

**THE THERMODYNAMICS OF SOLUTIONS AND
BINARY LIQUID MIXTURES.**

THESIS

**Submitted in fulfilment of the requirements for the Degree of
DOCTOR OF PHILOSOPHY
of Rhodes University**

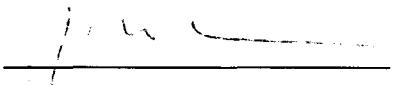
by

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December 1992

DECLARATION

I hereby certify that the work presented in this thesis is the result of my own investigation under the supervision of Professor T.M. Letcher, and has never been submitted in candidature for a degree in any other university.



June D. Mercer-Chalmers.

ACKNOWLEDGEMENTS

The author gratefully makes the following acknowledgements :

To Professor T.M. Letcher, under whose supervision this thesis was conducted, for his guidance and encouragement during the course of this study.

To Professor M.E. Brown, for being my co-supervisor.

To the technical staff of the Chemistry departments at Rhodes University and the University of Natal, for their help and advice.

To Professor Rubin Battino, for his help with the congruency theory.

To Professor John Bayles, for his invaluable help and advice.

To my good friends and colleagues, most especially Steve, Denise, Moira, Dean and Ashley, for their help during the ups and downs.

To Penny and Warren, for their help and cooperation in critical moments.

To my mother, for her forbearance, interest and moral support.

Financial support from the FRD is appreciated.

ABSTRACT

The thesis is presented in two parts. In part one, the excess thermodynamic properties have been determined for several binary liquid mixtures, with the aim of testing theories of liquid mixtures. The excess molar enthalpies, H_m^E , have been determined using an LKB flow microcalorimeter, and the excess molar volumes, V_m^E , have been determined using an Anton Paar densitometer.

The H_m^E s and V_m^E s have been measured at 298.15 K for binary systems involving an alkanol (methanol, ethanol, 1-propanol, 2-propanol) mixed with a hydrocarbon (1-hexene, 1-heptene, 1-octene, 1-hexyne, 1-heptyne, 1-octyne, toluene, mesitylene, *o*-, *m*-, or *p*-xylene, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane). The results show trends relating to the degree of unsaturation, or size, of component molecules as well as the position of the hydroxyl group on the alkanol. Measurements were also made on mixtures involving an (*n*-alkane + a pseudo-*n*-alkane) and (a cycloalkane + a pseudo-cycloalkane).

Two theories of liquid mixtures were tested in this work. The first theory tested was the theory of Congruency. This theory was tested, by means of a null test, on a novel set of mixtures involving an *n*-alkane (hexane, heptane, octane, decane, dodecane) + a pseudo-*n*-alkane, and mixtures of a cycloalkane (cyclopentane, cyclohexane, cycloheptane, cyclooctane) + a pseudo-cycloalkane. Deviations from the theory was less than the experimental error for the (*n*-alkane + pseudo-*n*-alkane) mixtures. However, significant deviations were observed for the mixtures of (a cycloalkane + a pseudo-cycloalkane).

The second theory tested was the Flory theory, which has been used to predict the excess molar enthalpies and excess molar volumes for the mixtures involving (a 1-alkene, or 1-alkyne, or methyl-substituted benzene) + an alkanol. The results show that the theory does not hold for hydrocarbon mixtures involving an alkanol.

In the second part of this thesis, the partial molar volumes, at infinite dilution, of binary solution involving a solid solute (18-crown-6 ether, dibenzo-18-crown-6 ether, dicyclohexano-

18-crown-6 ether, 15-crown-5 ether, or cryptand-222) are determined in various solvents. The results were repeated with a view to determine the volume changes at infinite dilution upon complexation, ΔV^∞ , of the crown ether or cryptand with a metal halide salt, MX (NaCl, NaI, KCl, KI, CsCl, CsI).

The ΔV^∞ results were compared with results in the literature for cryptand-222 (c-222) and dibenzo-18-crown-6 ether (B₂CE6) complexed with MX, and the study was extended to include further MX complexes with c-222 and B₂CE6, as well as MX complexes with 15-crown-5 ether and dicyclohexano-18-crown-6 ether. ΔV^∞ results were correlated with the Hepler prediction of the electrostriction solvent effect.

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CHAPTER 1

Introduction

There is a wealth of reference on the *ideal* behaviour of components for the mixing process,⁽¹⁾ thus it is often convenient to represent the changes in thermodynamic properties of mixing as deviations from this ideal behaviour. Experimental excess functions of liquid mixtures are useful in that they provide data to test theories of liquid mixtures and provide a guide for the formulation of new theories.⁽²⁾ For instance, excess molar enthalpies and excess molar volumes are useful to chemical engineers, both in chemical and petroleum industries, in the design of chemical plants such as reactors.⁽²⁾

One of the most important applications in the field of thermodynamics is the transformation of certain macroscopic data of a system into related data for that system through certain mathematical relationships, for prediction purposes. Prausnitz's *Molecular Thermodynamics of Fluid Phase Equilibria*⁽³⁾ includes examples of just such applications, concerning itself with methods for calculating the phase equilibrium behaviour of fluid mixtures from thermodynamic data and theories. Sufficient experimental data is essential in such applications. Another example of this type of work would be the use of the excess molar volume, V_m^E , to convert thermodynamic properties of mixing determined at constant pressure, to the properties at constant volume - to test theories which have the constraint of constant volume.

At present no satisfactory theory exists which can adequately predict thermodynamic data for binary liquid mixtures. The importance of such a theory would be two-fold, namely : (i) for the interpolation of limited experimental results available for the systems studied to systems not previously studied, and (ii) as an aid to understanding the nature of liquids and liquid mixtures.

Introduction

Molecular shape is an important and sensitive parameter in determining excess thermodynamic quantities.⁽⁴⁾ The *corresponding states* theory is useful in lending physical insight into the origin of excess functions for mixtures of molecules differing in size. Mixtures of normal alkanes have thus received considerable attention due to their simplicity, and to the fact that they serve as a model for polymeric systems. The theory does not however deal with a new effect which arises for molecules differing in shape. A considerable amount of work has been carried out in this regard by Patterson and co-workers,⁽⁵⁻⁸⁾ who attribute this effect to the short-range orientational order present in a system comprising of molecules of highly anisotropic shape, *eg.* *n*-alkanes. The mixing of molecules of different molecular shape, and consequently different degrees of orientational order, will result in a net decrease of order and a corresponding increase in the excess enthalpy for the mixture.⁽⁵⁾

The material in the first part of this thesis is primarily concerned with determining excess molar enthalpies, H_m^E , and excess molar volumes, V_m^E , for binary liquid mixtures, with the aim of testing various thermodynamic theories. A study has been made of excess properties for systems concerning molecules not only differing in shape and size, but also with mixtures where one of the components contains multiple bonds. H_m^E and V_m^E have been determined for binary systems involving a substituted benzene mixed with an alkanol. The substituted benzenes used were toluene, mesitylene, and *o*-, *m*- and *p*-xylene. These compounds were mixed with methanol, or ethanol, or 1-propanol, or 2-propanol, and the effect of the number and position of the $-CH_3$ -group on the excess properties was observed. These results were compared with previously reported work on benzene + alkanol mixtures.⁽⁹⁻¹¹⁾ Excess thermodynamic properties have also been measured for mixtures of a 1-alkene or a 1-alkyne + an alkanol. The various trends and observations have been compared with work previously carried out concerning systems involving *n*-alkanes mixed with alkanols.⁽¹²⁻¹⁴⁾ The final set of mixtures investigated in this section involve mixtures of cycloalkanes + alkanols. The effect of the ring size on the result was observed.

Introduction

The study of the above mixtures presented an opportunity to test the Flory theory.⁽¹⁵⁻²²⁾ This theory was postulated due to the need to explain the major discrepancies that exist between the experimental results and the results predicted by the lattice theory, which fails to account for the changes in volume and in local disorder with mixture composition. The one-parameter Flory theory was initially derived with the aim of explaining the thermodynamic properties of normal paraffin hydrocarbon mixtures⁽¹⁵⁻¹⁷⁾ and was subsequently extended to cover non-polar molecules differing in size and shape.⁽¹⁸⁾ In this thesis the experimental H_m^E and V_m^E results measured here have been fitted to the equations derived by Flory and co-workers. The adjustable interaction parameters, χ_{12} , which characterise the energetic weaknesses of unlike contacts, have been determined for each system from experimental H_m^E and V_m^E data.

The Flory theory considers excess thermodynamic properties of binary mixtures to be the sum of three contributions^(15,16): (i) a combinatorial term, (ii) an interactional term arising from the differences in the chemical nature of the two components, and (iii) a free volume contribution. More insight into the nature of these contributions is presented by the approximate equations of Patterson and co-workers,^(23,24) which lead to the separation of these contributions. The approximate form of their excess molar enthalpy equation⁽²³⁾ is divided into a free volume and an interactional contribution. The excess molar volume can be expressed as an interactional term, which is proportional to the χ_{12} parameter, a free volume contribution, which originates from a difference in the degrees of thermal expansion between the two components, and a P^* contribution, which arises from the differences in the internal pressure and the reduced volumes of the components.⁽²⁴⁾

A series of mixtures comprising an *n*-alkane and its pseudo-*n*-alkane⁽²⁵⁾ were made up to test the theory of congruency - first proposed by Bronsted and Koefoed⁽²⁶⁾ to correlate and predict activity coefficients. The principle has since been extended to correlate and predict several other thermodynamic properties, such as the excess Gibbs free energy of mixing,⁽²⁷⁾ the excess enthalpy of mixing,⁽²⁸⁾ and the excess volume of mixing.⁽²⁹⁾

Introduction

In this work, the V_m^E and H_m^E of a series of mixtures of an *n*-alkane + a pseudo-*n*-alkane, and a cycloalkane + a pseudo-cycloalkane were measured over the whole composition range -to test the theory by means of a novel null test.⁽³⁰⁾ This work has been discussed in terms of the effect of the difference in ring size and chain length of the cycloalkanes and *n*-alkanes.

In the second part of this thesis, the solution properties of binary solutions involving a solid solute such as a crown ether or a cryptand have been investigated. The partial molar volumes at infinite dilution, $V_i(x_i=0)$, of a solute *i* (18-crown-6 ether, dibenzo-18-crown-6 ether, dicyclohexano-18-crown-6 ether, 15-crown-5 ether, or cryptand-222) have been measured in various solvents. This information was then utilised to investigate the complexation properties of the crown ethers or cryptand with a selection of metal halide salts (NaCl, NaI, KCl, KI, CsCl, CsI), so that the volume changes upon complexation at infinite dilution, ΔV^∞ , could be calculated for each system. The equilibrium constant (*K*) for these reactions had to be large in order to ensure virtual complete complexation. The ΔV^∞ results are discussed in terms of similar, previously published, work⁽³¹⁻³⁶⁾ as well as in terms of electrostriction,⁽³⁷⁾ compressibilities,⁽³⁵⁾ and the effect of the equilibrium constant.^(38,39) A more detailed description of this work is given in the introduction to Part II of this thesis - Chapter 6.

CHAPTER 2

Excess Molar Volumes of Mixing

2.0 Introduction

The volume change on mixing of binary liquid mixtures, V_m^E , at constant pressure, is of interest to chemical thermodynamicists for two main reasons.⁽⁴⁰⁾ They serve as an accurate and sensitive indicator to the measure of the theories of solution, and they are relatively easy to obtain experimentally. V_m^E of a binary liquid mixture can arise out of a number of factors⁽⁴¹⁾ : (a) difference in size and/or shape of the component molecules, (b) changes in molecular orientations, (c) a difference in intermolecular interaction energies between like and unlike molecules, and (d) formation of products in solution. From these factors, it can be seen that V_m^E is a complex property. However, it can be obtained relatively easily experimentally, and with good precision, (0.01%).⁽⁴⁰⁾ The combination of these two facts is what makes V_m^E a desirable and useful property to test theories of liquid mixtures.

In this work, the interactions of alkanols with substituted benzenes or unsaturated hydrocarbons or cyclic hydrocarbons are investigated. The results obtained are discussed in terms of packing associations, dissociations and partial molar volumes at infinite dilution. These partial molar volumes are calculated from the V_m^E s, and this method as well as its limitations are discussed later on in this chapter. The V_m^E results are also treated (together with the H_m^E results from Chapter 3) in terms of the Flory theory - the discussion of this work is left to a later chapter (Chapter 5).

2.1 Measurement of Excess Molar Volumes

Volume changes for binary mixtures, V_m^E , can be determined in one of two ways. Namely, (i) indirectly by means of density measurements, or (ii) directly, by measuring the resultant volume change upon mixing of the two components.

Several reviews have been written on the subject of experimental methods of measuring volume changes. Detail is given in reviews by Letcher,⁽⁴²⁾ Battino,⁽⁴⁰⁾ and Handa and Benson.⁽⁴¹⁾ A more brief approach is made by Stokes and Marsh,⁽⁴³⁾ Swinton⁽⁴⁴⁾ and Marsh.^(45,46)

2.1.1 Indirect measurements

(a) Pycnometers

A variety of pycnometers, with varying characteristics, are made use of in the measurement of densities. Many of these are discussed by Bauer and Lewin.⁽⁴⁷⁾ Battino,⁽⁴⁰⁾ Wood and Brusie,⁽⁴⁸⁾ and Scatchard, Wood and Mochel.⁽⁴⁹⁾ The latter describe a single-arm pycnometer, depicted in Fig. 2.1, that can be used to obtain $0.00001 \text{ g.cm}^{-3}$ precision in

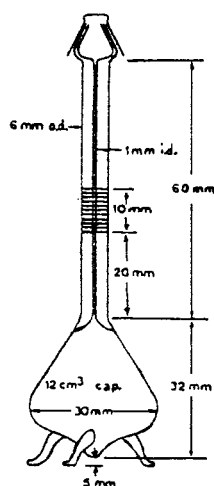


Fig. 2.1: Pycnometer of Scatchard et al, taken from ref.(49).

2.1 Measurement of V_m^E

density measurements. The bulb has an 11 cm³ capacity and the 1 mm internal diameter precision capillary has 11 lines lightly etched around the stems, and spaced 1 mm apart. The bulb is filled using a hypodermic syringe and cannula. Corrections for buoyancy and vapour space are feasibly applied.⁽³⁷⁾

When determining densities by means of this technique, it is important to be able to also determine the composition of the mixtures with precision. Many workers weighed the two components into the pycnometer. This also brings to the fore the problems of adequate mixing, evaporation, and vapour space composition. However, careful measurements using this method can provide very precise density values.

A better technique was devised, wherein use was made of a mixing bottle - originally described by Wood and Brusie⁽⁴⁸⁾ and improved upon by Battino.⁽⁵⁰⁾ With this bottle, as depicted in Fig. 2.2, the volume of mixing is determined at 298.2 K.

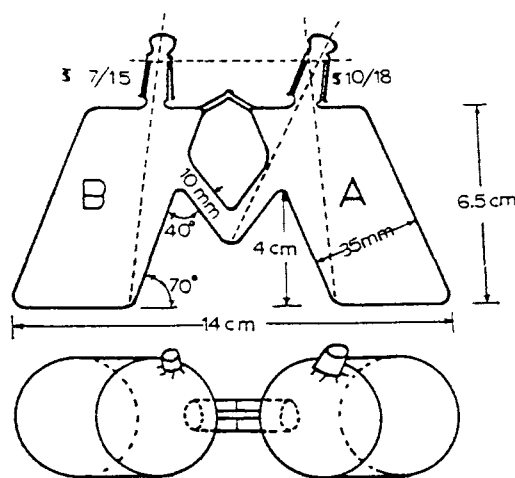


Fig. 2.2: Mixing bottle of Battino, taken from ref. (50).

Using male joints on the bottle minimizes the possibility of wetting the joints - used ungreased - during the mixing. The U-tube is filled with the mercury to prevent pre-mixing while the two liquids are introduced into their separate chambers. Kohler and Rott⁽⁵¹⁾ and Ruiter⁽⁵²⁾ also described good designs of mixing bottles.

2.1 Measurement of V_m^E

Kimura and Takagi⁽⁵³⁾ used a bicapillary pycnometer made of Pyrex glass. The capacity of the pycnometer was approximately 3.6 cm^3 , and the internal diameter of the capillary stems were approximately 0.5 mm. Sharp lines scored on each stem and magnified by a travelling microscope were used as reference points. The pycnometer was allowed to stand for 20 to 30 minutes in the balance case, before each weighing. Each capillary stem had a ground-glass stopper to prevent evaporation and wetting of the sample. The reproducibility for weighing the pycnometer was $\pm 0.01 \text{ mg}$ - which gave a precision of $0.00001 \text{ g.cm}^{-3}$ in density measurements.

(b) Magnetic float densimeters

Magnetic float densimeters operate on the principle of balancing the opposing effects of buoyancy, gravity and magnetic field on a float containing a permanent magnet. This is achieved by passing a current through a solenoid placed below the sample cell; the density is therefore related to the current at which the float first lifts off the bottom of the cell.⁽⁴¹⁾

Franks and Smith⁽⁵⁴⁾ described their apparatus, depicted in Fig. 2.3, which can be used for fifth and sixth place density measurements on mixtures. It has a sensitivity of $\pm 0.0001\%$ for a cell of 600 cm^3 capacity. The cell contained a quartz float which in turn contained a small bar magnet. Its weight was adjusted with lead shot so it just sank in water at 318.2-323.2 K. The optimum position of the solenoid relative to that of the magnet in the float was obtained by trial and error. The cell was mounted in a thermostated bath.

Limitations to this method are that temperature fluctuations may cause errors in density measurements; uncertainty in the values of the concentration; error in the placement of the solenoid; the viscosity of the solution may also introduce errors.⁽⁵⁴⁾ Other workers who have used similar apparatus are Benjamin,⁽⁵⁵⁾ Millero⁽⁵⁶⁾- who also reviewed earlier instruments, and Masterton and Seiler.⁽⁵⁷⁾

2.1 Measurement of V_m^E

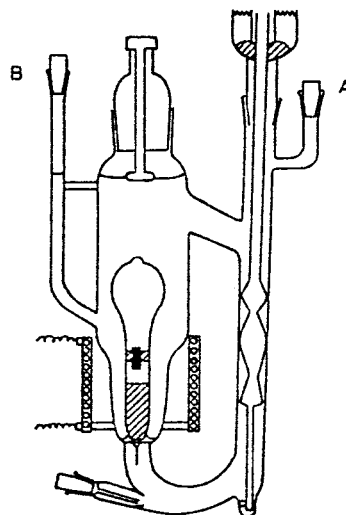


Fig. 2.3: Apparatus of Franks and Smith, taken from ref. (54).

(c) Mechanical Oscillator Densitometers or densimeters

The oscillating tube densimeter is widely used in the process and petroleum industries to measure densities, owing to the speed and precision with which results can be obtained.⁽⁵⁸⁾ The accuracy is limited to some extent by the calibration procedure, the viscosity of the sample, the pressure, the temperature control. The density of the sample is related to the resonance frequency of an electronically excited mechanical oscillator and the period of oscillation of the sample contained in the oscillator.

The effective mass (M) of the oscillator is composed of its own unknown mass (M_o) as well as the unknown mass of the sample, density d , contained in volume V - and is given by

$$M = M_o + Vd \quad 2.1$$

The resonant frequency is given by

$$2\pi\nu = (c/M)^{1/2} = [c/(M_o + Vd)]^{1/2} \quad 2.2$$

2.1 Measurement of V_m^E

where the mass M is attached to a spring of constant elasticity c , under the condition that the oscillator performs an undamped oscillation.⁽⁴¹⁾ Rearranging

$$d = -M_o/V + (c/4\pi^2V)(1/v^2) = A + B\tau^2 \quad 2.3$$

where $\tau = 1/v$, ie. the period of oscillation, and A and B are constants characteristic of the oscillator. Densities are measured relative to a reference material, thus :

$$d - d_o = B(\tau^2 - \tau_o^2) \quad 2.4$$

where d_o is the density of the reference material and τ_o its corresponding period of oscillation.

Kratky *et al*⁽⁵⁹⁾ designed a V-shaped hollow-glass sample tube. This design made filling and mixing procedures simpler and was readily adaptable to measurement involving flowing liquids. The vibrating tube densimeter method is popular due to its potential for high-precision measurements.

In this work, a densitometer, based on the design by Kratky *et al*,⁽⁵⁹⁾ manufactured by Anton Paar (Graz, Austria) is used. It employs a U-shaped borosilicate glass tube, with a volume of 0.7 cm³, mounted in a dual wall glass cylinder which serves as a water jacket. B is obtained by measuring τ for water and air. The precision obtained in τ is 0.000002 s.

Picker *et al*⁽⁶⁰⁾ developed a densimeter with a V-shaped stainless steel tube as the oscillator. This required a much shorter thermal equilibration period and is very suited to flow measurements. A change in flow rate of 100 per cent was found to affect the density results by only 3 ppm. It has been recommended⁽⁶¹⁻⁶³⁾ that B in equation 2.4 should be obtained by measuring τ for a number of liquids of known densities.

2.1 Measurement of V_m^E

In order to obtain a precision of $0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$ in V_m^E , Handa and Benson⁽⁴¹⁾ have calculated that the composition should be precise to five figures and density precise to six figures. Battino⁽⁴⁰⁾ states that the temperature must be controlled to $\pm 0.01 \text{ K}$ to accurately determine densities to $0.00001 \text{ g} \cdot \text{cm}^{-3}$.

Error analysis

To obtain an error of $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$ in V_m^E , the masses must be known to 0.00001 g , the τ values must be known to 0.000002 s , and the densities to $0.00001 \text{ g} \cdot \text{cm}^{-3}$. Refer to *Appendix A* for a detailed error analysis report.

2.1.2 Direct measurements

Direct measurements have generally been regarded⁽⁴¹⁾ as the more accurate and to yield higher precision results than indirect measurements. Apparatus for the direct measurement of volume change has been designed along two fundamental lines: (a) one composition per loading of the apparatus at a single temperature or batch dilatometers; and (b) a number of compositions per loading at a single temperature or continuous dilution dilatometers.

(a) Single composition per loading (batch dilatometry)

Keyes and Hildebrand⁽⁶⁴⁾ designed what was, arguably, the fundamental dilatometer in 1917 (seen in Fig. 2.4), which consisted of a U-tube with mercury filling the bottom in order to separate the two components. Graduated capillaries on the two arms gave the means by which the volumes, before and after mixing, could be determined. Mixing was achieved by rocking the apparatus which remained, throughout, in a thermostated bath. This particular apparatus was capable of precisions of $\pm 0.003 \text{ cm}^3 \cdot \text{mol}^{-1}$ in V_m^E , and was useful over the temperature range $280\text{--}350 \text{ K}$.⁽⁴⁰⁾

2.1 Measurement of V_m^E

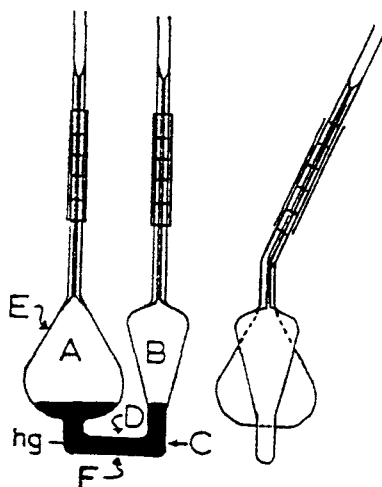


Fig. 2.4: Keyes and Hildebrand dilatometer, taken from ref. (64).

Many variations and modifications were made on this theme by subsequent workers - the majority of which have been reviewed by Battino.⁽⁴⁰⁾ Of these described methods, the simplest of the precise methods is the one employed by Duncan, Sheridan and Swinton.⁽⁶⁵⁾ This particular apparatus requires between 0.2 - 0.8 cm³ of each liquid and has changeable capillaries to accommodate different magnitudes of volume change. A negligible error is present due to a difference in pressure before and after mixing. The precision was found to be $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$ or $\pm 0.5\%$ in V_m^E .⁽⁴⁰⁾

Stookey *et al*⁽⁶⁶⁾ have reported on a detailed analysis of the errors associated with measurements made on batch dilatometers. They draw attention to the fact that failure to take into account a compressibility correction could result in errors of 0.5 to 1.0 per cent. Corrections for temperature fluctuations have to be made, and care has to be taken to avoid excessive amounts of grease on the joints.

The main disadvantage of these single composition dilatometers was: each loading only gave a single reading.

2.1 Measurement of V_m^E

(b) Many compositions per loading (dilution dilatometry)

Holleman⁽⁶⁷⁾ described a dilatometer in which a selection of chamber sizes and angles, as seen in Fig. 2.5, allows for four successive dilutions from one loading.

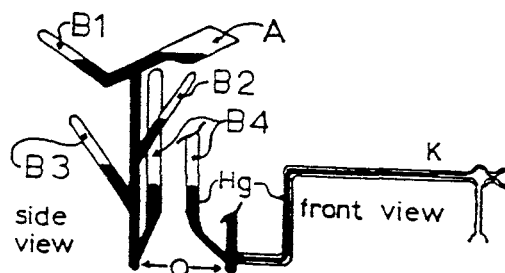


Fig. 2.5: Holleman dilatometer, taken from ref. (67).

The fundamental design by Geffcken, Kruis and Solana⁽⁶⁸⁾ has been adopted and modified by many workers.^(29,69-74) The original design by Geffcken *et al*⁽⁶⁸⁾ as seen in Fig. 2.6, has the mixing chamber C initially loaded with pure component A and

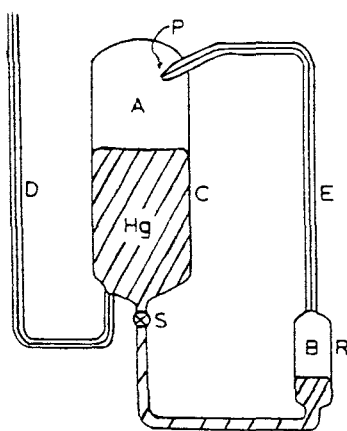


Fig. 2.6: Dilatometer of Geffcken *et al*, taken from ref. (68).

mercury. Stopcock S leads to reservoir R where pure component B is kept over mercury. The mercury level in the calibrated capillary D is read with respect to a fiduciary mark F. Some provision is made for stirring the contents of C, and the entire apparatus is thermostated. When S is opened, mercury from C forces some of component B into C via connecting tube E. S is then closed, and mixing begins. The change in level of mercury

2.1 Measurement of V_m^E

in capillary **D** is noted. Increments of **B** are added in a similar way in order to determine V_m^E as a function of composition at one temperature. The main difference between the different designs is in the method of separation of the two components at point **P**.

Stokes *et al*⁽⁷⁵⁾ designed a solution dilatometer along the lines of the one described above - component **B** being confined in a burette above which component **A** is confined in a bulb, over mercury. These two are attached by a fine stainless steel tube, and known fractions of component **B** are forced into the bulb by means of mercury flowing in the opposite direction via a stopcock. The advantage of this apparatus being that it is easier to load and use.

Bottomley and Scott⁽⁷⁶⁾ identified small errors in measurement due to grease in the diluent liquid. They reduced the error by designing a dilution dilatometer wherein no tap was opened or closed during a run - mixing was achieved by tilting. However, the apparatus proved to be tedious to work with, loading had to be done under vacuum, and only small volume changes could be measured.

Kumaran and McGlashan⁽⁷⁷⁾ redesigned Bottomley and Scott's⁽⁷⁶⁾ tilting dilatometer (see Fig. 2.7) so as to give easier calibration and loading, to eliminate the stopcock, and to allow for measurement of volume changes of any magnitude. Moreover, in the dilatometer designed by Kumaran and McGlashan,⁽⁷⁷⁾ the two liquids were separated by mercury at all stages of a run instead of only a diffusion boundary in a capillary as in the dilatometers of Stokes *et al*⁽⁷⁵⁾ and Bottomley and Scott.⁽⁷⁶⁾ The dilatometer by Kumaran and McGlashan is similar to the one shown in Fig. 2.7, except that the capillary **C** has a larger bore size and it has a calibrated bulb **AA** blown at the bottom of the calibrated burette **A**. The provision of the bulb **AA** eliminates the need to calibrate the mixing cell **B**. Before the start of a run, bulb **B** is filled with mercury and burette **A** with one of the components. After thermal equilibrium and with stopcock **T₁** removed, mercury from **B** is transferred into **AA** thus creating space of known volume in **B**. Kumaran and McGlashan have reported a standard deviation of $0.0007 \text{ cm}^3 \cdot \text{mol}^{-1}$ for the test system.

2.1 Measurement of V_m^E

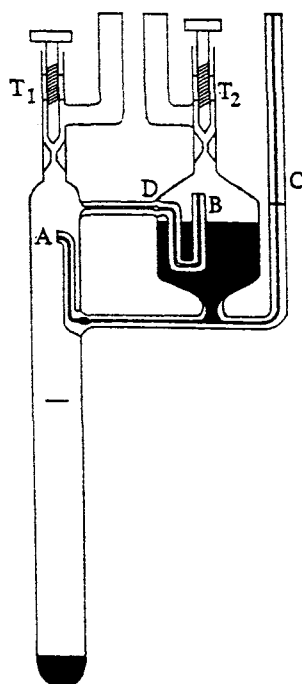


Fig. 2.7 : Bottomley and Scott's tilting dilution dilatometer, taken from ref. (76).

Both batch and continuous dilatometers are capable of producing results of equal accuracy, although the dilution technique is intrinsically more precise and useful for studying dilute solutions.⁽⁴⁰⁾ The disadvantage comes in that relatively large volumes (50 to 100 cm³) of highly purified components are required. More convenient are dilatometers needing only 5 to 15 cm³ of each component, as in the apparatus designed by Powell *et al.*⁽⁷⁸⁾ However, since loading was done by means of a hypodermic syringe, another possible source of error was introduced. Namely, evaporation of volatile components. Brennan *et al.*⁽⁷⁹⁾ and Ahmed *et al.*⁽⁸⁰⁾ designed an apparatus which overcomes this problem.

The minor disadvantage of most of the dilution dilatometers described here is that in order to measure a volume change at a constant pressure, a correction must be made. That is, a change in the height (Δh) of the mercury meniscus in the capillary causes a change in the mixing cell pressure equal to $\rho g \Delta h$, where ρ = density of mercury). Errors of up to 1.5 per cent can be introduced in this manner. However, this can be easily taken into account. Tanaka *et al.*⁽⁸¹⁾ (see Fig. 2.8) report on a simplified version of a design by Chareyron and Clechet.⁽⁸²⁾ Volume changes in the mixing cell F are accommodated by a piston controlled

2.1 Measurement of V_m^E

by a micrometer **Q**, which is turned to maintain the same level of the mercury menisci in the mixing cell **F** and the capillary **N**. By using a small-bore calibrated burette **D** containing the feed component, the precision in mole fraction is greatly improved. A reservoir **E** of the same component is used to recharge **D** once it has delivered its contents to **F**. This dilatometer, although difficult to operate, is capable of high precision. The reported standard deviation is $0.0004 \text{ cm}^3 \cdot \text{mol}^{-1}$. However, for the Tanaka *et al*⁽⁸¹⁾ dilatometer the greased stopcock, **A** remains a problem.

Other designs, unusual and otherwise, have been reviewed by Handa and Benson.⁽⁴¹⁾

See over the page for Schematic of dilatometer of Tanaka et al (Fig. 2.8)

2.1 Measurement of V_m^E

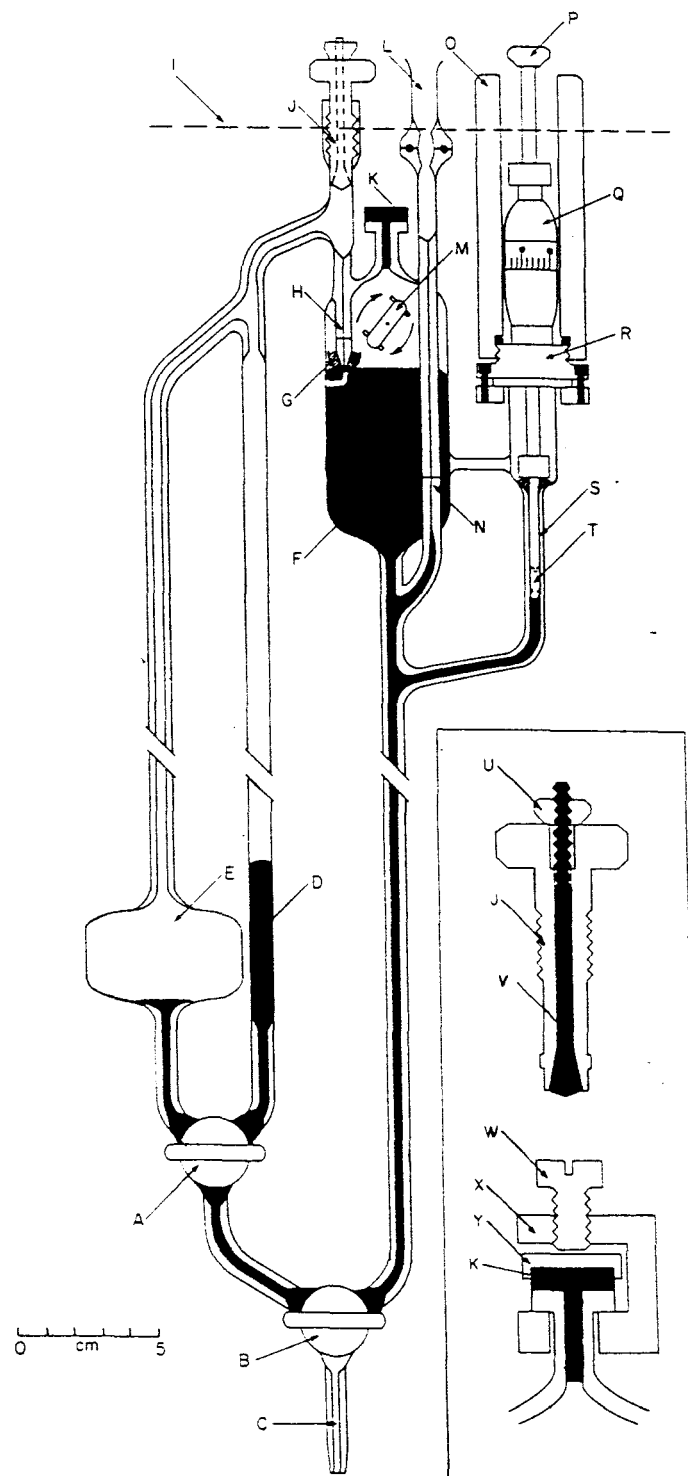


Fig. 2.8 : Schematic of dilatometer of Tanaka et al, taken from ref. (81).

2.2 Determining V_1^E

2.2 Determining excess partial molar volumes from data

The excess partial molar volumes at infinite dilution offer a way of interpreting the interactions which give rise to positive and negative V_m^E s.

The partial molar of a pure liquid 1 may be defined^(83,84) as

$$V_1 = (\partial V / \partial n_1)_{T,P,n_2}$$

and it is equal to the slope of the curve obtained when the volume of the solution is plotted against the molality m_1 of component 1. This follows since m_1 is the number of moles of component 1 in a constant quantity, namely 1000 g, of component 2.

The determination of partial molar volumes by this slope method is rather inaccurate; the *method of intercepts* is usually preferred. To use this method, a quantity (the molar volume of the solution V_m) is defined, which is the volume of the solution divided by the total number of moles of the various constituents. For a two component solution,

$$V_m = V / (n_1 + n_2)$$

Then,

$$V = V_m (n_1 + n_2)$$

and

$$V_1 = (\partial V / \partial n_1)_{n_2} = V_m + (n_1 + n_2) (\partial V_m / \partial n_1)_{n_2} \quad 2.5$$

Now the derivative with respect to the amount of component 1, n_1 , is transformed into a derivative with respect to mole fraction 2, x_2 .

$$(\partial V_m / \partial n_1)_{n_2} = dV_m / dx_2 (\partial x_2 / \partial n_1)_{n_2}$$

2.2 Determining V_1^E

since

$$x_2 = n_2/(n_1 + n_2) , (\partial x_2/\partial n_1)_{n_2} = -n_2/(n_1 + n_2)^2$$

Thus eqn. 2.5 becomes

$$V_1 = V_m - n_2/(n_1 + n_2)(dV_m/dx_2)$$

$$V_m = x_2(dV_m/dx_2) + V_1 \quad 2.6$$

The application of this equation is illustrated in Fig. 2.9, where V_m for a solution is plotted against the mole fraction.

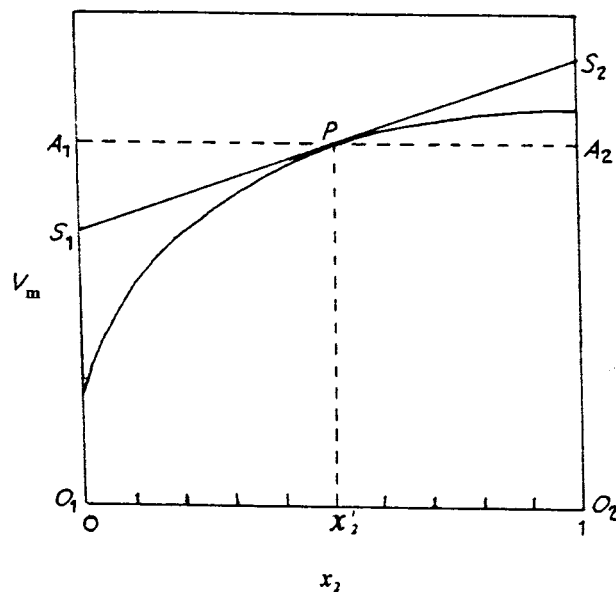


Fig. 2.9 : Determination of partial excess molar volumes - intercept method - a plot of V_m vs. x_2 .

The slope S_1S_2 is drawn tangent to the curve at point P , corresponding to a definite mole fraction x'_2 .

2.2 Determining V_1^E

$$V_1(x=x_2') = V_m - x_2'(A_1 - S_1)/x_2' = O_1 S_1$$

similarly,

$$V_2(x=x_2') = O_2 S_2$$

In a similar way, $V_1^E(x_1=0)$ can be obtained.

Redefining in terms of the excess partial molar volume, V_m^E ⁽⁸⁵⁾, where

$$V_m^E = V_m - V_{ideal}$$

and

$$V_{ideal} = x_1 V_1^o + x_2 V_2^o$$

where $x_i = n_i/(n_1 + n_2)$, 1 refers to a hydrocarbon, 2 refers to an alkanol and ^{o} refers to a pure liquid.

$$V_1^E = V_m^E - x_2(dV_m^E/dx_2) \quad 2.7$$

In this work the partial molar volumes at infinite dilution $V_1^E(x_1=0)$ and $V_2^E(x_2=0)$ have been calculated and used in the discussion. These properties can be readily calculated from the Redlich Kister equation (2.8)

$$V_m^E = x(1-x)\sum_{r=0}^n B_r(1-2x)^r \quad 2.8$$

where B_r represents the smoothing coefficients.

2.2 Determining V_1^E

V_m^E can be expressed as⁽⁸⁵⁾

$$V_m^E = x_1(1-x_1)[B_1 + B_2(1-2x_1) + B_3(1-2x_1)^2] \quad 2.9$$

The partial molar volume of mixing at mole fraction x_1 , is given by

$$V_1^E = (\partial V_m^E / \partial n_1)_{n_2} = (1-x) dV_m^E / dx_1 + V_m^E$$

At infinite dilution ($x_1=0$) this becomes

$$V_1^E(x_1=0) = dV_m^E / dx_1 = B_1 + B_2 + B_3$$

which can be expressed as

$$V_1^E(x_1=0) = \sum_{r=0}^n B_r \quad 2.10$$

Similarly,

$$V_2^E(x_2=0) = \sum_{r=0}^n (\text{even}) B_r - \sum_{r=0}^n (\text{odd}) B_r \quad 2.11$$

2.3 This work

In this work, the interactions in V_m^E between an alkanol (methanol, ethanol, 1-propanol, or 2-propanol) and a hydrocarbon are investigated. The excess molar volumes of mixing, V_m^E , of mixing benzene with C_1 , C_2 and C_3 alkanols have been reported.⁽⁹⁻¹¹⁾ However, very little has been reported on mixtures of substituted benzenes and C_1 , C_2 and C_3 alkanols.⁽⁸⁶⁻⁸⁸⁾ In this work, V_m^E of the following systems are reported on : mesitylene (1,3,5-trimethylbenzene), *o*-, *m*-, and *p*-xylene (isomer of $C_6H_4(CH_3)_2$), or toluene with methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH) or 2-propanol (2-PrOH). The effect of the methyl groups was

2.3 This work

observed.

Work has been reported on alkanol + *n*-alkane mixtures,⁽¹²⁻¹⁴⁾ and these were used as a basis for comparison for the 1-alkene or 1-alkyne + alkanol mixtures reported here. In this work, mixtures of 1-alkenes (1-hexene, 1-heptene or 1-octene) or 1-alkynes (1-hexyne, 1-heptyne or 1-octyne) with MeOH, EtOH, 1-PrOH, or 2-PrOH were investigated.

The V_m^E of a cycloalkane + an alkanol were also investigated, and the effect of increasing the cycloalkane ring size as well as increasing the alkanol chain length was observed.

The Flory theory has been applied to all of these abovementioned mixtures together with the H_m^E values from Chapter 3. These results are discussed in Chapter 5.

2.4 Experimental

The V_m^E results were determined from the density data using an Anton Paar DMA 601 vibrating tube densitometer. See 2.4.2 for a detailed description of the experimental procedure.

2.4.1 Materials

A summary of the materials, their suppliers and purities used in this work are given in Table 2.1. The materials were purified where necessary.⁽⁸⁹⁾

The toluene and mesitylene were vacuum distilled before use. The *o*-, *m*-, and *p*-xylene were each distilled at a reflux ratio of 0.1, using a 50 cm long insulated column filled with glass helices. The toluene was treated in the same way. The alkenes and alkynes were fractionally distilled twice before use. The cycloalkanes were fractionally distilled three times before use. The alkanols were purified using the method of Lund and Bjerrum⁽⁹⁰⁾: they

2.4 Experimental

were refluxed over magnesium turnings and iodine for 30 minutes, and then distilled through a 150 mm lagged, glass fragment-packed column. G.l.c. analyses indicated a purity of 99.8 mole percent after this procedure. Karl Fischer titrations on each of the alkanols showed that the water impurity was less than 0.02 mole percent. The purities were tested on a Hewlett-Packard 5890A gas chromatograph equipped with a 3393A integrator and a 25m carbowax 20M capillary column. All of the materials were stored in a drybox supplied with silica gel and a double access door.

2.4 Experimental

Table 2.1. Materials used, their suppliers and purities.

Compound	Supplier	Purity (mole %)
Mesitylene	Merck	99.65
<i>o</i> -xylene	Merck	99.5
<i>m</i> -xylene	Merck	99.5
<i>p</i> -xylene	Merck	99.5
toluene	BDH (AnalR grade)	99.8
1-hexene	Aldrich	99.8
1-heptene	Aldrich	99.8
1-octene	Aldrich	99.5
1-hexyne	Aldrich (Gold label)	99.5
1-heptyne	Aldrich	99.5
1-octyne	Aldrich	99.6
Cyclo-5	Fluka	> 99
Cyclo-6	SARchem	99
Cyclo-7	Aldrich	> 99
Cyclo-8	Janssen	> 99
Cyclo-10	Fluka	> 99
MeOH	Merck	99.9
EtOH	NCP (S.A.)	99.9
1-PrOH	BDH	99.8
2-PrOH	BDH	99.7

2.4.2 Experimental Procedure

In this work, volume changes were determined by density measurements using a commercially available Anton Paar DMA 601 vibrating tube densitometer.

2.4 Experimental

(i) Instrument description and operation

The laboratory arrangement of the density measurement apparatus is shown in Fig. 2.10. The measuring cell is contained within its own separate housing, and consists of a hollow U-shaped borosilicate glass tube fused into a dual wall glass cylinder through which the thermostat liquid is pumped. The volume of the cell is 0.7 cm³. The space between the U-tube and the cell is filled with a gas of high thermal conductivity, thus facilitating rapid equilibrium between the sample and the thermostat liquid flowing through the water jacket.

The determination of densities by this method⁽⁵⁰⁾ is based on the measurement of the period of oscillation of the undamped vibrating tube of volume, V , which in this case is filled with sample liquid. In this way, the natural frequency of vibration of the tube is influenced by the mass, and hence the density, of the sample. For the purposes of a mathematical derivation, the system is analogous to a hollow body of mass, M_o , which is suspended by a spring with a constant of elasticity, C . The volume of the hollow body is assumed to be filled with a sample of density, d . The natural vibrational frequency of such a system is then given by:⁽⁵⁰⁾

$$\nu = [(1/2\pi)(C/M_o + Vd)]^{(1/2)} \quad 2.12$$

In this instrument, two remote cells generate square wave signals in synchronism with the zero amplitude of the oscillating sample tube. These signals are separated by an optical isolator and are filtered from any resulting noise. The signal from any one of these sources, depending on the operators choice, is then fed into a period meter. Time based pulses every 10⁻⁵ seconds permit the determination of the time lapse of a preselected number of oscillator periods and hence allow the determination of the period of vibration, τ . The resulting period is related to the density of the sample through eqn. 2.3 which has been renumbered:⁽⁹¹⁾

$$d = B(\tau)^2 + A \quad 2.13$$

2.4 Experimental

where A and B are instrument constants, and are determined by calibration measurements with pure substances of accurately known density.

(ii) Temperature control and measurement

The accuracy of the density measurements depends to a large extent on the constant control of the temperature of both the environment in which the readings are being taken, as well as that of the thermostat liquid. A temperature stability of 0.01 K yields an uncertainty in the density of the order of $10^{-5} \text{ g.cm}^{-3}$.⁽⁵⁰⁾ For this reason, the temperature was controlled to ± 1 mK in this work. Deionised water was employed as the thermostat liquid.

A diagrammatic representation of the temperature control system is included in Fig. 2.10. The primary cooling system consisted of a rectangular copper bath, **A**, of dimensions 1000 x 500 x 500 mm. The bath had a glass front and was built around a steel cradle, thus making possible the clamping of stirrers and probes. The bath was insulated with sheets of 50 mm thick expanded polystyrene. A layer of polystyrene chips covered the water surface, reducing temperature fluctuations through evaporation. The apparatus was housed on a cushioned vibration-free surface in a constant temperature room. An ambient temperature of 296 K constant to ± 0.5 K was maintained.

A uniform temperature throughout the bath was achieved through the use of two variable speed mechanical stirrers, **B**. An auxiliary cooling system, **C**, comprising a 50 L water bath cooled by a Grants refrigeration coil, **D**, was incorporated to assist with the temperature control of the main water bath. Water from this auxiliary bath was pumped via a Braun or Haak immersion thermostat unit, **E**, at a rate of 2.8 L.min^{-1} through a four metre coiled-copper tube, **F**, (12 mm i.d.) placed inside the primary cooling bath. Since the auxiliary bath was maintained at a temperature of approximately 1 K below the operating temperature, this arrangement served to cool the main water bath.

2.4 Experimental

The thermostat system within the main water bath comprised of a permanent rheostated immersion heater, **G**, delivering up to 4W, and a 100W light bulb connected to a Tronac temperature controller, **H**. Water from the primary water bath was pumped through the water jacket by a submersible pump, **I**, at a rate of 3.4 L.min⁻¹. All rubber tubing to and from the densitometer was insulated to reduce heat losses. A Hewlett-Packard 2801 A quartz thermometer, **J**, calibrated as discussed in *Appendix B*, was employed to monitor the temperature within the main bath. A Paar digital thermometer, linked to a thermocouple, was used to monitor the temperature in the cell.

(iii) Sample injection

A warm-up time of at least 30 minutes for the apparatus, including temperature equilibration, was necessary before commencing experimental determinations. Before each run, the cell was flushed thoroughly with absolute alkanol and then acetone. After flushing, compressed air was blown through the cell. A constant period value obtained for the empty cell indicated that the cell had been thoroughly dried.

The sample was introduced into the cell by means of a glass syringe, which was equipped with a machined teflon nozzle, ensuring a leak-proof fit at the sample cell - syringe junction. The sample injection process was carried out slowly, enabling the liquid to properly wet the walls of the sample cell, and thus reducing the risk of trapping air bubbles in the U-tube. The sample cell was always filled to beyond its nodal points and the syringe was left in place during the period determination cycle. The other opening of the cell was sealed with a teflon plug to reduce evaporation.

2.4 Experimental

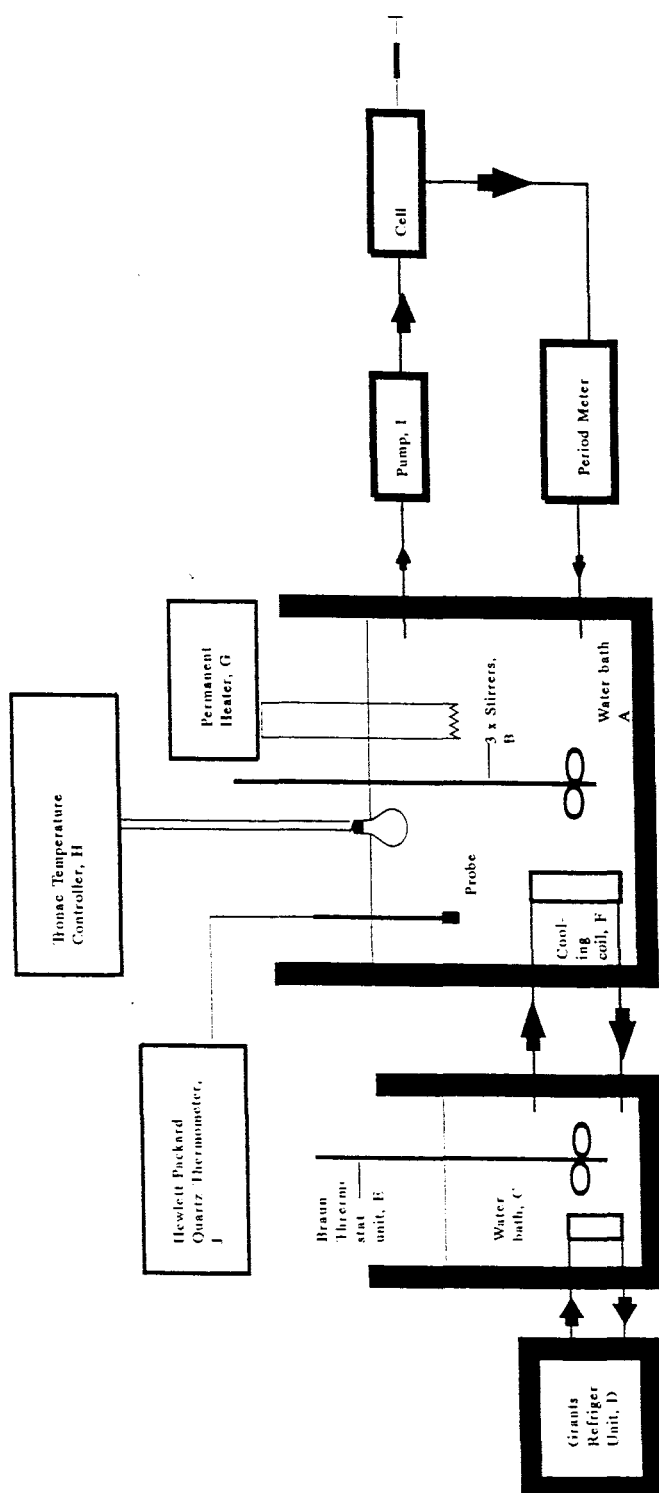


Fig. 2.10 : Laboratory arrangement.

2.4 Experimental

(iv) Preparation of mixtures

The mixtures were made up in 5 cm³ flasks fitted with ground glass stoppers. Care was taken to first add the least volatile component to the flask, and that the completed mixture left a small vapour space - large enough only to aid mixing. The mixtures were made up shortly before injecting into the densitometer, and were given a vigorous shake before injection.

(v) Density measurements

With the cell illumination light off, the photoelectric portion of the excitation system was automatically activated. Each measuring cycle was allowed to continue until a period value was obtained. Period values for water (deionised, distilled and degassed), pure solvent and air were determined between each solution injection. These values were not only required for the calculations, but also permitted a continuous check on both the samples and the densitometer operation, as well as reducing error due to minor fluctuations in temperature and solvent purity. The precision of τ , judged by repeated measurements for the same solution at different times, was estimated to be better than 0.000002 s.

(vi) Degassing of liquids

The liquids were degassed by immersing the flasks in a sonic bath for 10 minutes.

2.5 Results

The experimental results for each system are given in Tables 2.1-2.6, together with the deviations, Δ , calculated from the Redlich-Kister equation.

$$\Delta = V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^n B_r (1-2x)^r \quad 2.14$$

2.5 Results

The coefficients B_r for each system are given in Tables 2.7-2.13. The *Statgraphics 3.0* package was used to calculate these coefficients, and Δ . The V_m^E results were calculated using a GWBASIC program - details of which are given in *Appendix C*.

2.5 Results

Table 2.2. Molar excess volumes for $[x(\text{C}_6\text{H}_5\text{CH}_3) + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}]$ at 298.15 K, together with Δ calculated from eqn.2.14 and the coefficients in Table 2.8.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
MeOH								
0.0039	-0.001	12	0.3793	-0.076	-27	0.8588	0.012	-10
0.01318	-0.016	17	0.4173	-0.070	12	0.9399	0.017	26
0.0854	-0.041	5	0.4981	-0.059	25	0.9405	0.016	26
0.1315	-0.053	24	0.6433	-0.032	12	0.9877	0.005	8
0.1734	-0.066	-20	0.7794	-0.004	-37	0.9964	0.001	5
0.2039	-0.070	-11	0.8303	0.009	-2			
EtOH								
0.0031	-0.003	0	0.4537	-0.074	11	0.9058	0.050	-4
0.0428	-0.040	11	0.5132	-0.057	8	0.9542	0.036	28
0.1222	-0.086	16	0.6085	-0.022	13	0.9775	0.020	15
0.2269	-0.109	-14	0.7234	0.018	-27	0.9963	0.005	19
0.2792	-0.109	-16	0.8629	0.053	-4			

^aUnits : $\text{cm}^3\cdot\text{mol}^{-1}$

2.5 Results

Table 2.2 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
1-PrOH								
0.0042	-0.003	-1	0.5062	-0.011	18	0.9215	0.061	10
0.0528	-0.029	32	0.5603	0.007	26	0.9615	0.037	17
0.1443	-0.062	-2	0.6451	0.034	-3	0.9826	0.020	22
0.2787	-0.067	-25	0.7496	0.062	-41	0.9917	0.010	9
0.3504	-0.054	-4	0.8792	0.074	4			
2-PrOH								
0.0065	-0.001	8	0.5157	0.170	26	0.9289	0.120	31
0.1154	-0.002	6	0.5684	0.187	18	0.9716	0.052	18
0.1230	0.000	11	0.6488	0.205	-17	0.9879	0.024	-3
0.2349	0.040	-12	0.7422	0.214	-23	0.9929	0.014	-4
0.3467	0.092	-18	0.8957	0.153	4			

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

2.5 Results

Table 2.3 Molar excess volumes V_m^E at 298.15 K for $[x(C_9H_{12}) + (1-x)C_yH_{2y+1}OH]$ and the deviations Δ calculated from eqn. 2.14 and the coefficients of Table 2.9.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
CH₃OH								
0.0324	0.040	11	0.2770	0.158	28	0.7007	0.151	-28
0.0662	0.071	-8	0.3364	0.160	21	0.7537	0.143	-30
0.1101	0.103	-11	0.4243	0.165	35	0.8624	0.106	-40
0.1522	0.122	-32	0.5123	0.163	26	0.9320	0.068	20
0.1993	0.133	-32	0.5985	0.165	55			
C₂H₅OH								
0.0841	0.037	15	0.3470	0.129	25	0.7291	0.173	-36
0.1471	0.064	-3	0.5137	0.154	56	0.8382	0.167	-27
0.2097	0.086	-40	0.6023	0.164	45	0.8854	0.146	-22
0.2578	0.102	-40	0.6493	0.167	12	0.9483	0.090	14
1-C₃H₇OH								
0.1388	0.085	25	0.4350	0.203	49	0.7391	0.233	-28
0.2150	0.121	-47	0.5062	0.213	25	0.8332	0.214	-26
0.2701	0.150	-3	0.6038	0.228	27	0.9188	0.150	11
0.3393	0.171	-34						

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.3 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
2-C ₃ H ₇ OH								
0.0788	0.098	21	0.4607	0.365	57	0.7727	0.356	-15
0.1417	0.161	39	0.5190	0.364	17	0.8396	0.305	-65
0.2589	0.265	-12	0.6007	0.391	79	0.9024	0.230	-20
0.3622	0.320	-51	0.6868	0.381	-3	0.9320	0.181	-32

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.4. Molar excess volumes for $[x\{o-, m-, \text{ or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}]$ at 298.15 K, together with Δ calculated from eqn. 2.14 and the coefficients in Table 2.10.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
xo-xylene + (1-x)MeOH								
0.0147	-0.004	13	0.1942	-0.033	-7	0.7831	0.012	-7
0.0236	-0.007	12	0.3205	-0.033	-20	0.8600	0.018	-16
0.0304	-0.010	2	0.3544	-0.031	-15	0.9256	0.019	9
0.0388	-0.012	9	0.4388	-0.024	12	0.9694	0.014	41
0.0736	-0.021	3	0.5659	-0.012	27	0.9807	0.010	39
0.1249	-0.029	-8	0.6415	-0.003	22	0.9893	0.006	24
0.1746	-0.030	17	0.7422	0.003	-42	0.9934	0.003	13
xo-xylene + (1-x)EtOH								
0.0117	-0.009	31	0.2370	-0.096	-29	0.7888	0.053	13
0.0195	-0.017	29	0.2936	-0.091	-35	0.8471	0.064	0
0.0247	-0.022	22	0.3786	-0.074	13	0.8742	0.070	-20
0.0303	-0.030	-8	0.4730	-0.046	28	0.9345	0.059	36
0.0462	-0.041	11	0.5192	-0.030	51	0.9706	0.034	35
0.0604	-0.051	8	0.6052	-0.002	21	0.9798	0.025	35
0.0917	-0.068	3	0.6774	0.021	-24	0.9889	0.014	13
0.1543	-0.086	13	0.7304	0.038	-63	0.9911	0.011	14

^aUnits : $\text{cm}^3\cdot\text{mol}^{-1}$

2.5 Results

Table 2.4 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
<i>o</i> -xylene + (1-x)1-PrOH								
0.0106	-0.008	2	0.2683	-0.047	5	0.7666	0.094	-3
0.0197	-0.015	-4	0.3231	-0.038	-1	0.7998	0.100	-11
0.0316	-0.023	-13	0.3851	-0.027	-7	0.9010	0.094	8
0.0427	-0.029	-4	0.4678	-0.005	9	0.9574	0.055	5
0.0716	0.038	24	0.5324	0.013	7	0.9777	0.032	7
0.1248	-0.052	10	0.6174	0.042	-1	0.9804	0.028	0
0.1984	-0.057	-22	0.7097	0.076	-1	0.9942	0.009	0
<i>o</i> -xylene + (1-x)2-PrOH								
0.0298	-0.009	-6	0.2988	0.042	-12	0.7223	0.194	58
0.0356	-0.012	-16	0.3313	0.057	-12	0.7457	0.193	-16
0.0580	-0.014	0	0.3819	0.083	-7	0.7968	0.190	-21
0.0788	-0.017	-10	0.4595	0.117	-17	0.8742	0.165	-20
0.1353	-0.013	-3	0.5156	0.142	3	0.8961	0.151	-9
0.1433	-0.012	2	0.5390	0.152	11	0.9442	0.106	43
0.1915	0.002	26	0.6245	0.176	0	0.9707	0.061	8
0.2523	0.024	18	0.6885	0.193	35	0.9848	0.034	10

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.4 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
<i>xm</i> -xylene + (1-x)MeOH								
0.1193	0.003	2	0.5154	0.026	10	0.8346	0.046	-10
0.1735	0.002	16	0.6006	0.032	21	0.8639	0.045	-13
0.2058	0.004	2	0.6755	0.038	12	0.9398	0.035	37
0.2845	0.009	-19	0.7622	0.042	-24	0.9642	0.024	27
0.3509	0.015	-10	0.8117	0.046	-8	0.9821	0.013	13
0.4371	0.020	-3	0.8250	0.047	-6	0.9907	0.007	8
<i>xm</i> -xylene + (1-x)EtOH								
0.0172	-0.009	3	0.2647	-0.034	5	0.7655	0.086	-11
0.0377	-0.019	1	0.3541	-0.020	-4	0.8265	0.093	-2
0.0484	-0.021	27	0.4165	-0.006	2	0.8802	0.085	-16
0.0667	-0.028	19	0.4643	0.006	10	0.9374	0.065	35
0.1064	-0.038	-1	0.5155	0.019	7	0.9674	0.037	8
0.1725	-0.043	-11	0.5604	0.032	15	0.9789	0.026	7
0.2206	-0.042	-27	0.6833	0.066	-16	0.9907	0.014	21

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.4 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
<i>xm</i> -xylene + (1-x)1-PrOH								
0.0122	-0.005	1	0.3011	0.016	10	0.8548	0.133	10
0.0260	-0.008	21	0.3795	0.032	-5	0.9212	0.102	26
0.0409	-0.011	29	0.4646	0.060	62	0.9627	0.058	12
0.0701	-0.015	30	0.5301	0.071	6	0.9756	0.040	9
0.1198	-0.017	13	0.6050	0.092	-3	0.9859	0.025	8
0.1977	-0.011	-34	0.7077	0.118	-37	0.9948	0.009	2
0.2565	-0.000	-50	0.7904	0.134	-20			
<i>xm</i> -xylene + (1-x)2-PrOH								
0.0151	0.003	-20	0.3148	0.148	-11	0.7831	0.293	-10
0.0273	0.005	-42	0.3865	0.193	-4	0.8668	0.256	-27
0.0411	0.011	-18	0.4768	0.239	-9	0.9311	0.183	15
0.0519	0.016	-10	0.5286	0.260	0	0.9722	0.090	5
0.1218	0.045	37	0.6010	0.283	22	0.9811	0.065	18
0.1967	0.080	31	0.6655	0.294	14	0.9905	0.039	58
0.2664	0.115	-24	0.7285	0.297	-7			

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

2.5 Results

Table 2.4 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
<i>mp</i> -xylene + (1-x)MeOH								
0.0206	-0.009	5	0.1915	-0.046	-4	0.7857	0.012	3
0.0268	-0.012	11	0.2503	-0.048	-23	0.8392	0.016	-14
0.0361	-0.016	-1	0.3105	-0.045	-13	0.9015	0.017	-6
0.0498	-0.021	8	0.3694	-0.039	8	0.9591	0.015	42
0.0606	-0.024	5	0.4535	-0.030	14	0.0907	0.009	7
0.1097	-0.036	5	0.5819	-0.014	18	0.9851	0.005	3
0.1600	-0.042	10	0.6879	-0.003	-21	0.9943	0.002	2
<i>mp</i> -xylene + (1-x)EtOH								
0.0207	-0.021	-2	0.4014	-0.061	-10	0.8480	0.074	-24
0.0302	-0.029	1	0.4770	-0.036	33	0.9100	0.068	-8
0.0513	-0.042	37	0.5293	-0.024	-6	0.9344	0.062	45
0.0944	-0.069	-2	0.5612	-0.009	37	0.9594	0.043	20
0.1594	-0.086	-2	0.6133	0.004	-13	0.9754	0.029	20
0.2174	-0.089	-10	0.6818	0.031	-5	0.9850	0.017	1
0.2583	-0.085	10	0.7506	0.055	-8	0.9885	0.014	1
0.3234	-0.079	-31	0.7915	0.067	-13			

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.4 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
<i>xp</i> -xylene + (1-x)1-PrOH								
0.0213	-0.011	19	0.3066	-0.038	14	0.8498	0.108	-4
0.0445	-0.026	-13	0.3802	-0.026	-9	0.9075	0.092	6
0.0576	-0.027	25	0.4421	-0.007	14	0.9558	0.056	8
0.0726	-0.033	17	0.4897	0.007	26	0.9740	0.037	16
0.1283	-0.047	2	0.5312	0.017	-14	0.9827	0.026	16
0.1886	-0.052	-17	0.6137	0.050	9	0.9923	0.012	4
0.2522	-0.050	-29	0.7342	0.090	-25			
<i>xp</i> -xylene + (1-x)2-PrOH								
0.0234	-0.004	0	0.3139	0.101	-10	0.7458	0.229	-6
0.0439	-0.001	-3	0.3891	0.136	-13	0.8158	0.216	6
0.0582	0.000	34	0.4668	0.172	29	0.8654	0.187	-17
0.0754	0.002	31	0.5308	0.194	27	0.9049	0.157	25
0.1281	0.012	-18	0.5809	0.208	15	0.9612	0.079	14
0.1862	0.037	-17	0.6236	0.216	-10	0.9793	0.045	8
0.2616	0.075	-7	0.6835	0.223	-39	0.9853	0.032	7

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.5. Excess molar volumes for $[x(C_mH_{2m}) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K, together with Δ , calculated from eqn. 2.14 and the coefficients in Table 2.11.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
x1-C ₆ H ₁₂ + (1-x)MeOH								
0.0979	0.121	25	0.3934	0.275	36	0.7934	0.229	-55
0.1434	0.160	-18	0.5430	0.280	75	0.8602	0.191	-60
0.2499	0.224	-81	0.7162	0.261	56	0.9414	0.112	20
x1-C ₇ H ₁₄ + (1-x)MeOH								
0.0843	0.188	6	0.4709	0.364	-8	0.7964	0.276	-47
0.2066	0.315	-31	0.5063	0.368	46	0.8565	0.231	33
0.3553	0.364	19	0.6531	0.343	-7	0.8968	0.180	-4
0.3586	0.362	-7						
x1-C ₈ H ₁₆ + (1-x)MeOH								
0.0501	0.148	13	0.4170	0.395	-1	0.7753	0.313	3
0.0994	0.248	-6	0.5372	0.383	48	0.8738	0.217	-123
0.1588	0.325	-34	0.5704	0.379	57	0.9544	0.107	30
0.2510	0.384	-34	0.6809	0.356	48			
x1-C ₆ H ₁₂ + (1-x)EtOH								
0.1005	0.034	20	0.3978	0.158	12	0.7546	0.230	22
0.1582	0.052	-25	0.4622	0.186	37	0.8030	0.209	-49
0.2414	0.089	-10	0.5488	0.213	27	0.8534	0.181	-39
0.2807	0.103	-39	0.6884	0.236	22	0.9405	0.099	14

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.5 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
x1-C ₇ H ₁₄ + (1-x)EtOH								
0.0854	0.097	14	0.5024	0.292	85	0.7871	0.268	-52
0.2307	0.201	-47	0.6620	0.305	59	0.8997	0.189	44
0.2629	0.217	-52	0.7693	0.278	-89	0.9603	0.088	-4
0.3586	0.263	42						
x1-C ₈ H ₁₆ + (1-x)EtOH								
0.0478	0.084	24	0.5375	0.352	87	0.8596	0.245	-106
0.1042	0.155	-47	0.5488	0.354	99	0.8955	0.206	-73
0.2457	0.275	-83	0.6943	0.338	20	0.9421	0.144	63
0.3947	0.334	14						
x1-C ₆ H ₁₂ + (1-x)1-PrOH								
0.0394	-0.320	123	0.3773	-0.038	-26	0.8027	0.116	-8
0.1273	-0.071	6	0.4873	0.012	-25	0.8362	0.112	-18
0.1995	-0.081	2	0.5917	0.056	73	0.9100	0.084	-4
0.2673	-0.071	-38	0.7237	0.108	18			
x1-C ₇ H ₁₄ + (1-x)1-PrOH								
0.0276	0.032	61	0.4013	0.123	-1	0.8314	0.180	-7
0.0779	0.001	35	0.4706	0.154	10	0.8736	0.151	-3
0.1747	0.031	-42	0.5563	0.189	0	0.9276	0.100	-8
0.3181	0.084	-4	0.6964	0.214	10			

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.5 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
x1-C ₈ H ₁₆ + (1-x)1-PrOH								
0.0492	0.023	120	0.3195	0.179	-48	0.6133	0.270	100
0.0900	0.053	71	0.4401	0.230	-71	0.7134	0.278	138
0.1673	0.100	13	0.5232	0.253	-32	0.8703	0.225	-191
0.2333	0.137	-44						
x1-C ₆ H ₁₂ + (1-x)2-PrOH								
0.0557	0.021	-54	0.3694	0.276	123	0.7268	0.397	-78
0.1294	0.061	2	0.4687	0.382	35	0.8254	0.296	54
0.1950	0.115	27	0.6039	0.427	-75	0.8910	0.205	57
0.2680	0.185	-10						
x1-C ₇ H ₁₄ + (1-x)2-PrOH								
0.0566	0.069	98	0.3505	0.393	26	0.7241	0.492	-57
0.1031	0.131	-59	0.4667	0.480	6	0.8704	0.312	14
0.1866	0.227	-9	0.6027	0.525	26	0.9409	0.160	37
0.2516	0.299	-24						
x1-C ₈ H ₁₆ + (1-x)2-PrOH								
0.0419	0.074	-11	0.3305	0.434	-1	0.7012	0.529	-4
0.0916	0.153	-13	0.4383	0.511	13	0.8534	0.363	-22
0.1633	0.253	-9	0.5435	0.555	-11	0.9401	0.170	51
0.2304	0.332	17						

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.6. Molar excess volumes for $[x(C_mH_{2m-2}) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K, together with Δ calculated from eqn. 2.14 and the coefficients in Table 2.12.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
x1-C ₆ H ₁₀ + (1-x)MeOH								
0.0569	-0.0342	-4	0.3897	-0.135	5	0.7610	-0.085	10
0.1004	-0.0568	9	0.0547	-0.125	-1	0.8573	-0.065	-27
0.1585	-0.0850	7	0.6810	-0.101	16	0.9283	-0.037	7
0.2456	-0.1187	-24						
x1-C ₇ H ₁₂ + (1-x)MeOH								
0.0996	-0.0171	1	0.04753	-0.029	1	0.7940	-0.006	13
0.2313	-0.0294	5	0.5985	-0.024	-23	0.8839	-0.001	6
0.3192	-0.0334	-5	0.7093	-0.013	8	0.9586	-0.000	-3
0.4035	-0.0328	-3						
x1-C ₈ H ₁₄ + (1-x)EtOH								
0.0482	0.0049	-6	0.4689	0.028	10	0.7266	0.020	-14
0.0937	0.0106	5	0.5331	0.026	-13	0.8035	0.016	-14
0.2453	0.0231	20	0.6477	0.023	-15	0.8990	0.011	13
0.3426	0.0266	14						
x1-C ₆ H ₁₀ + (1-x)EtOH								
0.0987	-0.0822	40	0.2958	-0.146	-86	0.6990	-0.026	29
0.1540	-0.1180	-33	0.3940	-0.120	48	0.8396	0.003	24
0.2474	-0.1398	-28	0.5382	-0.079	25	0.9166	0.004	-19

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.6 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
x1-C ₇ H ₁₂ + (1-x)EtOH								
0.0593	-0.033	14	0.3584	-0.047	-2	0.6985	0.039	7
0.0983	-0.050	-11	0.3997	-0.038	7	0.7939	0.050	-45
0.1642	-0.063	-13	0.4778	-0.016	34	0.9113	0.043	-24
0.1755	-0.063	-6	0.5466	0.002	38	0.9513	0.032	9
0.2292	-0.066	-28	0.5997	0.014	15	0.9579	0.028	5
x1-C ₈ H ₁₆ + (1-x)EtOH								
0.0997	-0.010	7	0.4006	0.026	56	0.6730	0.088	-57
0.1411	-0.014	-14	0.4711	0.040	11	0.7615	0.099	-40
0.2475	-0.009	-7	0.5355	0.068	97	0.0842	0.088	-56
0.3302	-0.001	-50	0.6132	0.082	17	0.9241	0.054	31
x1-C ₆ H ₁₀ + (1-x)1-PrOH								
0.0637	-0.054	66	0.5097	-0.085	12	0.7558	-0.050	17
0.1123	-0.083	108	0.6332	-0.073	74	0.8260	-0.033	-49
0.2544	-0.094	-11	0.7128	-0.060	57	0.9009	-0.015	-98
0.3968	-0.092	-66						
x1-C ₇ H ₁₂ + (1-x)1-PrOH								
0.0509	-0.036	89	0.3495	-0.034	-25	0.7378	0.059	47
0.0997	-0.047	27	0.4721	0.001	-7	0.8037	0.065	-51
0.1811	-0.055	-19	0.5744	0.028	31	0.8771	0.060	-65
0.2497	-0.052	-27						

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.6 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
x1-C ₈ H ₁₄ + (1-x)1-PrOH								
0.0400	-0.013	-117	0.3277	-0.005	-13	0.6815	0.089	95
0.0899	-0.025	-211	0.4429	0.039	32	0.7830	0.096	98
0.1657	-0.026	-251	0.5386	0.061	62	0.8960	0.080	72
0.2248	-0.017	-208						
x1-C ₆ H ₁₀ + (1-x)2-PrOH								
0.0560	-0.012	275	0.2954	0.102	135	0.7737	0.203	-77
0.0779	-0.010	327	0.3899	0.155	24	0.8970	0.110	74
0.1129	0.117	-815	0.5284	0.209	-41	0.8425	0.151	85
0.2067	0.055	198	0.6151	0.226	-71			
x1-C ₇ H ₁₂ + (1-x)2-PrOH								
0.0356	0.007	17	0.3668	0.188	32	0.7319	0.258	94
0.1008	0.025	87	0.5033	0.262	-31	0.8506	0.195	-20
0.1889	0.084	-32	0.5840	0.282	-13	0.9205	0.126	-85
0.2523	0.125	-52						
x1-C ₈ H ₁₄ + (1-x)2-PrOH								
0.0939	0.036	17	0.455	0.266	32	0.7899	0.236	94
0.1678	0.076	88	0.555	0.296	-31	0.8561	0.174	-20
0.2377	0.125	-32	0.697	0.290	-13	0.9322	0.094	-85
0.3422	0.205	-52						

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.7. Molar excess volumes for $[x(c\text{-C}_m\text{H}_{2m}) + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}]$ at 298.15 K, together with Δ calculated from eqn. 2.14 and the coefficients in Table 2.13.

x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$	x	V_m^{Ea}	$10^4\Delta^a$
$x\text{c-C}_5\text{H}_{10} + (1-x)\text{MeOH}$								
0.0343	0.094	-65	0.3369	0.490	13	0.6929	0.411	-8
0.0585	0.165	15	0.4634	0.488	-56	0.7579	0.364	-34
0.1212	0.296	19	0.5702	0.474	59	0.8086	0.326	30
0.2066	0.410	1	0.6397	0.439	-3	0.9234	0.167	-7
$x\text{c-C}_5\text{H}_{10} + (1-x)\text{EtOH}$								
0.0609	0.092	-12	0.2769	0.329	-7	0.6229	0.391	20
0.1158	0.167	-33	0.3286	0.360	-8	0.6813	0.372	-4
0.1432	0.203	-13	0.3848	0.383	2	0.8236	0.290	2
0.1511	0.218	41	0.4756	0.398	-22	0.9279	0.156	-9
0.2404	0.306	29						
$x\text{c-C}_5\text{H}_{10} + (1-x)1\text{-PrOH}$								
0.1401	0.044	32	0.4493	0.195	6	0.6763	0.235	31
0.2388	0.086	-65	0.4922	0.210	15	0.7812	0.208	0
0.3392	0.150	40	0.5624	0.226	2	0.8503	0.174	32
0.4015	0.175	-2	0.6193	0.226	-63	0.9088	0.118	-31
$x\text{c-C}_5\text{H}_{10} + (1-x)2\text{-PrOH}$								
0.0548	0.052	22	0.3971	0.341	-10	0.6713	0.415	-62
0.1431	0.131	-28	0.5007	0.399	27	0.7996	0.363	56
0.2469	0.232	32	0.5601	0.420	41	0.8623	0.286	-7
0.3347	0.296	-28	0.6203	0.422	-21	0.9608	0.101	-30

^aUnits : $\text{cm}^3\cdot\text{mol}^{-1}$

2.5 Results

Table 2.7 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
xc-C ₆ H ₁₂ + (1-x)EtOH								
0.0981	0.235	-26	0.3027	0.500	8	0.5686	0.548	-12
0.1896	0.388	5	0.4063	0.549	-8	0.7464	0.445	33
0.2479	0.456	20	0.4763	0.559	-11	0.8910	0.242	-25
xc-C ₆ H ₁₂ + (1-x)1-PrOH								
0.0939	0.213	-9	0.4851	0.418	-2	0.7152	0.317	-19
0.1769	0.328	23	0.5567	0.400	-1	0.7927	0.254	-21
0.2595	0.387	-16	0.6455	0.365	32	0.9068	0.133	21
0.3903	0.424	-3						
xc-C ₆ H ₁₂ + (1-x)2-PrOH								
0.0377	0.073	1	0.3741	0.501	-37	0.7838	0.489	-15
0.1276	0.229	-2	0.4682	0.557	25	0.8798	0.354	47
0.2313	0.372	-6	0.5319	0.471	-9	0.9355	0.212	-43
0.3041	0.452	27	0.6424	0.572	1			
xcC ₇ H ₁₄ + (1-x)EtOH								
0.0467	0.125	10	0.3636	0.496	-9	0.6484	0.516	-5
0.0689	0.180	52	0.4354	0.520	3	0.7015	0.495	4
0.1806	0.357	-21	0.5230	0.535	27	0.8020	0.414	-3
0.2292	0.409	-17	0.5893	0.528	-7	0.9137	0.234	-7

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.7 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
xc-C ₇ H ₁₄ + (1-x)1-PrOH								
0.0581	0.079	10	0.4253	0.342	9	0.7375	0.337	-20
0.1027	0.130	3	0.4894	0.358	12	0.8114	0.294	-2
0.1957	0.217	-11	0.5414	0.365	3	0.8619	0.249	42
0.2694	0.270	3	0.5956	0.367	-7	0.9477	0.112	-35
0.3356	0.305	-11	0.6696	0.360	-2			
xc-C ₇ H ₁₄ + (1-x)2-PrOH								
0.0328	0.056	-17	0.4382	0.452	15	0.7622	0.438	-1
0.1186	0.189	27	0.5108	0.477	-1	0.8290	0.372	18
0.2086	0.286	-28	0.6049	0.489	-23	0.8751	0.301	-8
0.2832	0.356	4	0.6821	0.481	8	0.9465	0.153	-10
0.3459	0.400	2						
xc-C ₈ H ₁₆ + (1-x)EtOH								
0.0609	0.119	-19	0.2161	0.310	-18	0.6531	0.381	-43
0.1026	0.189	15	0.4358	0.399	5	0.7518	0.351	39
0.1726	0.274	14	0.5361	0.403	13	0.9047	0.196	-15
xc-C ₈ H ₁₆ + (1-x)1-PrOH								
0.0499	0.056	9	0.3137	0.229	-23	0.8027	0.260	-7
0.0656	0.071	9	0.4041	0.266	11	0.8275	0.244	-9
0.0848	0.088	0	0.4689	0.285	28	0.8597	0.225	63
0.1896	0.170	24	0.5668	0.302	15	0.9133	0.156	-6
0.2525	0.199	-38	0.7171	0.292	-44	0.9689	0.064	-13

^aUnits : cm³.mol⁻¹

2.5 Results

Table 2.7 continued...

x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$	x	V_m^{Ea}	$10^4 \Delta^a$
$xc-C_8H_{16} + (1-x)2-PrOH$								
0.0515	0.064	29	0.3221	0.281	14	0.7381	0.356	-39
0.1002	0.107	-41	0.4044	0.326	21	0.8203	0.305	19
0.1958	0.193	-9	0.4848	0.357	-4	0.8959	0.213	27
0.2631	0.243	4	0.5854	0.381	-9			
$xc-C_{10}H_{20} + (1-x)EtOH$								
0.0418	0.047	57	0.2983	0.184	-7	0.6249	0.237	-2
0.0787	0.073	-18	0.3798	0.206	-11	0.7239	0.225	-6
0.1168	0.099	-9	0.4356	0.220	-8	0.8640	0.155	-29
0.1535	0.123	5	0.5600	0.238	22	0.9364	0.092	37
0.1800	0.136	-13						
$xc-C_{10}H_{20} + (1-x)1-PrOH$								
0.1036	0.022	20	0.3675	0.123	11	0.7749	0.193	-12
0.1546	0.038	7	0.4403	0.151	16	0.8682	0.156	43
0.2225	0.061	-27	0.5377	0.181	6	0.9683	0.045	-41
0.2776	0.0848	-14	0.7003	0.2019	-23			
$xc-C_{10}H_{20} + (1-x)2-PrOH$								
0.0975	-0.005	0	0.3736	0.092	8	0.7290	0.155	-42
0.1548	0.004	18	0.4457	0.122	17	0.8003	0.140	13
0.2283	0.029	0	0.5442	0.151	0	0.8763	0.104	30
0.2857	0.053	3	0.6022	0.161	-8	0.9421	0.053	1

^aUnits : $cm^3 \cdot mol^{-1}$

2.5 Results

Table 2.8. The coefficients B_r of eqn 2.14 for $[x(C_6H_5CH_3) + (1-x)C_yH_{2y+1}OH]$.

Alkanol	B_0	B_1	B_2	B_3
CH ₃ OH	-0.2463	-0.2965	0.1194	-0.2258
C ₂ H ₅ OH	-0.2486	-0.6345	0.1594	-0.4243
C ₃ H ₇ OH	-0.0596	-0.6348	0.2381	-0.3143
CH ₃ CH(OH)CH ₃	0.6456	-0.7757	0.2396	-0.4685

2.5 Results

Table 2.9. Coefficients B_r of eqn. 2.14 for $[x(C_6H_3(CH_3)_3) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K.

Alkanol	B_0	B_1	B_2	B_3
CH ₃ OH	0.6453	0.0073	0.6128	0.0827
C ₂ H ₅ OH	0.5870	-0.2251	0.6629	-0.6792
1-C ₃ H ₇ OH	0.8400	-0.3249	0.6706	-0.6989
2-C ₃ H ₇ OH	1.4764	-0.4158	0.7916	-0.6067

2.5 Results

Table 2.10. Coefficients B_r of eqn. 2.14 for $[x(o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2) + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}]$ at 298.15 K.

Mixture	B_0	B_1	B_2	B_3	B_4
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.0846	-0.1627	-0.0830	-0.2420	-
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.1653	-0.6280	-0.2215	-0.5512	-
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.0126	-0.5895	0.3745	-0.6326	-
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.5454	-0.7850	0.1610	-0.5709	0.4474
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	0.0966	-0.0998	0.1679	-0.3538	-
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	0.0569	-0.5360	0.2856	-0.4520	-
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.2529	-0.5250	0.4220	-0.6306	-
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.9985	-0.7949	0.1011	-0.8667	0.9347
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.1071	-0.2359	0.0198	-0.2153	-
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.1336	-0.6146	0.2107	-0.5969	-
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.0335	-0.6524	-0.4005	-0.4766	-
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.7254	-0.7028	0.2999	-0.5819	-

2.5 Results

Table 2.11. The coefficients B_i of eqn. 2.14 for $[x(C_mH_{2m}) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K.

Mixture	B_0	B_1	B_2	B_3
$x1-C_6H_{12} + (1-x)CH_3OH$	1.0991	0.0467	0.7376	-0.5219
$x1-C_7H_{14} + (1-x)CH_3OH$	1.4549	0.1019	1.0999	0.2344
$x1-C_8H_{16} + (1-x)CH_3OH$	1.5362	0.2938	1.4724	0.1275
$x1-C_6H_{12} + (1-x)C_2H_5OH$	0.7833	-0.6741	0.3180	-0.1842
$x1-C_7H_{14} + (1-x)C_2H_5OH$	1.1562	-0.2835	0.7447	-0.3740
$x1-C_8H_{16} + (1-x)C_2H_5OH$	1.3709	-0.0895	1.0080	-0.4342

2.5 Results

Table 2.12. The coefficients B_r of eqn 2.14 for $[x(C_mH_{2m-2}) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K.

Mixture	B_0	B_1	B_2	B_3
$x1-C_6H_{10} + (1-x)CH_3OH$	-0.5233	-0.2129	-0.1059	0.2374
$x1-C_7H_{12} + (1-x)CH_3OH$	-0.1149	-0.1064	0.0139	-
$x1-C_8H_{14} + (1-x)CH_3OH$	0.1098	0.0031	0.0098	-
$x1-C_6H_{10} + (1-x)C_2H_5OH$	-0.3808	-0.6484	-0.1054	-
$x1-C_7H_{12} + (1-x)C_2H_5OH$	-0.0566	-0.5312	0.0811	-0.2481
$x1-C_8H_{14} + (1-x)C_2H_5OH$	0.1929	-0.5917	0.2409	-

2.5 Results

Table 2.13. The coefficients B_r for eqn. 2.14 for $[x(c-C_mH_{2m}) + (1-x)C_yH_{2y+1}OH]$ at 298.15 K.

Mixture	B_0	B_1	B_2	B_3
$x C_5H_{10} + (1-x)CH_3OH$	1.9514	0.4342	0.9656	-0.1687
$x C_5H_{10} + (1-x)C_2H_5OH$	1.6064	-0.0402	0.5416	-0.5086
$x C_5H_{10} + (1-x)C_3H_7OH$	0.8450	-0.5754	0.0151	-0.2571
$x C_5H_{10} + (1-x)CH_3CH(OH)CH_3$	1.5852	-0.8136	0.3208	-0.1953
$x C_6H_{12} + (1-x)C_2H_5OH$	2.2415	0.0929	0.5840	-
$x C_6H_{12} + (1-x)C_3H_7OH$	1.6630	0.4139	0.5662	0.2748
$x C_6H_{12} + (1-x)CH_3CH(OH)CH_3$	2.2612	-0.5714	0.7348	-0.4252
$x C_7H_{14} + (1-x)C_2H_5OH$	2.1221	-0.1844	1.0334	-
$x C_7H_{14} + (1-x)C_3H_7OH$	1.4371	-0.3566	0.5649	-0.1863
$x C_7H_{14} + (1-x)CH_3CH(OH)CH_3$	1.8969	-0.6406	0.6743	-
$x C_8H_{16} + (1-x)C_2H_5OH$	1.6103	-0.0137	0.8618	-0.2123
$x C_8H_{16} + (1-x)C_3H_7OH$	1.1572	-0.4122	0.5879	-0.1477
$x C_8H_{16} + (1-x)CH_3CH(OH)CH_3$	1.4506	-0.6456	0.4786	-
$x C_{10}H_{20} + (1-x)C_2H_5OH$	0.9207	-0.2672	0.4438	-
$x C_{10}H_{20} + (1-x)C_3H_7OH$	0.6797	-0.6150	0.2116	-0.2023
$x C_{10}H_{20} + (1-x)CH_3CH(OH)CH_3$	0.5563	-0.6250	-0.1743	-

2.6 Discussions

2.6.1 Mixtures of benzene or a substituted benzene + an alkanol

(a) Previous work

Results for V_m^E for mixing benzene with C_1, C_2 , and C_3 alkanols have been reported previously by several workers.⁽⁹⁻¹¹⁾ These values have been used as a comparison for the work reported here. Values for V_m^E (toluene + an alkanol) have been reported in the literature. The (toluene + MeOH) system by Washburn and Lightfoot,⁽⁹²⁾ the (toluene + ethanol) system by Pardo and Van Ness⁽⁹³⁾ and by Myers and Clever,⁽⁹⁴⁾ the (toluene + 1-PrOH or 2-PrOH) by Narayana *et al.*⁽⁸⁴⁾ The more precise work of Pardo and Van Ness is very similar to the work presented here over most of the composition range, but is less negative than the values reported here by $0.010 \text{ cm}^3 \cdot \text{mol}^{-1}$ at the V_m^E (minimum) region at $x_1 = 0.25$. The results reported here are within the experimental errors calculated for the Myers and Clever data.⁽⁸³⁾ The results in this work, for both 1-PrOH and 2-PrOH, differ by $0.050 \text{ cm}^3 \cdot \text{mol}^{-1}$ from those of Narayana *et al.*⁽⁹⁵⁾

V_m^E at 298.15 K has previously been measured for $\{xo\text{-}C_6H_4(CH_3)_2 + (1-x)C_kH_{2k+1}OH\}$, ($k = 2$ or 3),^(93,96) $\{xm\text{-}C_6H_4(CH_3)_2 + (1-x)C_kH_{2k+1}OH\}$, ($k = 2$ or 3),^(93,96) and $\{xp\text{-}C_6H_4(CH_3)_2 + (1-x)C_kH_{2k+1}OH\}$, ($k = 2$ or 3).^(13,93,96) The V_m^E s reported in this work compare well with the literature values. In no case is the difference between the results reported here and those reported in the literature greater than $0.010 \text{ cm}^3 \cdot \text{mol}^{-1}$.

(b) This work

Studying the comparative plots of all the aromatic compounds in an alkanol, which are plotted in Fig. 2.11 (i) to (iv) - one observes that, for benzene, the general trend is an increase in V_m^E (maximum) as the carbon number of the alkanol increases. (See Table 2.14).

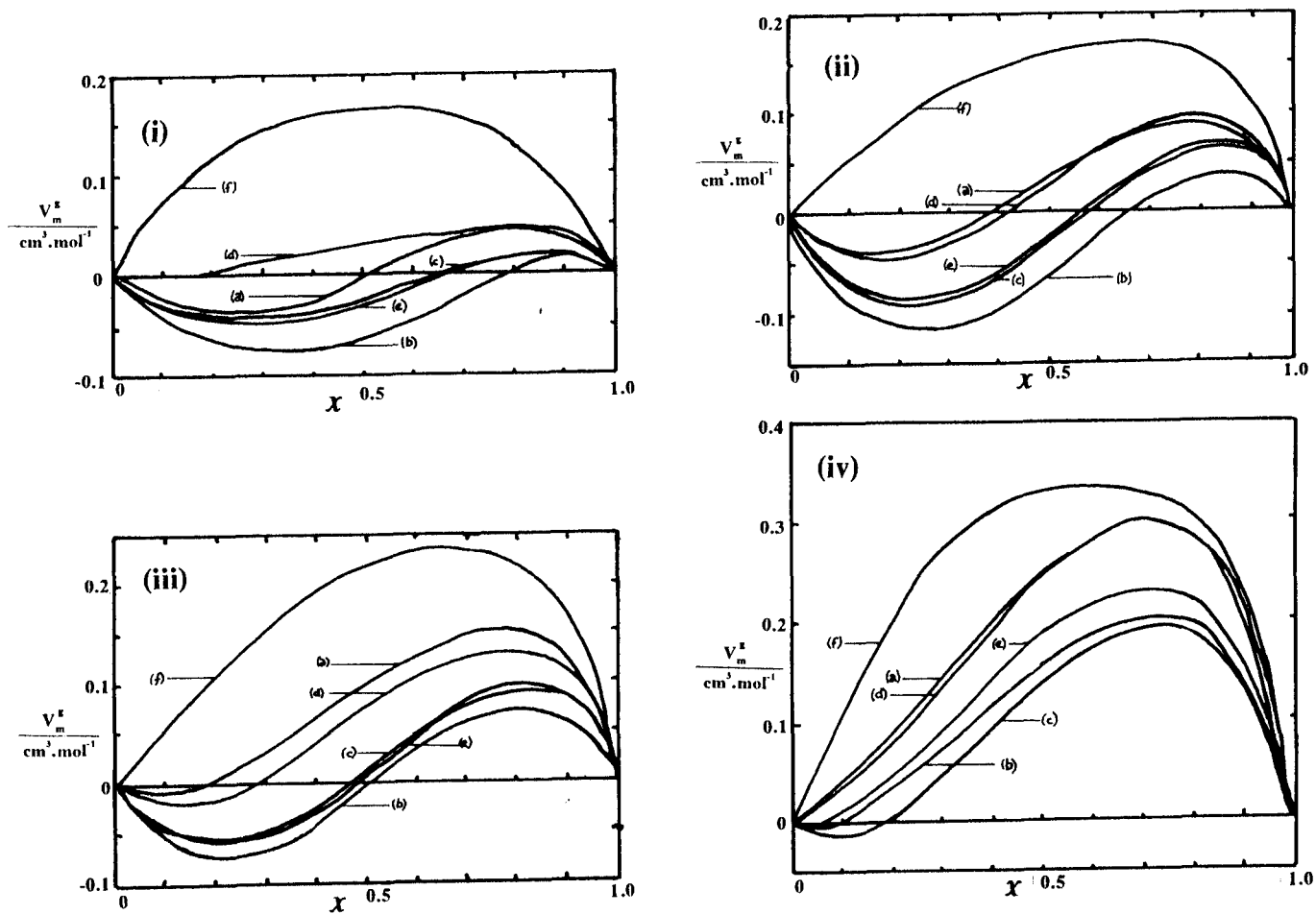


Fig. 2.11 : V_m^E for $\{xC_6H_{6-m}(CH_3)_m + (1-x)C_nH_{2n+1}OH\}$ at 298.15K: (a) C_6H_6 ; (b) $C_6H_5CH_3$; (c) $o\text{-}C_6H_4(CH_3)_2$; (d) $m\text{-}C_6H_4(CH_3)_2$; (e) $p\text{-}C_6H_4(CH_3)_2$; (f) $1,3,5\text{-}C_6H_3(CH_3)_3$. Where (i) methanol systems; (ii) ethanol systems; (iii) 1-propanol systems; (iv) 2-propanol systems. Taken from publication 8.

2.6 Discussions

Table 2.14. The $V_m^E(\text{maximum})$ for $x\text{C}_9\text{H}_{12} + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}$ and for $x\text{C}_6\text{H}_6 + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}$. The values of $x(\text{maximum})$ are given in parentheses. The results for the benzene mixtures have been obtained from the literature quoted in the discussion text.⁽⁹⁻¹¹⁾

Alkanol	$V_m^E(\text{maximum})^a$	
	C_9H_{12}	C_6H_6
CH_3OH	0.17(0.60)	0.03(0.80)
$\text{C}_2\text{H}_5\text{OH}$	0.17(0.75)	0.09(0.80)
1- $\text{C}_3\text{H}_7\text{OH}$	0.24(0.70)	0.15(0.70)
2- $\text{C}_3\text{H}_7\text{OH}$	0.39(0.62)	0.29(0.65)

^aUnits : $\text{cm}^3.\text{mol}^{-1}$

The (toluene + alkanol) and [(*o*-, *m*- or *p*-xylene) + alkanol] plots follow a similar trend - as can be seen from Fig. 2.11. To try and clarify these results, use was made of a qualitative interpretation of the excess volumes of (some component + an alkanol) outlined by several workers.^(41,97-99) According to the hypothesis put forward by these workers, V_m^E depends on the balance between two opposing contributions : (a) a positive term from the rupture of alkanol-alkanol hydrogen bonds and physical dipole-dipole interactions between alkanol monomers and polymers; and (b) a negative term from the formation of OH- π -electron hydrogen-bonded complexes, changes of free volume, and interstitial accommodation.

The $V_m^E(x)$ curves for most of the mixtures reported here, are sine-shaped, being negative at low x values and positive at high x values, see Fig. 2.11 (i), (ii), (iii) and (iv). This is probably due⁽⁹⁶⁾ to (a)-contributions being relatively important at high values of x , where the effect of the breaking of alkanol-alkanol H-bonds is proportionally very large. At lower values of x the dissociation of the alkanol is of less importance and the balance is essentially dependent on the magnitude of negative (b)-contributions.⁽⁹⁶⁾ This observation is confirmed by the results of mixtures of (a cycloalkane + an alkanol), (see later), where the OH- π -

2.6 Discussions

The mesitylene curves do *not* fit the pattern generated by the other five aromatic systems (see Fig. 2.11). This could be as a result of the molecular packing of mesitylene and highlights the difficulties in interpreting excess molar volume data. No other sets of excess volume data for mesitylene mixtures are available for comparison.

Studying the results, it has become apparent that the addition of, and position of, the $-\text{CH}_3$ group does not affect the V_m^E result as much as a variation in the alcohol-type does. For the set of results $V_m^E\{xo\text{- or }xm\text{- or }xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)(\text{C}_k\text{H}_{2k+1}\text{OH})\}$, ($k = 1, 2$ or 3), the $V_{m,\max}^E(\text{CH}_3\text{OH}) < V_{m,\max}^E(\text{C}_2\text{H}_5\text{OH}) < V_{m,\max}^E(\text{C}_3\text{H}_7\text{OH}) < V_{m,\max}^E(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)$ and in most cases $V_{m,\min}^E(\text{C}_5\text{H}_5\text{OH}) < V_{m,\min}^E(\text{CH}_3\text{OH}) < V_{m,\min}^E(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)$. Narayana *et al*⁽⁹⁵⁾ observed similar behaviour in mixtures of toluene + MeOH or EtOH or 1-PrOH. They argue that the almost equal values of V_m^E for the mixtures suggest that the positive V_m^E values are insensitive to the chain length. However, negative contributions get more and more sterically hindered⁽⁹⁵⁾ when the alkyl group in the alkanol becomes increasingly more branched, eg. toluene + 2-PrOH.

The excess partial molar volumes of these systems have been calculated in order for a more complete picture of the interactions to be obtained. In this work $V_1^E(x_1=0)$ and $V_2^E(x_2=0)$ (where 1 refers to the aromatic compound and 2 to an alkanol) have been calculated from equations 2.10 and 2.11, which in turn were calculated from the Redlich Kister coefficients B_r given in Table 2.10 from eqn 2.7. These results support the conclusions made above, as to the interactions and contributions that afford the V_m^E results. The $V_1^E(x_1=0)$ results are given in Table 2.15. In all systems, except for the (mesitylene + methanol) system, $V_1^E(x_1=0) \ll V_2^E(x_2=0)$. As in the case of $H_2^E(x_2=0)$ (see Chapter 3), the relatively large $V_2^E(x_2=0)$ is probably a result of the breakdown of the hydrogen bonding between the alkanol molecules when one mole of alkanol is added to an infinite amount of the aromatic component. Furthermore, the largest values of $V_2^E(x_2=0)$ are associated with the six systems involving 2-propanol. The relatively low values (usually negative values) for $V_1^E(x_1=0)$ could be a reflection of the association of the aromatic component and the alkanol. At low xylene

2.6 Discussions

concentrations relatively few alkanol-alkanol bonds break and one imagines that the alkanol network is largely intact. This is supported by the fact that methanol does not mix with *m*-xylene at low *m*-xylene concentrations.

The negative or small and positive values for $V_1^E(x_1=0)$ are likely to be due to the formation of π electron-hydrogen-bond (π -HO) interactions and also to interstitial accommodation of the aromatic compound between the hydrogen bonded alkanol network. The positive values of $V_2^E(x_2=0)$ are most likely due to the rupture of the alkanol-alkanol hydrogen bonds and alkanol dipole-dipole interactions.

It would be interesting to note the interactions between a chloro-substituted benzene and an alkanol. The electron withdrawing property of the Cl-group (as opposed to the electron-releasing property of the CH₃-group), should perhaps have more of an influence on the alkanol interactions - possible through H-Cl interactions. (See Chapter 3 for comments on H_m^E values of a chloro-substituted benzene + an alkanol).

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Table 2.15. $V_1^E(x_1=0)$ and $V_2^E(x_2=0)$ (where 1 = the aromatic component and 2 = the alkanol)

Mixture	$V_1^E(x_1=0)^a$	$V_2^E(x_2=0)^a$
$x\text{C}_6\text{H}_5(\text{CH}_3) + (1-x)\text{CH}_3\text{OH}$	-0.65	0.40
$x\text{C}_6\text{H}_5(\text{CH}_3) + (1-x)\text{C}_2\text{H}_5\text{OH}$	-1.15	0.97
$x\text{C}_6\text{H}_5(\text{CH}_3) + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.77	1.13
$x\text{C}_6\text{H}_5(\text{CH}_3) + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	-0.36	2.13
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.57	0.24
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-1.57	0.79
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.84	1.61
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	-0.20	2.51
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.19	0.72
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.65	1.33
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.48	1.83
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	+0.37	3.70
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.54	0.36
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.87	1.29
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.70	1.56
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	-0.26	2.31
$x\text{C}_9\text{H}_{12} + (1-x)\text{CH}_3\text{OH}$	+1.35	1.17
$x\text{C}_9\text{H}_{12} + (1-x)\text{C}_2\text{H}_5\text{OH}$	+0.35	2.15
$x\text{C}_9\text{H}_{12} + (1-x)\text{C}_3\text{H}_7\text{OH}$	+0.49	2.54
$x\text{C}_9\text{H}_{12} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	+1.25	3.29

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

2.6 Discussions

2.6.2 Mixtures of 1-alkenes or 1-alkynes + an alkanol

(a) 1-alkene + alkanol mixtures

At 298.15 K, CH_3OH does not mix in all proportions with the n-alkanes, n-hexane, n-heptane and n-octane,^(12-14,100) but does mix with the 1-alkenes, 1-hexene, 1-heptene, 1-octene, and the 1-alkynes, 1-hexyne, 1-heptyne and 1-octyne. These observations could be considered as evidence for specific interactions between the double bond of the 1-alkene and the hydroxyl group of the alkanol. The $V_m^E(\text{maximum})$ for 1-hexene, 1-heptene and 1-octene + ethanol (0.23, 0.30 and 0.35 $\text{cm}^3\cdot\text{mol}^{-1}$, respectively), and are less positive than those for hexane, heptane or octane + ethanol (0.45, 0.47 and 0.51 $\text{cm}^3\cdot\text{mol}^{-1}$ respectively).^(12-14,100) The fact that the $V_m^E(\text{maximum})$ for the 1-alkene + ethanol mixtures studied in the work are less positive than those for the related n-alkane + ethanol^(12-14,100) mixtures could be a result of the specific interaction of the double bond and the OH group. The $V_m^E(\text{maximum})$ for 1-alkene + ethanol is less positive than the $V_m^E(\text{maximum})$ for the respective 1-alkene + methanol mixture. As the alkanol chain length increases, at low x values the double bond-OH interactions become less significant in relation to the rupture of the OH-OH interaction - the latter becoming increasingly more contributive to the V_m^E result. The 2-propanol results are significantly larger than the 1-propanol results, this could be due to the steric effect of the methyl group adjacent to the C-OH bond on the 2-propanol.

The V_m^E results for 1-alkene + an alkanol are given in Table 2.5, and are plotted in Fig. 2.12.

2.6 Discussions

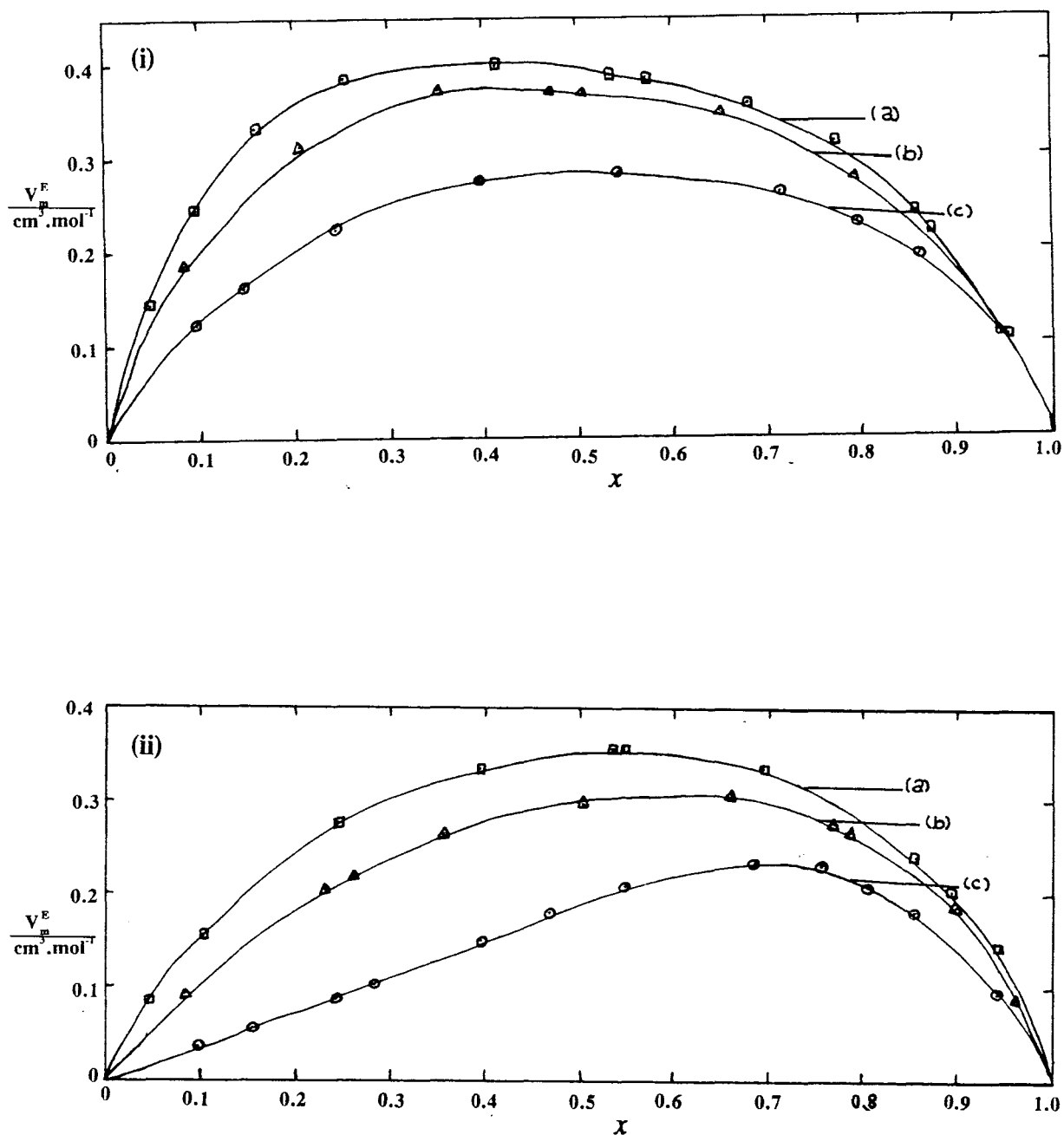
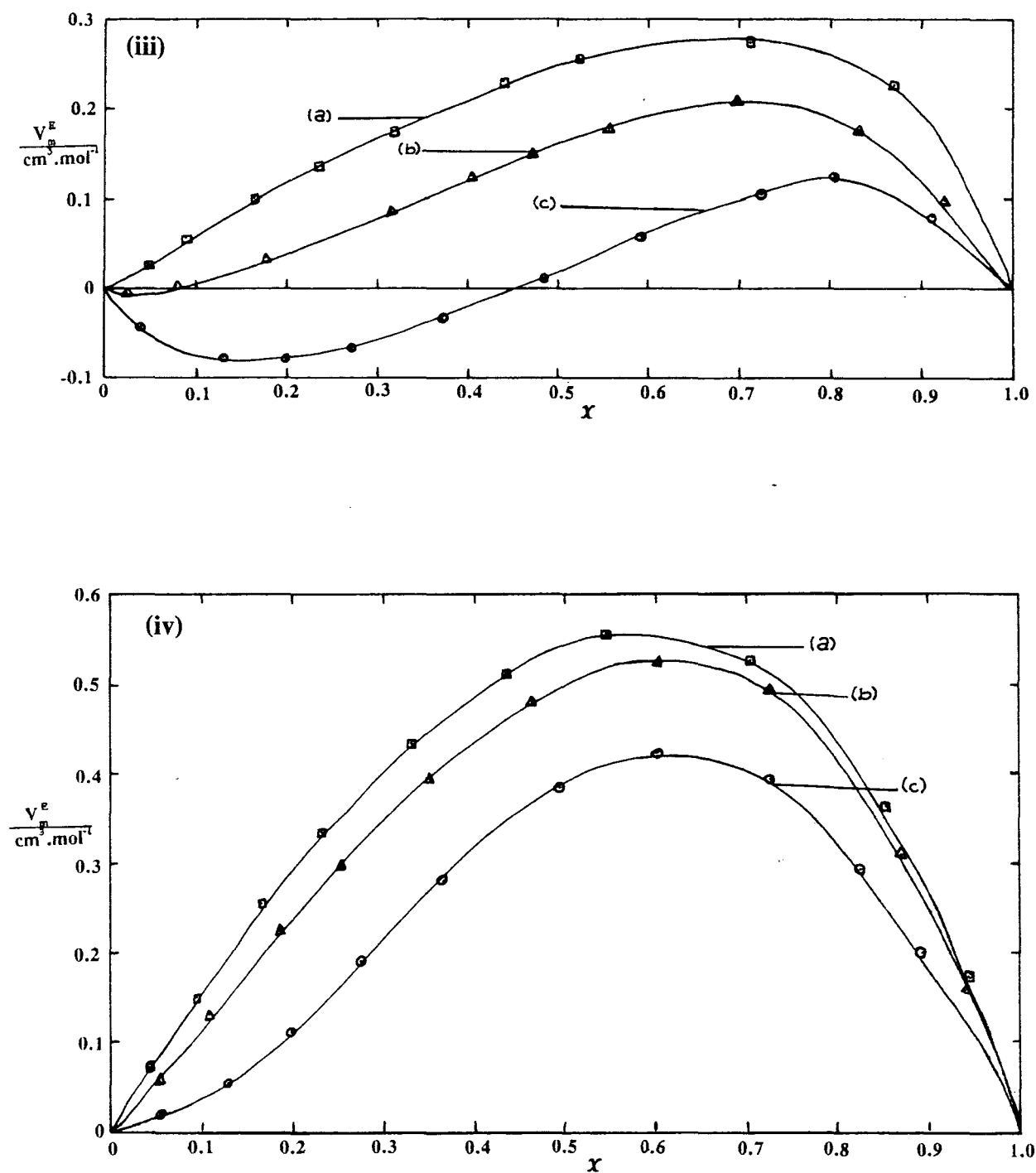


Fig. 2.12 : V_m^E for 1-alkenes + (i) methanol, or + (ii) ethanol; (a) 1-octene; (b) 1-heptene; (c) 1-hexene.



2.6 Discussions

(b) 1-alkyne + alkanol mixtures

The V_m^E values for 1-alkyne + an alkanol are given in Table 2.6, and are graphed in Fig. 2.13. Results for the 1-alkyne systems together with literature values for the n-alkane⁽⁹⁻¹¹⁾ systems are given in Table 2.16. The V_m^E for 1-hexyne, 1-heptyne or 1-octyne + methanol or ethanol reported here are dependent on the carbon number of the 1-alkyne. In both sets the V_m^E at any particular mole fraction is more positive the greater the carbon number of the 1-alkyne. All of these V_m^E results are significantly less positive than the V_m^E for n-hexane, n-heptane or n-octane + methanol or + ethanol. The fact that the V_m^E for 1-alkyne + ethanol is less positive than V_m^E for n-alkane + ethanol could be a result of the packing effect induced by the specific interaction of the triple bond of the 1-alkyne and the OH group of the alkanol.

Table 2.16. $V_m^E(x=0.5)$ for $x\text{C}_y\text{H}_{2y+2}$ and $x\text{C}_y\text{H}_{2y-2} + (1-x)\text{C}_z\text{H}_{2z+1}\text{OH}$ at 298.15 K.

Compound	$V_m^E(x=0.5)^a$			
	CH_3OH	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
C_6H_{14}	-	0.45	-	-
1- C_6H_{10}	-0.13	-0.08	0.09	0.20
C_7H_{16}	-	0.47	-	-
1- C_7H_{12}	-0.03	0.00	0.00	0.26
C_8H_{18}	-	0.51	-	-
1- C_8H_{14}	+0.03	0.06	0.05	0.28

^aUnits : $\text{cm}^3\cdot\text{mol}^{-1}$

As the chain length of the alkanol increases, so the $V_m^E(\text{maximum})$ increases. This can be seen from Fig. 2.13 (i) to (iv). The 2-propanol results, however, are significantly more positive than the 1-propanol results - this could be due to a larger contribution from the rupture of the OH-OH interactions. The partial molar excess volumes at infinite dilution

2.6 Discussions

have been determined, using the data in Table 2.12, in an attempt to gain further insight into the interactions involved. The partial molar excess volumes at infinite dilution at both ends of the concentration gradient for 1-alkyne + methanol or + ethanol mixtures again give some clue to the contributions of the overall V_m^E . The partial molar excess volumes for 1-hexyne, 1-heptyne or 1-octyne at infinite dilution in methanol or in ethanol are all negative except for one value. This is in contrast to the partial molar excess volumes for ethanol at infinite dilution in 1-hexyne, 1-heptyne or 1-octyne which are all positive except for one value. The values are given in Table 2.17.

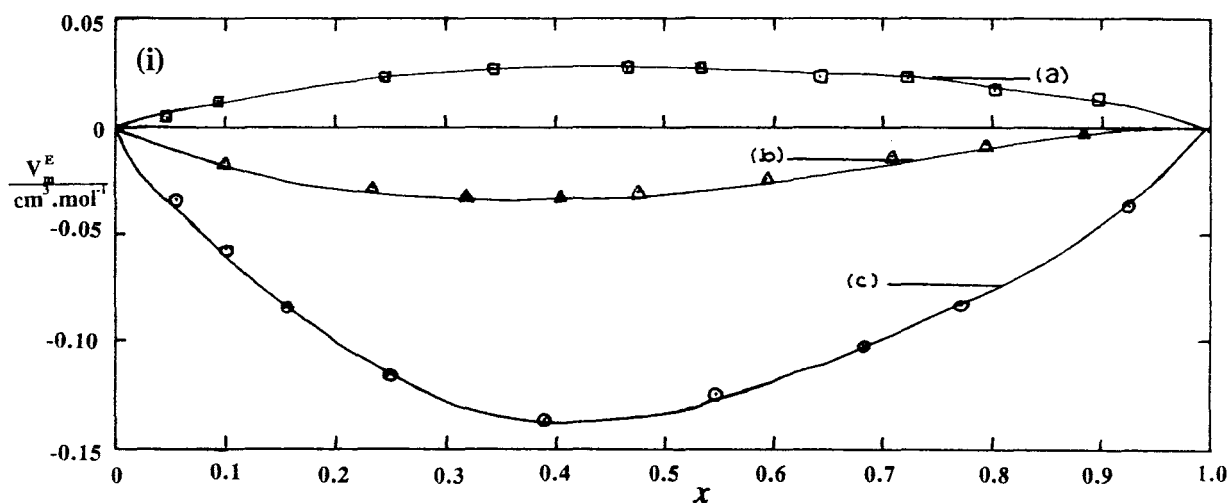


Fig. 2.13 : V_m^E for 1-alkynes + (i) methanol; (a) 1-octyne; (b) 1-heptyne; (c) 1-hexyne.

2.6 Discussions

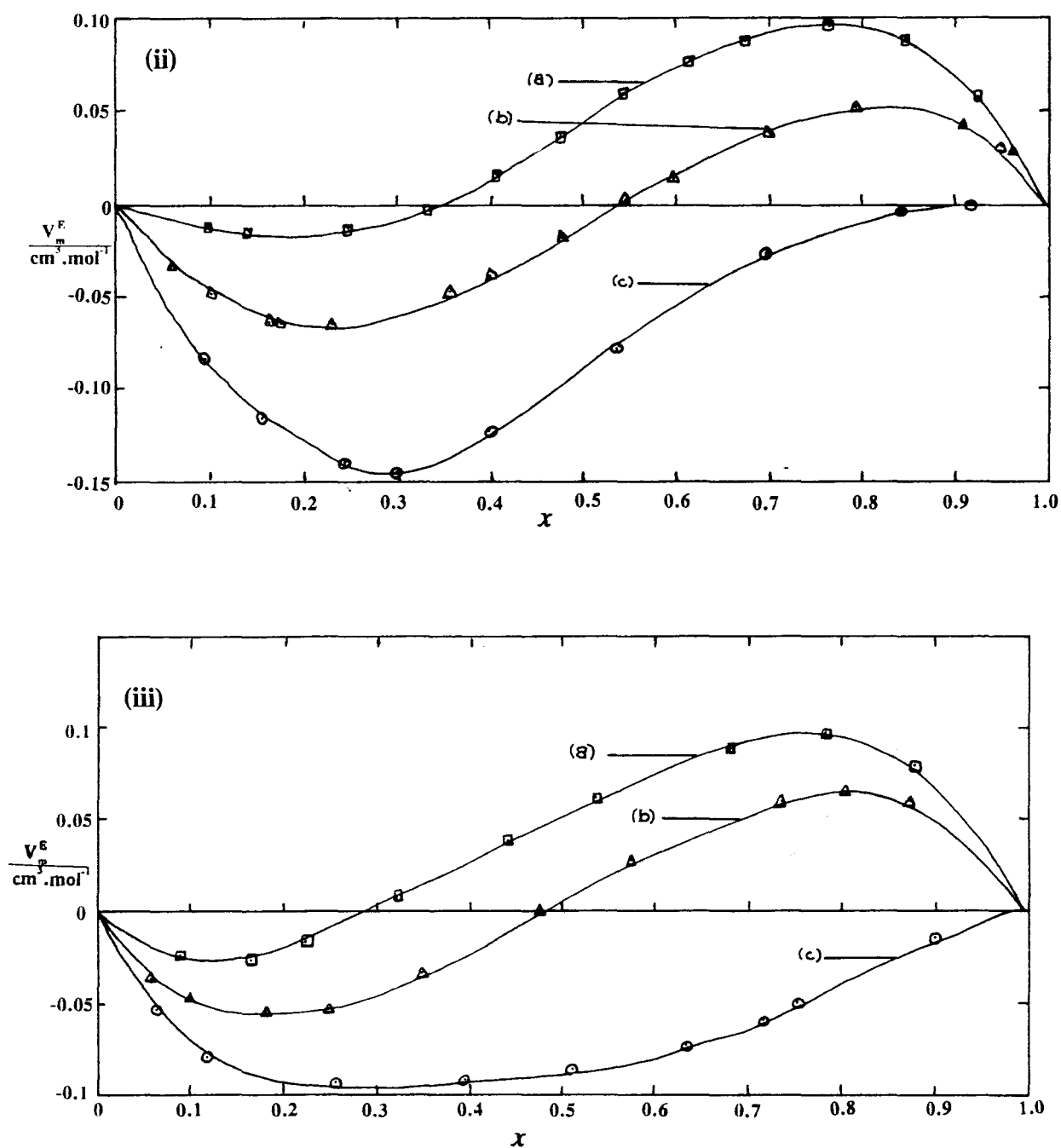


Fig. 2.13: V_m^E for 1-alkynes + (ii) ethanol, or + (iii) 1-propanol; (a) 1-octyne; (b) 1-heptyne; (c) 1-hexyne.

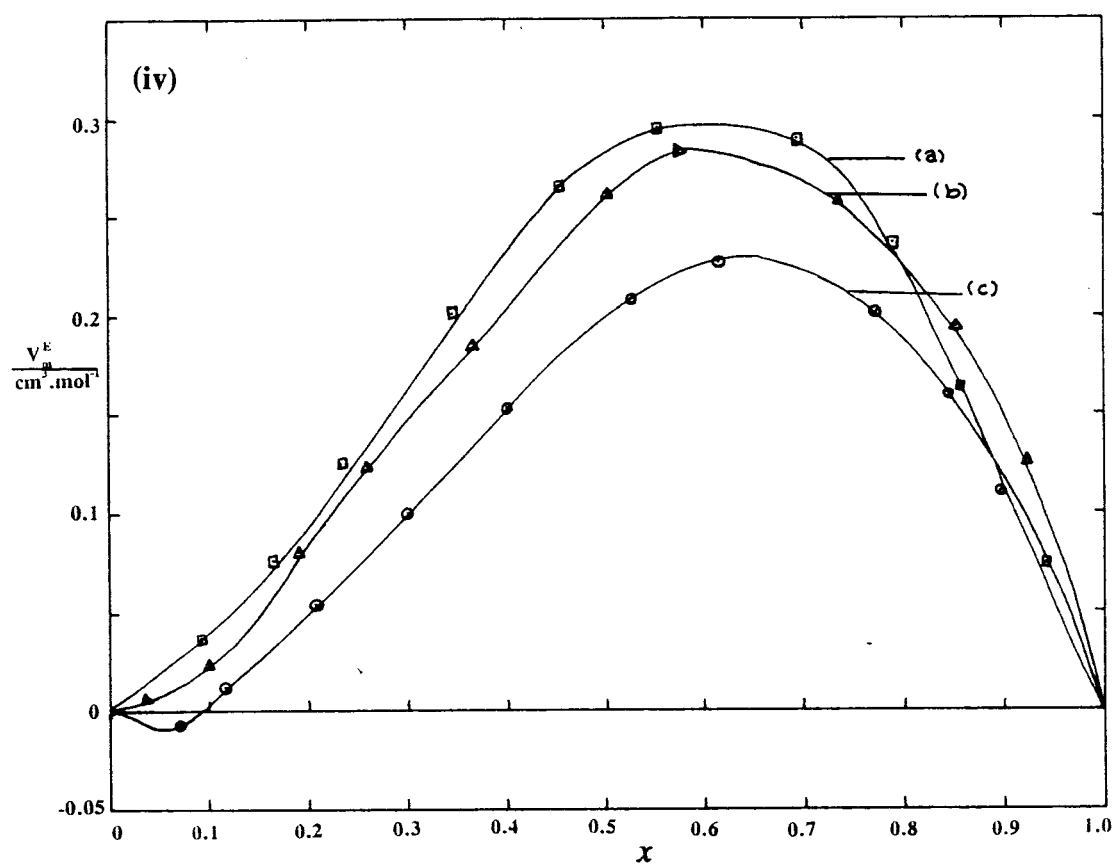


Fig. 2.13: V_m^E for 1-alkynes + (iv) 2-propanol; (a) 1-octyne; (b) 1-heptyne; (c) 1-hexyne.

Table 2.17. Excess molar volumes at infinite dilution, $V_1^E(x_1=0)$ and $V_2^E(x_2=0)$ for $x1\text{-C}_y\text{H}_{2y-2} + (1-x)\text{C}_z\text{H}_{2z+1}\text{OH}$.

y	z	$V_1^E(x_1=0)^a$	$V_2^E(x_2=0)^a$
6	1	-0.61	-0.65
6	2	-1.13	0.16
7	1	-0.21	0.01
7	2	-0.75	0.80
8	1	+0.12	0.12
8	2	-0.16	1.03

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

2.6 Discussions

The largely negative partial molar excess volumes for $V_1^E(x_1=0)$ reflect the weak dissociation of 1-alkyne molecules (small positive effect) and the association of 1-alkyne and ethanol (a negative contribution). This latter effect increases with decreasing 1-alkyne chain length. The positive partial molar excess volumes $V_2^E(x_2=0)$ for all systems other than 1-hexyne + methanol, is a result of the total dissociation of alkanol at infinite dilution (a positive effect) and the association of the 1-alkyne and alkanol (a negative contribution). The latter contribution again increasing with decreasing 1-alkyne chain length.

In conclusion, it can be seen that replacing the single bond by a double bond, followed by replacing the double bond by a triple bond - the effect produced is a decrease in V_m^E . As suggested earlier in the discussion, the possible explanation for this trend is the specific interaction of the multiple bond and the OH-group of the alkanol, this is superimposed on a positive effect of the (OH-OH) breakdown.

2.6.3 Mixtures of a cycloalkane + an alkanol

(a) Previous work

The V_m^E results for (cyclopentane + ethanol) and (cyclohexane + ethanol) are within $0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$ of the results reported by Marsh and Burfitt.⁽¹³⁾ The V_m^E s reported here for (cyclohexane + ethanol) and those of Marsh and Burfitt⁽¹³⁾ compare well to those reported by Pardo and van Ness⁽⁹³⁾ but differ by as much as $0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$, in the worst case, when compared to the published results of Scatchard and Satkiewicz.⁽¹⁰¹⁾ The results for (cyclohexane + 1-propanol) compare reasonably well with those published by Janssens and Ruez⁽¹⁰²⁾ and differ by only $0.012 \text{ cm}^3 \cdot \text{mol}^{-1}$ from their smoothing curve.

(b) This work

Only the MeOH V_m^E results for cyclopentane are presented here, as the other cycloalkanes

2.6 Discussions

were immiscible in MeOH. The V_m^E s for all the mixtures, except for (cyclodecane + 2-propanol) at low cyclodecane concentrations, are positive over the whole composition range. This is most likely a result of the breakdown of the hydrogen bonding between the alkanol molecules on addition of the cycloalkane. The $V_m^E(x=0.5)$ results for all sixteen systems has been plotted as a function of cycloalkane carbon number, k , in Fig. 2.14.

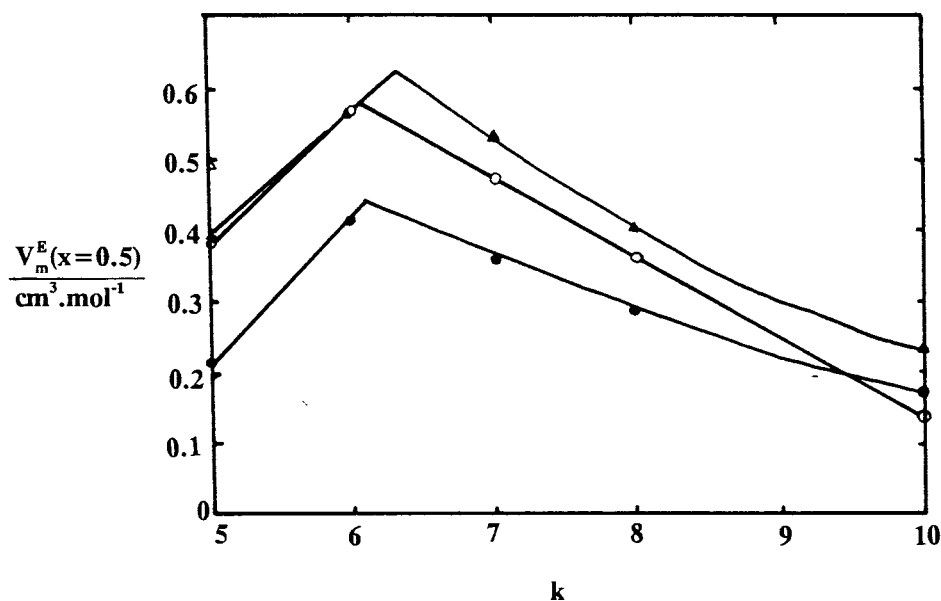


Fig. 2.14 : $V_m^E(x=0.5)$ for $\{xc-C_kH_{2k} + (1-x)C_lH_{2l+1}OH\}$ against k . $\triangle$, CH_3OH ; $\blacktriangle$, C_2H_5OH ; $\bullet$, C_3H_7OH ; $\circ$ $CH_3CH(OH)CH_3$.

The values for the cyclopentane systems are very much lower than the values predicted by the pattern generated by the other cycloalkanes. This is reminiscent of the $V_m^E(x=0.5)$ values obtained for cycloalkane + n-alkane mixtures.^{(103(a))} For these mixtures the $V_m^E(x=0.5)$ values for the cyclopentane systems are all less positive than the $V_m^E(x=0.5)$ predicted by the pattern generated by the cyclohexane, cycloheptane cyclooctane and cyclodecane systems. It is possible that the small size of the cyclopentane molecule results in a compact packing structure within the hydrogen bonded network of alkanol molecules, resulting in a small overall volume of mixing.

The magnitude of $V_m^E(x=0.5)$, for mixtures of a cycloalkane + a 1-alkanol is also dependant on the 1-alkanol chain length. From Fig. 2.14 for any given cycloalkane, $V_m^E(x=0.5)$

2.6 Discussions

decreases with increasing alkanol chain length. This could be a direct result of the fact that hydrogen bonding decreases in alkanols with increasing chain length. The breakdown of this hydrogen bonding on mixing results in methanol producing a more positive V_m^E than ethanol, and ethanol in turn producing a more positive effect than 1-propanol. The effect of the branched alkane chain in 2-propanol produces an effect which lies between that of ethanol and 1-propanol.

CHAPTER 3

Excess Molar Enthalpies of Mixing

3.0 Introduction

In principle⁽²⁾, the excess molar enthalpy H_m^E , may be derived from the temperature dependence of the excess molar Gibbs free energy

$$H_m^E = G_m^E - T(\partial G_m^E / \partial T)_p \quad 3.1$$

Practically, this is not considered a satisfactory method - as measurements of G_m^E rarely extend over a temperature range of more than 15 per cent of the temperature. Williamson⁽¹⁾ has reported that for measurements of G_m^E at two temperatures 30 K apart in the 300 K region, the relative error in the calculated H_m^E is roughly 15 times that of the error in the calculated G_m^E . It is thus necessary to measure H_m^E directly by means of a calorimeter.

In this work, an LKB flow-mix calorimeter was used to obtain results for the same systems described in Chapter 2 : mixtures of hydrocarbons (substituted benzenes or 1-alkenes or 1-alkynes or cycloalkanes) + an alkanol (methanol, ethanol, 1-propanol or 2-propanol). These results are discussed with reference to benzene + alkanol and alkane + alkanol results. In Chapter 5, the work reported in this chapter together with the V_m^E results from Chapter 2, are discussed in terms of the Flory theory.

3.1 Mixing calorimeters

Many types of calorimeters have been described.^(2,104-106) For precise measurements, the

3.1 Mixing Calorimeters

requirements are: there must be *no* vapour space - if this requirement is not adhered to, errors may arise due to evaporation or condensation of the components onto the walls of the mixing vessel - resulting in a heat effect and uncertainties of the composition of the mixture.⁽²⁾ McGlashan⁽¹⁰⁴⁾ has reported that a 20 per cent error of H_m^E can arise from a $0.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ vapour space. Care must be taken that no air bubbles are formed in the mixing vessel of a flow calorimeter - as, apart from forming a vapour space, the movement of bubbles may be interpreted as a thermal event. This last problem can be avoided by degassing the liquids before introducing them into the mixing vessel.

The liquids must be adequately mixed in the reaction vessel - and the composition of this mixture must be accurately known. The liquids must be at the correct measuring temperature. Finally, the volume change upon mixing must also be taken into account.⁽¹⁰⁴⁾ The latter can be a little difficult to evaluate - but for endothermic systems, where electrical energy is added simultaneously with mixing, equations relating H_m^E to the areas can be derived.⁽²⁾

3.1.1 Measurement of H_m^E by means of a mixing calorimeter

Calorimeters have been divided into 3 types in this short review, namely : (a) adiabatic, (b) isothermal and (c) flow.

McGlashan⁽¹⁰⁴⁾ has extensively reviewed the published work for mixing calorimeters used prior to 1961. Since then, shorter review articles have been published by Marsh,^(2,45,46) Becker⁽¹⁰⁵⁾ and McGlashan.⁽¹⁰⁶⁾ Hansen and Eatough⁽¹⁰⁷⁾ reported on a comparison of calorimetric methods in terms of the minimum energy effects that can be detected. The conclusion made was that the adiabatic flow method has the best potential detection limit - but that other criteria, such as sample size and the expected magnitude of the enthalpy change, need to be taken into account when a method of detection is chosen.

3.1 Mixing Calorimeters

(a) Adiabatic calorimeters

In this case, the liquid components are mixed in a vessel which is thermally isolated from its surroundings. If H_m^E is endothermic (positive) then the mixing vessel temperature is lowered. Usually, electrical energy is supplied to counteract this temperature drop. The addition of electrical energy thus reduces errors arising from heat losses, and H_m^E is exothermic (negative), then a second experiment is necessary to determine the amount of energy required to produce the same temperature *rise* - or, two identical calorimeters can be used.⁽¹⁰⁸⁾ A known amount of electrical energy is added to the second calorimeter such that the temperature difference between the two calorimeters is minimised.

In his review, McGlashan⁽¹⁰⁴⁾ concluded that the adiabatic calorimeters had two major problems: (i) the presence of a vapour space and (ii) they did not allow for volume changes which occurred on mixing. An improvement on this state of affairs was introduced by the calorimeter of Larkin and McGlashan⁽¹⁰⁹⁾ (see Fig. 3.1). It consists of a glass vessel with two compartments, **A** and **B**, in its upper half, and a side arm connected by a capillary, **C**, to an expansion bulb, **D**, via a greased joint, **EF**. A heating element, **H**, and four thermistors (**T**₁ to **T**₄) distributed over the surface of the mixing vessel form part of a Wheatstone bridge assembly. The vessel is filled completely with, and immersed in a bowl of, mercury. The mercury is displaced from the upper compartment by introducing weighed components of the mixture through the opening **F** by means of a hypodermic syringe. However, this is a cumbersome procedure and is prone to error.

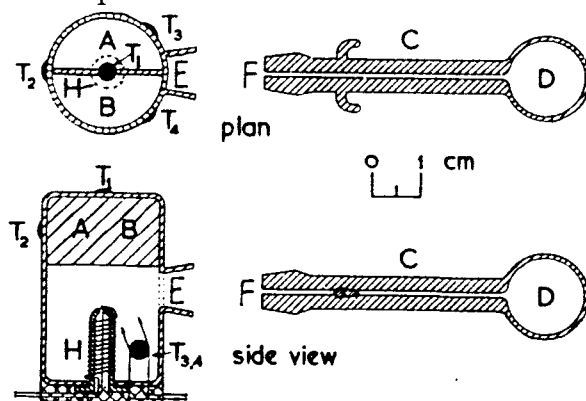


Fig. 3.1 : Adiabatic calorimeter of Larkin and McGlashan, taken from ref. (109).

3.1 Mixing Calorimeters

The loaded vessel with the capillary tube, C, half filled with mercury and attached at the ground joint, F, is placed in an evacuated enclosure within a thermostat until temperature equilibration is achieved. After temperature equilibration, the liquids are mixed in the absence of a vapour space by rotation of the apparatus through 180° , the direction of rotation being such that the liquid never comes into contact with the greased joint. The temperature change on mixing is measured by the four thermistors.

The precision of the apparatus has been quoted at $0.7 \text{ J} \cdot \text{mol}^{-1}$ or 0.5% of the maximum value of H_m^E .⁽²⁾ The method is particularly useful when only small quantities of sample are available, as measurements can be made on sample sizes as small as 1 cm^3 . One of the major disadvantages of the technique is that it is very slow, with each measurement requiring a separate loading.

Most of the subsequent measurements of H_m^E by means of the adiabatic method were made on modifications of the above calorimeter.⁽¹¹⁰⁻¹¹⁵⁾ These include a reduction in heat leaks and in the thermistor heat dissipation, and an amplification of the output bridge signal to a chart recorder.⁽¹¹²⁾ A modification of the filling port by Howell and Stubley⁽¹¹¹⁾ eliminates the need for immersing the calorimeter in a mercury trough when loading the reagents. The apparatus of Hill and Swinton⁽¹¹³⁾ only weighs 90 g, and thus the reagents can be weighed directly into the vessel placed on an analytical balance. A major limitation of these calorimeters is the possible chemisorption of the components onto the mercury⁽¹¹⁶⁾ - an unpredictable source of error.

(b) Isothermal calorimeters

Malcolm and co-workers^(117,118) described an isothermal apparatus based on the Bunsen calorimeter.⁽¹⁾ The mixing vessel of a Bunsen calorimeter is completely surrounded by a vessel containing a liquid - part of which is frozen to give a "mantle" around the inner walls - to which a capillary side-arm is attached. Any energy released or absorbed during the mixing

3.1 Mixing Calorimeters

process causes melting or freezing of the mantle. The volume change accompanying this process is measured by the movement of the mercury in the capillary tube. One advantage of a calorimeter of this type is that it can be used for measuring heat effects for slow processes. The major disadvantage of this technique is that measurements can only be made at the melting point of the calorimetric fluid.

An alternative to this is the isothermal dilution calorimeter.⁽²⁾ For an endothermic system, one component is slowly injected into the second with the simultaneous addition of sufficient electrical energy to maintain isothermal conditions. The excess enthalpy is again related to the composition of the mixture and the amount of energy required to maintain isothermal conditions. The apparatus is normally designed so that the entire composition range can be covered in two experimental runs.

The majority of the stepwise dilution calorimeters which are suitable for endothermic measurements⁽¹¹⁹⁻¹²⁵⁾ are based on the original design of Mrazek and Van Ness.⁽¹⁰⁾ An uncertainty of 2% in H_m^E is estimated using this apparatus. The instrument had a disadvantage that complete mixing of the two liquids was sometimes not achieved for mixtures of components possessing very different densities. The heating contribution resulting from the mechanical stirrer⁽¹¹⁹⁾ was eliminated by the addition of a cooling module in a later refinement by Winterhalter and Van Ness.⁽¹²⁰⁾ In these cases, a moving piston was employed to enclose the liquid and an error of 1% in H_m^E was reported.

Dilution calorimeters usually required approximately 50 cm³ of each component for analyses covering the entire composition range.⁽²⁾ The isothermal displacement calorimeter of Stokes *et al*⁽¹¹⁹⁾ and sample sizes of approximately 20 cm³ were used. A stirrer modification solved the problem of phase separation that had been observed in previous calorimeters of this type. The difficulty associated with sealing the mechanical piston without frictional heat being generated was overcome by the introduction of a mercury piston : the added liquid was accommodated through the displacement of mercury. Stokes *et al*⁽¹²²⁾ reported results with this

3.1 Mixing Calorimeters

instrument at 298.15 K for (cyclohexane + *n*-hexane) with a standard deviation of 0.09 J.mol⁻¹ and an absolute deviation of 0.07 J.mol⁻¹ compared to the IUPAC reference curve.⁽²⁾

A further modification to the apparatus by Stokes and co-workers^(122,123) in the form of a directly driven stirrer, initially introduced an undesirable dead volume of 0.03 cm³ around the stirrer shaft. This dead volume was later reduced to 0.008 cm³. Mixtures at various compositions were prepared by injecting known quantities of the pure components into the calorimeter from thermostated calibrated syringes, rather than by the method of Savini and co-workers,⁽¹¹⁹⁾ in which method mercury is weighed into feed bottles to restore the volume. An advantage of the Stokes and co-workers⁽¹²²⁾ apparatus, is that individual results at one temperature can be obtained much quicker by this apparatus than by a batch calorimeter, since the volume of sample added can be obtained directly from the calibrated syringes. Isothermal conditions are maintained either by direct electrical heating, for positive excess enthalpies, or through the use of a Peltier cooler, for negative excess enthalpies.

There are several disadvantages attributable to the use of mercury pistons - such as adsorption of the components onto the mercury surface. A modification by Stokes⁽¹²⁶⁾ incorporates a capillary exit in the mixing vessel. The mixture is thus allowed to escape from the mixing vessel as the second component is added. The reported error in H_m^E was of the order of 1.0 J.mol⁻¹ using this instrument.

An apparatus more suitable for measuring exothermic enthalpies was described by Gibbs and Van Ness.⁽¹²⁷⁾ A thermoelectric cooling module was used to remove energy at a constant rate - this energy is removed uniformly from the calorimeter, and no cold spots are produced. A similar apparatus was constructed by Murakami and Benson,⁽¹²¹⁾ with the adaptation of the cooling unit being situated in a second plug at the base of the vessel. Tanaka *et al*⁽¹²⁵⁾ reported on an apparatus which uses the Van Ness type⁽¹²⁷⁾ calorimeter, with a vessel of fixed dimensions in which mercury is displaced in the same manner as in the calorimeter of Stokes and Marsh.^(122,123)

3.1 Mixing Calorimeters

(c) Flow calorimetry

The most recent advances in calorimetry have been in the design of flow calorimetry. The two liquids are injected at a steady, known, rate into a mixing vessel, where complete mixing is achieved in the absence of a vapour space. The excess enthalpy is related to the power output of the heating element and the molar flow rates of the two components,⁽²⁾ (see later in the experimental section for the description of the relationship). The major advantage of the flow technique is that it gives rapid results while a precision of 1 % or better⁽¹²⁸⁻¹³⁰⁾ can be achieved. The system can be adapted to be either adiabatic or isothermal.⁽¹³¹⁾ The adiabatic condition is achieved when the flow cell and the temperature-sensitive elements are thermally insulated from their surroundings. In the isothermal mode, the heat of mixing in the reaction vessel is transferred to a heat sink.⁽¹³¹⁾

McGlashan and Stoeckli⁽¹³²⁾ have constructed a single cell flow calorimeter. The apparatus is represented in Fig. 3.2 - it was constructed of Teflon, with a mixing cell of 2.5 cm³.

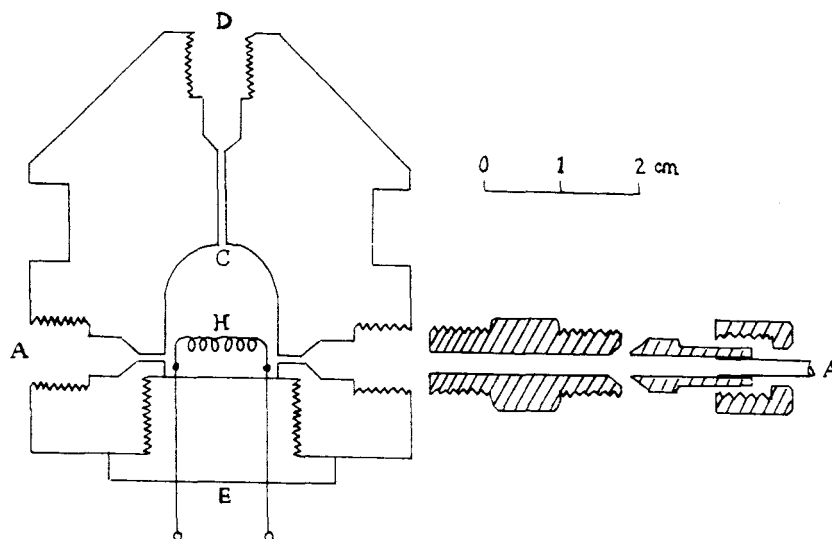


Fig. 3.2 : Flow calorimeter of McGlashan and Stoeckli.

This minimised any heat transfer from the mixing zone to the surroundings. The liquids are introduced at opposite sides of the mixing zone through the inlet ports, A, and mixing takes place in the mixing chamber, C. In the case of endothermic mixing, four thermistors sense the

3.1 Mixing Calorimeters

temperature drop. The temperature can be restored to the pure component temperature by passing an electrical current through the heater, H. McGlashan and Stoeckli⁽¹³²⁾ calculated an error in H_m^E of approximately 1%. However, a drawback of the apparatus was that 200 cm³ of component liquid was required to cover the whole composition range. In addition, heat losses *via* the heating wire and the thermistor leads were not accounted for. A similar calorimeter, designed by Sturtevant and Lyons,⁽¹³³⁾ used smaller sample sizes. However, the reproducibility of the results was only of the order of 2%.

Stoesser and Gill⁽¹³⁴⁾ reported on a twin flow microcalorimeter, with the aim of overcoming the problems of vapour space, mechanical stirring effects and wall effects, which occurred in some earlier batch type instruments. However, there was some doubt as to whether complete mixing of the liquids was achieved. The authors reported an error of 1% in H_m^E .

Monk and Wadso⁽¹²⁹⁾ designed a twin heat conduction calorimeter. The apparatus consists of a metal block heat sink, containing a centrally located heat exchanger unit surrounded by calorimetric units in a twin arrangement. The calorimetric units comprise two flow reaction cells surrounded by surface thermopiles in contact with primary heat sinks. The heat sinks are thermally isolated and are immersed in a water bath. Heat evolved or absorbed during the mixing process is thus conducted to or from a heat sink arrangement *via* the semi-conductor thermopile. Peristaltic pumps were used to introduce the liquids into the mixing cell. Monk and Wadso⁽¹²⁹⁾ observed a decrease in mixing efficiency when air bubbles became trapped within the mixing vessel. Thermal breaks within the flow lines were achieved by using PVC connections; these were ignored by previous workers such as Stoesser and Gill.⁽¹³⁴⁾

Hsu and Clever⁽¹³⁵⁾ observed that the use of peristaltic pumps with silicone tubing in the LKB microcalorimeter, a commercial instrument based on the design of Monk and Wadso,⁽¹²⁹⁾ presented limitations in the accuracy of the flows delivered. A maximum deviation of 22 J.mol⁻¹ was reported⁽¹²⁹⁾ from the IUPAC smoothing curve⁽²⁾ for the measured H_m^E of the system (cyclohexane + *n*-hexane). A heating effect due to frictional flow effects was not

3.1 Mixing Calorimeters

compensated for in this calculation.

Tanaka *et al*⁽¹³⁶⁾ have improved the performance of the LKB flow microcalorimeter. The temperature control of the air bath, in which the calorimeter unit is housed, was improved - in addition to the digitization of the thermopile and calibration circuits. Piston displacement pumps improved the quality of the liquid flows. A precision of better than 0.5 % for systems where the H_m^E at equimolar concentrations were of the order of 100 J.mol⁻¹ was estimated.

In an attempt to reduce the sensitivity of the apparatus to flow parameters such as the fluid velocity and the heat capacity of the fluids, Randzio and co-workers⁽¹³⁷⁾ modified a commercial UNIPAK 600 microcalorimeter. These modifications included active heat exchangers in a negative feedback loop - insuring that the temperatures of the pure components flowing into the cell are always equal to the thermostat temperature, irrespective of the flow parameters. Raal and Webley⁽¹³⁸⁾ have reported that these modifications are unnecessary if passive heat exchangers are designed in accordance with the guidelines set out in their publication.

Picker *et al*⁽¹³⁹⁾ used thermocouples instead of thermopiles in their isothermal differential flow calorimeter, as the large heat capacity of the thermopiles lengthened the thermal equilibration time. Mixing was achieved through turbulence as a result of reducing the inner diameter of the mixing cell to 0.2 mm. These workers estimated an accuracy of 1 % in their H_m^E data - this was supported by Grolier *et al*⁽¹⁴⁰⁾ who obtained an average deviation of less than 1.6 J.mol⁻¹ from the IUPAC smoothing equation⁽²⁾ for the (cyclohexane + *n*-hexane) system.

Picker and co-workers⁽¹⁴¹⁾ have investigated heat losses and boundary effects on calorimeter performance. They observed that the dilution of the second component by the first may occur through a process of molecular diffusion as a result of a thin film of liquid remaining on the walls of the mixing vessel. Errors of greater than 30 % in heating effects in some cases were attributed to this effect.

3.1 Mixing Calorimeters

Heat losses through heated lead wires have been minimized in a flow calorimeter design of Coomber and Wormald.⁽¹⁴²⁾ Lost energy is readsorbed by the pure liquids flowing over the lead wires. However, this calorimeter suffered a frictional heating effect through the stirrer shaft. The authors⁽¹⁴²⁾ estimated an error of 2% for endothermic H_m^E .

Raal and Webley⁽¹³⁸⁾ have developed a differential microflow calorimeter, in an attempt to reduce frictional effects arising from using the more viscous organic liquids. The priorities addressed in their study were : (i) complete temperature equilibration of the mixture components before mixing, (ii) separation of the frictional energy from the H_m^E , (iii) the elimination of heat leaks, and (iv) complete mixing of the components. The H_m^E results for the (cyclohexane + *n*-hexane) never differed by more than 0.53 J.mol⁻¹ from the IUPAC commission recommended values.⁽²⁾

The most recent developments are those on instruments capable of measuring H_m^E at high temperatures and pressures.^(130,143,144)

3.2 Experimental

3.2.1 Materials

A summary of the materials used in this work, their suppliers and purity, as well as methods of purification are given in the experimental section of Chapter 2.

3.2.2 Apparatus and experimental procedure

H_m^E results for the binary liquid mixtures reported in this work were carried out on a commercial LKB 2107-101 flow-mix microcalorimeter.

3.2 Experimental

(a) Instrument description and principle of operation

The mixing vessel arrangement for the LKB microcalorimeter is represented in Fig. 3.3.

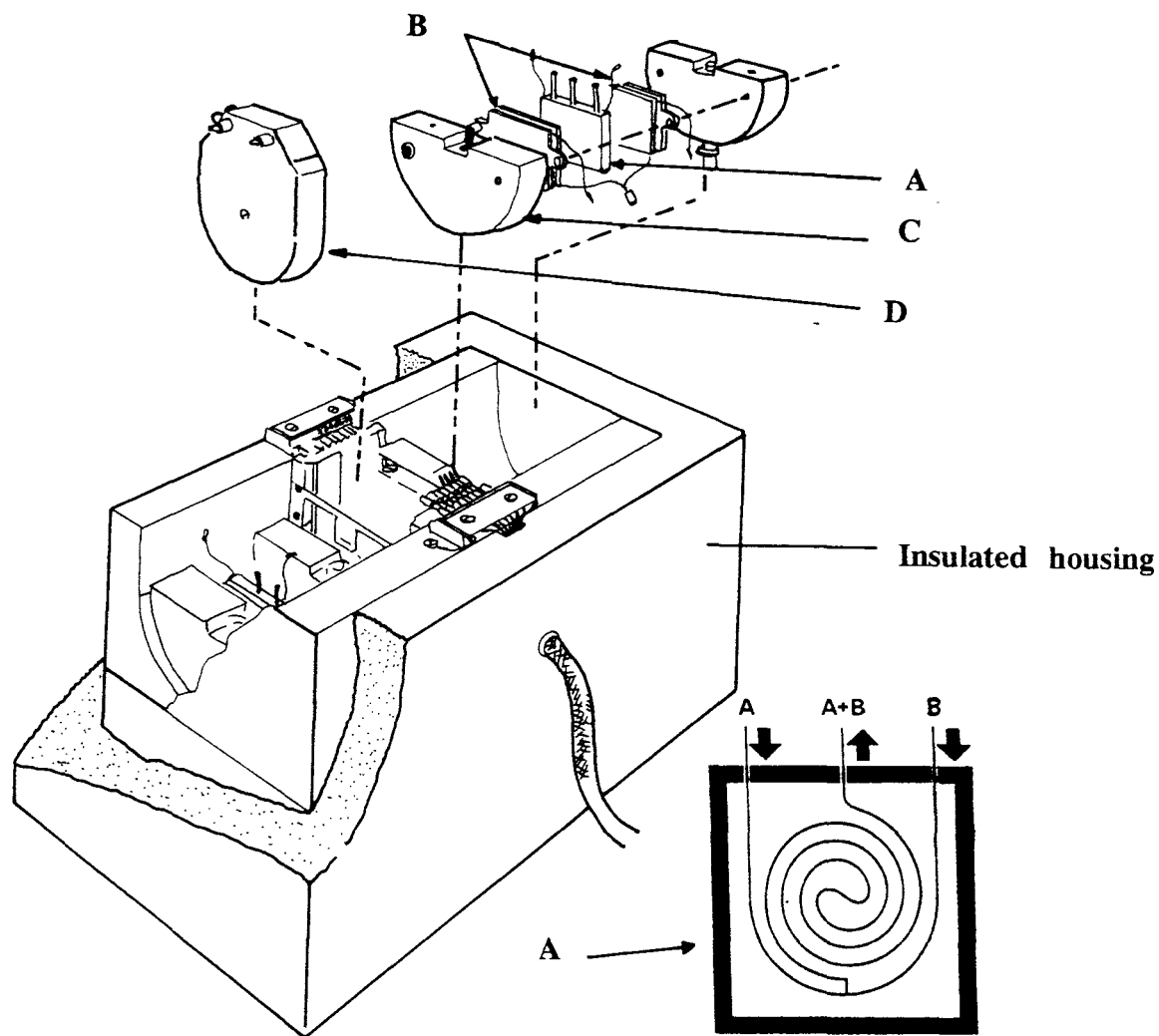


Fig. 3.3 : Representation of the LKB microcalorimeter and flow cell, taken from LKB manual.

3.2 Experimental

The mixing vessel, **A**, has two separate inlets and comprises a bifilar spiral-wound 24 carat gold tube of 1 mm i.d. and with a volume of 0.5 cm³. The cell design is such that adequate mixing occurs in the absence of a vapour space. The mixing vessel is in thermal contact with a pair of matched thermocouples in the thermopiles, **B**, and an aluminium heat-sink assembly, **C**, with heat sink compound covering all the surfaces of these items. An exothermic reaction results in heat flowing to the heat-sink assembly, while the opposite effect is observed for endothermic reactions. In each case the resultant temperature difference is detected by the thermopile positioned between the vessel and the heat-sink. The output from the thermopiles is amplified and fed to a digital readout system and a Perkin-Elmer 561 chart recorder.

The aluminium block heat-sink assembly is contained within an insulated housing. A heater and a temperature sensor are mounted within the main heat-sink. The entire arrangement is contained within an LKB thermostatically controlled air bath. To maintain the temperatures required for this investigation water, cooled to 278 K by a Grants refrigeration coil, was pumped through the thermostat by a Haak circulator at a rate of 500 cm³.min⁻¹.

The LKB microcalorimeter system was used in conjunction with an LKB control unit. The unit incorporates a power supply - this can be used to supply an adjustable current to the calibration heaters contained within the insulated mixing vessel assembly, and it also has a facility for heating and monitoring the temperature of the calorimeter heat-sink assembly. This heating facility may be used to reduce the equilibration time when raising the operating temperature - and must always be switched off when measurements are made.

Since liquids entering the microcalorimeter are required to be within 0.05 K of the experimental temperature, they were first routed through an external heat exchanger fitted into a recess in the bottom of the air bath of the thermostat unit and then through the internal heat exchangers, **D**, situated inside the insulated housing containing the mixing vessel assembly. Samples were introduced using two LKB 2102 Varioperpex II peristaltic pumps, capable of stable flow rates ranging from 0.03 - 2.0 cm³.min⁻¹. Viton tubing, 1.5 mm. *i.d.*, and Teflon

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tubing, 1.2 mm *i.d.*, were utilised in the pumps and flow lines, respectively, both types of which were unaffected by the liquids pumped through them. The calorimeter temperature - constant to within 0.01 K - was monitored by a Hewlett Packard 2804A quartz thermometer.

(b) Excess molar enthalpy measurements

An initial equilibration time of at least three days was required. Power to the equipment was left on continuously for the duration of the experimental determinations to ensure that thermal equilibrium was maintained in the temperature control units. The flow lines were filled with water overnight. In the morning, absolute alkanol was pumped through each flow line at a rate of 5 cm³.min⁻¹ for 15 minutes before the introduction of the component liquids. The two inlets were then separately flushed and primed with the two degassed components.

The calibration procedure discussed in the LKB instruction manual involves pumping a mixture, similar to the one under investigation, through the reaction vessel at a speed similar to that for the actual experimental determinations, which are henceforth conducted with respect to this new baseline. The procedure takes into account the heating effects due to friction resulting from pumping the liquids. However, the process is time consuming and wasteful of chemicals - thus a method similar to that described by Spiteri⁽¹⁴⁵⁾ was used.

A typical recorder output as a function of time, for a steady state H_m^E measurement is represented in Fig. 3.4.

3.2 Experimental

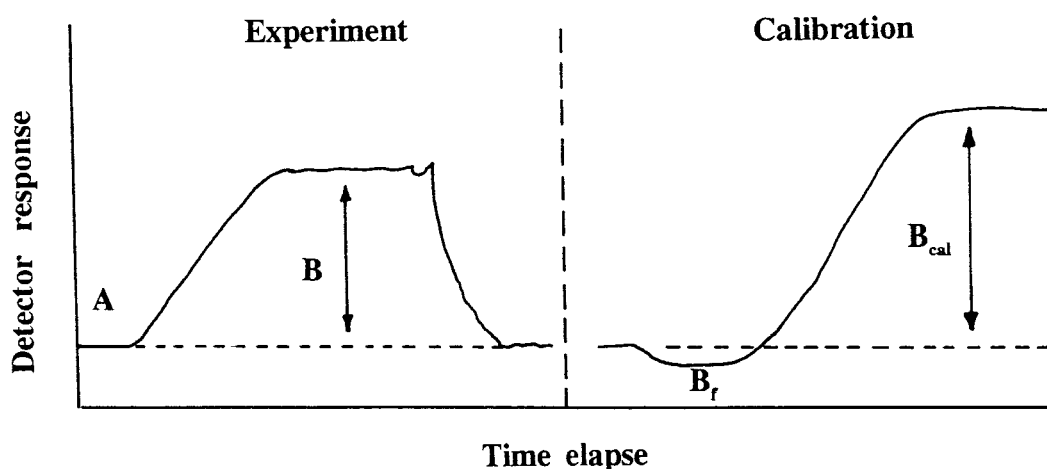


Fig. 3.4 : Representation of a chart recording for a flow calorimeter experiment .

Section A represents the steady state baseline obtained without any liquid flowing through the mixing vessel. This was always recorded before commencing a set of experimental measurements. Since accurate time elapse values were required for the determination of sample flow-rates, the pumps and a stop-watch were activated simultaneously, together with the addition of a calibration current to the calibration heater. This current was applied in order to restore the original baseline, in the case of an endothermic reaction. In the case of an exothermic reaction, enough current was supplied to reproduce this base line deflection, **B**. In practice, noise and non-uniform flow-rates, occurring at low flow-rates, produced regular baseline deflections on the recorder. The current was then adjusted so that the deflections were equal about the mean value (the zero-flow baseline).

Once the original baseline had been regained, the pumps were switched off. The molar flow rates f_1 and f_2 , were determined by weighing the two component flasks before and after each run - from these masses and the time elapsed for the experiment, the molar flow rates were calculated. A Mettler AE 240 electronic balance, accurate to 0.1 mg, was used for the mass determinations. The component flasks were 25 cm³ Quickfit conical flasks, fitted with modified B14 stoppers - which had two 1.8 mm *l.d.* inlets, one connected by Teflon tubing

3.2 Experimental

to the pump, and the other loosely capped with a rubber plug. The masses of effluent collected after each run were compared to the amounts of pure component consumed, thus serving as a constant check against liquid leaks in the system. For each new run, a new pumping rate was set, and the process repeated for each run.

(c) Friction effects and flow rate determinations

The values of the baseline deflections, B , and the corresponding currents, I , required to nullify these deflections were plotted for each system. In each case, the resulting graph together with the mixture from each run were employed to adjust the experimental readings for frictional effects. These calibrations were carried out collectively at the end of a series of experimental runs for a system. Each calibration involved purging the mixing vessel with the effluent from a particular run. With the same pumping parameters as were employed for that particular run, any heating effect due to friction exhibited a deflection, B_f , in Fig. 3.4. The experimental detector voltage shift was thus corrected to:

$$B_o = B - B_f \quad 3.2$$

The indicated calibration current, I_{cal} , corresponding to B_o , was then interpolated from the experimentally determined graph and was passed through the calorimeter heater, thereby producing a baseline deflection corresponding to B_{cal} in Fig. 3.4. The excess enthalpy was thus calculated from :

$$H_m^E = \{[B_o(I_{cal})^2 R]/B_{cal}\}/(f_1 + f_2) \quad 3.3$$

where R is the resistance of the calorimeter heater. However, it was observed that $B \cong B_{cal}$ for flow rates less than $0.70 \text{ cm}^3 \cdot \text{min}^{-1}$. Since the majority of the experimental runs were carried out at flow rates less than this, the above calibration became unnecessary in many cases, and H_m^E was then determined by

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$$H_m^E = (I^2R)/(f_1 + f_2) \quad 3.4$$

3.3 Results

The measured excess molar enthalpies H_m^E , are given in Tables 3.1-3.5, together with the deviations, Δ , calculated from the Redlich-Kister equation

$$\Delta = H_m^E/(J.mol^{-1}) - x(1-x)\sum_{r=0}^n A_r(1-2x)^r \quad 3.5$$

by the method of unweighted least squares. The coefficients A_r are given in Tables 3.6-3.10.

3.3 Results

Table 3.1. Molar excess enthalpies for $[x(C_9H_{12}) + (1-x)C_yH_{2y+1}OH]$ at 298.2 K, and the deviations Δ calculated from eqn 3.5 and the coefficients in Table 3.6.

x	H_m^E	Δ^a	x	H_m^E	Δ^a	x	H_m^E	Δ^a
CH₃OH								
0.0494	141.1	1.2	0.2885	569.4	-2.9	0.7039	812.9	-3.4
0.0882	235.0	-1.4	0.3992	682.5	5.1	0.8211	719.2	-2.8
0.1332	333.5	-0.7	0.4706	732.9	3.6	0.8915	550.4	-2.4
0.2159	475.8	-2.1	0.5686	788.6	2.4	0.9021	520.3	3.6
C₂H₅OH								
0.0738	222.4	1.8	0.4200	757.8	7.4	0.7350	883.1	-6.6
0.1532	402.5	-4.7	0.5255	830.8	3.7	0.8303	785.1	-2.2
0.2345	548.2	-1.2	0.6342	888.7	5.8	0.8680	700.3	3.1
0.3243	660.5	-1.8						
1-C₃H₇OH								
0.0998	286.8	1.7	0.5029	963.3	4.1	0.7951	956.9	-3.4
0.2069	538.7	-5.9	0.5904	1025.5	6.8	0.8679	785.3	-0.1
0.2976	714.7	3.2	0.7176	1029.2	-4.5	0.9254	537.2	1.0
0.4053	862.7	0.0						
2-C₃H₇OH								
0.0865	375.4	-1.7	0.4411	1176.5	-1.9	0.7251	1188.2	-1.2
0.1607	630.1	2.5	0.5696	1267.9	-0.9	0.7632	1132.0	8.6
0.2383	837.9	4.1	0.5983	1265.7	-6.9	0.8009	1038.2	4.2
0.3326	1023.8	-0.9	0.6360	1263.4	-2.9	0.8947	680.2	-2.8

^aUnits : J.mol⁻¹

3.3 Results

Table 3.2. Excess molar enthalpies for $[x(\text{C}_6\text{H}_4(\text{CH}_3)_2) + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}]$ at 298.2 K and the deviations calculated from eqn 3.5 and the coefficients of Table 3.7.

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
<i>o</i> -xylene + (1-x)MeOH								
0.0575	138.8	1.7	0.4259	643.3	-1.0	0.7547	752.1	-4.9
0.1058	223.4	-6.0	0.4995	696.7	0.2	0.8260	704.7	-3.5
0.1617	325.8	3.6	0.6070	746.6	1.3	0.9004	563.3	7.3
0.2373	433.6	0.4	0.6755	762.6	1.4	0.9473	360.4	-2.2
0.3120	530.6	1.3						
<i>o</i> -xylene + (1-x)EtOH								
0.0835	178.4	-0.2	0.4070	683.5	-5.8	0.6954	865.3	-2.0
0.1512	311.3	-0.7	0.5430	810.2	6.8	0.7788	840.2	-5.1
0.2252	448.1	4.2	0.5993	840.7	4.5	0.8512	753.6	6.2
0.3234	587.9	-2.9	0.6435	852.8	-2.5	0.8852	656.0	-2.5
<i>o</i> -xylene + (1-x)1-PrOH								
0.1064	256.2	-1.1	0.4854	906.8	-4.8	0.7480	963.2	-4.2
0.1893	428.4	4.5	0.6081	982.3	4.4	0.8138	912.1	-2.5
0.2828	606.0	-4.1	0.6513	990.7	6.7	0.8699	810.9	2.3
0.3859	791.9	0.7	0.6963	980.3	-1.7	0.9284	580.4	-0.2
<i>o</i> -xylene + (1-x)2-PrOH								
0.0898	331.8	0.3	0.4888	1168.9	1.1	0.6563	1220.7	-1.0
0.1978	676.0	-1.6	0.5132	1183.7	-1.0	0.7000	1203.4	-1.8
0.2881	896.8	1.4	0.5517	1204.7	-1.0	0.8213	1029.4	0.5
0.3961	1076.3	1.7	0.6207	1226.4	2.5			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.2 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
<i>xm</i> -xylene + MeOH								
0.0567	133.4	-1.3	0.4301	633.3	-4.6	0.7670	733.9	-4.1
0.1046	230.4	2.4	0.5189	699.7	7.8	0.8423	675.1	-1.0
0.1589	323.2	3.3	0.5872	727.5	7.2	0.9077	530.5	4.7
0.2382	434.2	-2.2	0.6727	742.2	-0.3	0.9344	419.2	-2.1
0.3187	529.4	-6.1	0.7025	742.2	-3.6			
<i>xm</i> -xylene + (1- <i>x</i>)EtOH								
0.0777	157.8	-1.3	0.4249	696.2	-0.4	0.7186	850.3	-7.0
0.1402	287.5	4.7	0.4897	757.9	6.9	0.7569	849.4	-2.5
0.2079	405.1	-1.8	0.5221	775.9	1.8	0.8364	780.4	0.1
0.2968	545.8	-1.5	0.5803	818.7	8.8	0.8896	661.4	7.2
0.3951	658.4	-8.8	0.6822	849.9	-2.4	0.9206	531.7	-3.5
<i>xm</i> -xylene + (1- <i>x</i>)1-PrOH								
0.1002	239.9	-0.8	0.5152	921.0	3.6	0.7724	947.6	0.9
0.1796	408.9	3.1	0.5797	958.8	2.6	0.8017	914.9	-2.8
0.2637	570.1	-1.0	0.6325	980.4	6.6	0.8612	814.1	4.6
0.3721	752.2	-4.1	0.6791	975.0	-3.7	0.9078	650.8	-1.3
0.4631	868.5	-2.5	0.7297	964.9	-5.2			

3.3 Results

Table 3.2 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
<i>xm</i> -xylene + (1-x)2-PrOH								
0.1008	349.1	0.8	0.4716	1141.9	-0.7	0.7314	1165.1	-3.6
0.1795	613.1	1.6	0.5326	1180.6	2.8	0.8002	1075.8	-5.6
0.2604	827.3	-6.0	0.5714	1199.0	7.1	0.8676	891.6	-7.1
0.3680	1029.1	-5.7	0.6042	1205.4	6.4	0.9123	700.5	5.3
0.4211	1100.7	1.8	0.6692	1200.5	2.8			
<i>xp</i> -xylene + (1-x)MeOH								
0.0680	139.5	-2.0	0.4368	615.7	-2.7	0.7142	720.8	3.6
0.1174	227.2	4.3	0.5616	680.5	-3.2	0.7430	715.0	-3.0
0.2186	376.1	4.2	0.6058	705.3	8.3	0.8174	689.6	-5.1
0.2934	465.9	-6.2	0.6519	709.4	1.7	0.8754	617.4	-2.5
0.3419	526.8	-3.1	0.6739	715.0	3.2	0.9136	520.5	2.4
<i>xp</i> -xylene + (1-x)EtOH								
0.0701	123.5	-1.2	0.5106	740.2	-0.6	0.7381	806.2	-2.7
0.1289	222.3	1.8	0.5693	778.0	5.5	0.7700	801.3	-1.9
0.1958	336.7	5.2	0.6095	790.5	2.6	0.8188	774.2	-0.5
0.2819	470.6	-3.8	0.6589	805.3	3.8	0.8748	685.8	-2.5
0.3860	615.6	-8.6	0.7039	810.0	1.5	0.9226	535.7	1.5

3.3 Results

Table 3.2 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xp-xylene + (1-x)1-PrOH								
0.0986	212.1	-1.0	0.5113	867.0	-5.4	0.7281	942.7	4.8
0.1780	358.5	2.1	0.5756	915.3	2.5	0.7963	899.8	-7.1
0.2604	513.5	3.6	0.6242	935.0	4.3	0.8900	732.5	-1.8
0.3549	674.6	-4.9	0.6543	940.3	3.1	0.9364	530.1	1.2
0.4605	820.2	-4.5	0.6981	942.7	2.1			
xp-xylene + (1-x)2-PrOH								
0.0539	190.0	1.6	0.4549	1090.6	2.6	0.7144	1156.0	-5.6
0.0936	324.5	1.7	0.5032	1140.6	13.0	0.7884	1065.2	-13.1
0.1672	550.4	-6.0	0.5649	1170.4	7.3	0.8585	905.1	3.9
0.2476	760.0	-5.8	0.6115	1181.4	3.2	0.8895	780.9	2.6
0.3614	978.4	0.9	0.6619	1175.9	-4.5			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.3. Excess molar enthalpies at 298.2 K for $[x(1-C_kH_{2k}) + (1-x)C_yH_{2y+1}OH]$ and the deviations calculated from eqn. 3.5 and the coefficients in Table 3.8.

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
x1-hexene + (1-x)MeOH								
0.0473	123.6	1.0	0.3462	497.4	3.7	0.6632	573.4	-0.1
0.1249	274.6	-0.8	0.4113	529.1	4.9	0.7693	530.9	-1.2
0.1915	363.2	-4.9	0.4845	553.2	3.4	0.8166	480.9	-5.6
0.2732	442.4	-4.0	0.5614	570.1	1.9	0.9221	285.0	1.8
x1-heptene + (1-x)MeOH								
0.0842	234.5	2.2	0.3346	516.3	-3.3	0.6852	590.8	1.4
0.1388	330.7	-4.8	0.4268	560.9	5.5	0.7775	540.1	-5.5
0.1833	399.6	1.1	0.5428	587.7	3.4	0.9065	340.0	1.1
0.2360	453.5	-0.5	0.6548	592.5	-0.7			
x1-octene + (1-x)MeOH								
0.0630	201.5	1.3	0.4650	596.3	1.8	0.7798	585.9	-4.9
0.1550	385.7	-2.1	0.5394	617.4	4.5	0.8273	550.2	6.6
0.2161	457.3	-6.6	0.6425	626.1	1.4	0.8655	480.1	-1.6
0.3216	546.3	5.3						

^aUnits : J.mol⁻¹

3.3 Results

Table 3.3 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
x1-hexene + (1-x)EtOH								
0.1220	167.1	0.7	0.5421	575.6	2.0	0.7798	585.9	-4.9
0.2417	332.3	-3.0	0.6556	616.1	0.9	0.8273	550.2	6.6
0.3196	414.7	-1.1	0.7132	613.1	-4.1	0.8655	480.1	-1.6
0.4466	521.3	4.3						
x1-heptene + (1-x)EtOH								
0.0696	136.8	2.3	0.3751	518.0	4.7	0.7310	648.1	-7.7
0.1289	235.9	-0.6	0.4855	591.9	8.2	0.8105	601.9	-4.3
0.1687	290.2	-6.8	0.6489	655.6	2.1	0.8712	513.0	3.9
0.1879	322.0	-1.8						
x1-octene + (1-x)EtOH								
0.0898	186.5	2.2	0.6120	660.7	7.3	0.8823	548.4	-4.9
0.1638	323.5	-3.2	0.7018	686.0	4.3	0.9102	478.7	4.2
0.2579	458.7	-5.4	0.7891	668.3	-6.9	0.9189	448.8	4.3
0.3385	538.6	-0.3	0.8669	580.4	-6.3	0.9384	365.5	-7.5
0.4576	605.0	5.6						

^aUnits : J.mol⁻¹

3.3 Results

Table 3.4. Excess molar enthalpies at 298.2 K for $[x(1-C_yH_{2y-2}) + (1-x)C_zH_{2z+1}OH]$ and the deviations Δ , calculated from eqn. 3.5 and the coefficients in Table 3.9.

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
x1-C ₆ H ₁₀ + (1-x)CH ₃ OH								
0.1073	115.8	-1.7	0.5727	573.6	-6.2	0.7863	628.5	4.0
0.2201	230.6	2.1	0.6439	623.1	-7.0	0.8260	590.8	10.0
0.2955	305.7	3.2	0.6800	641.4	-3.9	0.8818	477.5	4.3
0.3652	378.1	5.0	0.6439	623.1	-7.0	0.9550	224.1	2.5
0.4387	450.8	1.5	0.7331	647.7	-1.9			
x1-C ₇ H ₁₂ + (1-x)CH ₃ OH								
0.0750	89.7	1.3	0.3873	478.9	2.7	0.7695	754.2	-6.1
0.1558	200.4	-3.2	0.4631	550.6	4.9	0.8774	634.8	2.2
0.2342	322.4	-0.4	0.5683	644.7	4.1	0.9118	524.0	-0.1
0.3010	385.3	-3.4	0.6498	708.4	-1.9			
x1-C ₈ H ₁₄ + (1-x)CH ₃ OH								
0.1064	160.2	1.9	0.4200	573.6	1.7	0.7304	682.2	-5.1
0.1524	243.3	-0.2	0.4844	610.7	6.2	0.8089	660.4	-5.1
0.2025	328.9	-3.2	0.5771	648.5	6.9	0.9051	497.5	2.2
0.3005	465.2	-6.1	0.6555	670.9	0.7			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.4. continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
x1-C ₆ H ₁₀ + (1-x)C ₂ H ₅ OH								
0.1468	220.8	2.6	0.4844	612.6	3.7	0.7130	767.5	-3.2
0.2278	335.6	-3.1	0.5998	709.4	5.8	0.7493	773.1	-2.6
0.2879	410.7	-5.4	0.6660	754.4	5.1	0.7893	754.1	-9.7
0.3504	485.6	0.3	0.6923	766.4	3.5	0.8972	576.0	2.7
x1-C ₇ H ₁₂ + (1-x)C ₂ H ₅ OH								
0.1578	261.2	1.8	0.6123	816.6	6.8	0.7660	863.0	-1.1
0.2415	412.0	-2.8	0.6434	836.6	6.1	0.7955	842.6	-6.3
0.3814	605.8	-4.8	0.6789	850.2	0.1	0.8961	650.0	2.2
0.5012	727.2	3.1	0.7083	857.2	-4.8			
x1-C ₈ H ₁₄ + (1-x)C ₂ H ₅ OH								
0.0978	157.1	4.1	0.4259	615.2	3.9	0.6984	806.4	-0.2
0.1714	271.4	-10.3	0.5087	684.9	1.4	0.7460	808.8	-2.9
0.2981	470.9	-1.2	0.5967	753.7	2.4	0.8728	660.4	-2.7
0.3652	555.5	4.7	0.6641	792.4	-0.3	0.9451	380.2	1.1

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5. Excess molar enthalpies at 298.2 K for $[x(c-C_kH_{2k}) + (1-x)C_yH_{2y+1}OH]$ and the deviations Δ calculated from eqn. 3.5 the coefficients in Table 3.10.

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
$xc-C_3H_{10} + (1-x)CH_3OH$								
0.0747	249.8	-4.9	0.3754	556.1	-0.2	0.6735	513.6	-0.7
0.1332	375.9	4.0	0.4072	562.0	-0.7	0.7964	438.1	0.7
0.1953	452.5	1.3	0.4817	566.3	-0.6	0.8523	375.4	-3.7
0.2410	491.4	0.2	0.5762	553.7	2.7	0.9188	269.5	3.3
0.3009	526.0	-2.1						
$xcC_5H_{10} + (1-x)C_2H_5OH$								
0.0639	119.1	-4.7	0.4114	482.8	-4.3	0.6659	537.2	3.2
0.1251	210.3	-1.2	0.4836	519.4	-0.1	0.7752	497.7	-9.4
0.1911	297.0	5.9	0.5732	538.7	2.2	0.8863	404.5	3.6
0.2398	346.8	2.7	0.6205	541.0	3.7	0.9493	240.7	1.8
0.3365	430.9	-3.9						

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xc-C ₅ H ₁₀ + (1-x)C ₃ H ₇ OH								
0.1005	127.2	-2.2	0.5839	455.0	-5.0	0.7215	528.4	2.0
0.1833	200.4	1.0	0.5220	478.2	-1.9	0.7965	512.3	-5.2
0.3001	311.7	3.8	0.5610	500.7	4.6	0.8512	480.7	-3.3
0.4070	405.1	-0.7	0.6195	520.3	7.4	0.9183	376.4	6.6
0.4536	437.5	3.3	0.6833	521.0	-2.5	0.9581	232.8	-0.3
cx-C ₅ H ₁₀ + (1-x)CH ₃ CH(OH)CH ₃								
0.1025	192.7	-3.5	0.4137	604.8	-4.2	0.7757	662.8	-6.7
0.1745	304.3	-0.1	0.5225	685.9	-0.9	0.8427	595.6	0.2
0.1806	317.0	3.7	0.6040	715.3	3.7	0.9183	419.4	2.4
0.2971	477.8	2.5	0.6302	715.8	2.0	0.9503	291.2	0.8
0.3497	539.6	-1.2	0.7251	699.6	1.8			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xc-C ₆ H ₁₂ + (1-x)C ₂ H ₅ OH								
0.0983	241.1	0.7	0.4884	632.0	-2.4	0.7150	602.5	2.8
0.1736	361.5	-1.9	0.5317	637.7	-2.1	0.8009	540.5	-8.7
0.2558	473.5	4.2	0.5844	639.4	2.3	0.8619	475.0	-5.6
0.2586	570.1	0.2	0.6533	627.5	5.6	0.8967	426.2	9.9
0.4530	621.5	-2.7						
xc-C ₆ H ₁₂ + (1-x)C ₃ H ₇ OH								
0.1436	230.7	-1.7	0.5543	604.5	-3.8	0.7483	592.3	-5.0
0.2511	356.7	3.2	0.6018	619.5	2.8	0.8198	554.2	-1.5
0.3642	479.4	-0.9	0.6415	621.3	3.6	0.8936	451.6	1.1
0.4157	528.0	-1.4	0.6935	614.8	2.7	0.9344	338.2	1.4
xc-C ₆ H ₁₂ + (1-x)CH ₃ CH(OH)CH ₃								
0.1347	313.6	-4.2	0.5536	826.1	-0.9	0.7455	766.2	-6.1
0.2619	542.1	10.2	0.5942	836.7	4.6	0.8362	651.4	-7.6
0.3557	663.0	-5.5	0.6251	835.3	5.4	0.8991	517.6	8.4
0.4471	762.3	-6.1	0.6895	812.0	2.8			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xc-C ₇ H ₁₄ + (1-x)C ₂ H ₅ OH								
0.0889	243.6	-2.2	0.5299	660.9	-3.6	0.7526	592.1	-6.0
0.1641	383.4	0.1	0.6003	657.6	3.2	0.8369	530.3	-1.7
0.2447	499.7	4.0	0.6646	639.8	4.3	0.8891	449.3	-0.7
0.3431	594.8	-1.2	0.6856	630.6	2.7	0.9521	265.0	5.2
0.4076	635.9	2.1						
xc-C ₇ H ₁₄ + (1-x)C ₃ H ₇ OH								
0.0913	171.6	-5.2	0.4174	557.7	-2.6	0.6589	636.0	1.8
0.1685	296.5	4.6	0.5438	619.2	-2.1	0.7026	626.7	-2.4
0.2519	402.8	3.1	0.5850	633.6	3.4	0.8655	495.7	-9.8
0.3516	503.0	-3.6	0.6073	636.2	3.2	0.9132	407.2	10.1
xc-C ₇ H ₁₄ + (1-x)CH ₃ CH(OH)CH ₃								
0.0969	259.8	0.9	0.5051	837.1	2.7	0.6320	865.2	-7.0
0.1776	440.6	0.4	0.5462	860.1	3.3	0.7298	815.2	6.3
0.3191	656.4	-5.5	0.5732	865.0	-1.9	0.7998	690.6	1.9
0.4205	774.6	5.9	0.6003	867.9	-4.6	0.9008	388.0	-3.0

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xc-C ₈ H ₁₆ + (1-x)C ₂ H ₅ OH								
0.0793	237.1	-1.6	0.4362	615.0	-3.6	0.7244	575.8	2.2
0.1473	369.4	-1.7	0.4718	623.2	-1.4	0.8065	517.3	-6.1
0.2182	472.6	3.1	0.5023	624.6	-1.6	0.8695	442.8	-5.9
0.3047	557.2	3.9	0.5632	623.4	1.9	0.9219	345.1	9.7
0.3791	596.3	-2.7	0.6237	614.0	5.5			
xc-C ₈ H ₁₆ + (1-x)C ₃ H ₇ OH								
0.0430	95.5	-2.0	0.5220	617.6	3.6	0.8202	563.4	-1.8
0.1531	284.5	-0.5	0.5663	632.2	1.1	0.8772	476.6	-6.3
0.2314	394.2	2.8	0.6095	638.7	3.3	0.9151	395.2	3.9
0.3902	552.7	-6.0	0.6433	637.9	2.4	0.9542	255.3	5.0
0.4402	584.6	-1.8	0.7015	628.2	-0.2			

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
xc-C ₈ H ₁₆ + (1-x)CH ₃ CH(OHCH ₃)								
0.0631	192.9	-5.2	0.5287	788.6	0.2	0.7033	767.4	-4.6
0.1371	377.2	2.4	0.5852	796.1	2.1	0.7828	712.9	-7.2
0.2371	558.2	5.4	0.6093	796.8	3.5	0.8512	630.3	5.5
0.3402	675.3	-5.6	0.6459	793.1	4.4	0.9217	430.1	0.3
0.4458	757.1	-2.6						
xc-C ₁₀ H ₂₀ + (1-x)C ₂ H ₅ OH								
0.1168	450.2	0.7	0.4037	489.6	1.1	0.6513	450.4	1.5
0.2081	367.4	-1.3	0.4818	496.5	-1.3	0.7512	370.9	-1.4
0.3034	445.6	-0.5	0.5362	490.1	2.4	0.8921	211.0	0.7
0.3523	473.0	1.7	0.6034	474.3	1.7	0.9317	117.4	-0.5
xc-C ₁₀ H ₂₀ + (1-x)C ₃ H ₇ OH								
0.1394	246.2	-2.4	0.5350	489.4	-1.6	0.7236	460.2	1.5
0.2453	353.7	4.1	0.5736	494.2	0.9	0.7850	419.9	-0.7
0.3465	420.8	0.1	0.6019	494.0	1.8	0.8693	320.1	-10.0
0.4502	466.6	-4.2	0.6575	485.6	2.8	0.9321	223.1	10.3

^aUnits : J.mol⁻¹

3.3 Results

Table 3.5 continued...

x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a	x	H_m^{Ea}	Δ^a
$x\text{c-C}_{10}\text{H}_{20} +$ $(1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$								
0.0729	233.1	6.1	0.5037	662.2	-4.1	0.6512	658.2	1.7
0.1467	353.2	-6.7	0.5448	668.2	-4.7	0.7126	636.2	9.9
0.2172	448.0	-1.1	0.5819	670.0	-2.5	0.8382	493.3	-11.9
0.3560	593.3	8.7	0.6156	668.9	1.7	0.9301	312.6	7.3
0.4362	638.2	-1.1						

^aUnits : J.mol⁻¹

3.3 Results

Table 3.6. Coefficients of A_r eqn. 3.5 for $[x(C_9H_{12}) + (1-x)C_yH_{2y+1}OH]$ at 298.2 K.

Alkanol	A_0	A_1	A_2	A_3
CH ₃ OH	2922.4	-1236.8	2161.6	-894.6
C ₂ H ₅ OH	3239.7	-1376.5	2555.0	-1123.3
1-C ₃ H ₇ OH	3827.0	-1679.6	2236.2	-1447.9
2-C ₃ H ₇ OH	4933.5	-1499.9	1700.9	-147.9

3.3 Results

Table 3.7. Coefficients A_r for eqn 3.5 for $[x(C_6H_4(CH_3)_2) + (1-x)C_kH_{2k+1}OH]$ at 298.2 K.

Mixture	A_0	A_1	A_2	A_3	A_4
$xo-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2787.0	-1189.1	1337.5	-1810.8	1633.9
$xo-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	3091.0	-1533.7	1784.0	-1901.6	791.6
$xo-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3696.2	-1605.1	594.4	-2558.5	3001.9
$xo-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4703.6	-1404.5	2235.3	-1813.1	-
$xm-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2782.6	-1070.8	1455.0	-1917.2	1508.4
$xm-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	3034.4	-1452.4	1843.2	-2230.6	868.3
$xm-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3621.0	-1665.1	1080.2	-2216.9	2012.9
$xm-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4644.5	-1168.6	2332.9	-2665.6	-
$xp-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2631.2	-1021.0	988.4	-2368.2	2285.1
$xp-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	2934.6	-1389.0	796.7	-2665.0	2339.5
$xp-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3452.6	-1716.7	607.9	-2565.8	3031.9
$xp-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4500.9	-1449.8	2296.9	-1890.7	-

3.3 Results

Table 3.8. Coefficients A_r for eqn. 3.5 for $[x(1-C_kH_{2k}) + (1-x)C_yH_{2y+1}OH]$ at 298.2 K.

Mixture	A_0	A_1	A_2	A_3
$x1-C_6H_{12} + (1-x)CH_3OH$	2216.7	-548.8	1506.5	-314.9
$x1-C_7H_{14} + (1-x)CH_3OH$	2300.8	-467.2	1793.4	-244.3
$x1-C_8H_{16} + (1-x)CH_3OH$	2415.0	-502.4	1955.0	-116.7
$x1-C_6H_{12} + (1-x)C_2H_5OH$	2202.2	-1169.6	1346.3	-926.1
$x1-C_7H_{14} + (1-x)C_2H_5OH$	2366.8	-1079.2	1732.2	-1011.2
$x1-C_8H_{16} + (1-x)C_2H_5OH$	2457.1	-680.1	2336.6	-2204.9

3.3 Results

Table 3.9. Coefficients A_r for eqn. 3.5 for $[x(C_yH_{2y-2}) + (1-x)C_zH_{2z+1}OH]$ at 298.2 K.

Mixture	A_0	A_1	A_2	A_3
$x1-C_6H_{10} + (1-x)CH_3OH$	2048.0	-1994.2	1438.0	-292.0
$x1-C_7H_{12} + (1-x)CH_3OH$	2315.5	-1802.9	2368.5	-1987.5
$x1-C_8H_{14} + (1-x)CH_3OH$	2444.6	-840.4	1885.5	-2638.0
$x1-C_6H_{10} + (1-x)C_2H_5OH$	2488.3	-1692.1	2252.7	-1916.9
$x1-C_7H_{12} + (1-x)C_2H_5OH$	2892.2	-1668.9	2259.2	-2666.7
$x1-C_8H_{14} + (1-x)C_2H_5OH$	2705.1	-1660.5	2165.9	-1992.4

3.3 Results

Table 3.10. Coefficients A_r for eqn. 3.5 for $[x(c-C_kH_{2k}) + (1-x)C_lH_{2l+1}OH]$ at 298.2 K.

k	Alkanol	A_0	A_1	A_2	A_3	A_4
5	CH ₃ OH	2262.1	194.0	958.3	-226.7	1345.0
5	C ₂ H ₅ OH	2097.1	-542.5	507.3	-1288.6	1582.6
5	C ₃ H ₇ OH	1876.2	-1068.9	300.3	-1407.0	2295.6
5	CH ₃ CH(OH)CH ₃	2699.9	-1149.8	493.0	-1254.6	1666.8
6	C ₂ H ₅ OH	2546.4	-324.6	495.3	-1270.7	1876.9
6	C ₃ H ₇ OH	2350.1	-1005.1	104.3	-1197.5	2467.1
6	CH ₃ CH(OH)CH ₃	3223.4	-1104.3	280.7	-1034	1978.1
7	C ₂ H ₅ OH	2655.7	-153.3	643.9	-1463.8	1935.0
7	C ₃ H ₇ OH	2425.1	-828.2	762.7	-1331.1	1346.1
7	CH ₃ CH(OH)CH ₃	3324.0	-1307.3	1437.0	661.1	-1402.0
8	C ₂ H ₅ OH	2505.1	-24.3	961.5	-1114.6	1533.1
8	C ₃ H ₇ OH	2456.4	-719.4	793.3	-1372.3	1369.4
8	CH ₃ CH(OH)CH ₃	3125.7	-590.4	1262.9	-1378.6	1197.5
10	C ₂ H ₅ OH	1988.6	133.5	360.3	198.4	76.0
10	C ₃ H ₇ OH	1940.8	-434.6	507.8	-205.4	956.1
10	CH ₃ CH(OH)CH ₃	2661.3	-538.8	452.4	-301.8	1905.9

3.4 Discussion

3.4.1 Mixtures of substituted benzenes + alkanols

(a) Previous work

With the exception of two results, the results reported here are in good agreement with the values reported in the literature.⁽¹⁴⁶⁻¹⁴⁸⁾ For the mixtures $\{xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 \text{ or } xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}\}$ the results for $H_m^E(\text{maximum})$ are approximately $30 \text{ J}\cdot\text{mol}^{-1}$ lower than that reported by Rodriguez-Nunez *et al*,⁽¹⁴⁶⁾ who based his conclusions on his own results for $H_m^E\{x(o\text{-}, m\text{- or } p\text{-})\text{C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$ where $k = 3, 4, 5, 6, 7$ and 8 and all the alkanols are primary. The results for $H_m^E\{xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}\}$ agree within experimental error of the results of Nagata⁽¹⁴⁸⁾ and also of Christensen,⁽¹⁴⁷⁾ although Christensen's work was measured at 170 kPa .

(b) This work

The heats of mixing for each of the sets of data for $H_m^E(\text{aromatic component} + \text{an alkanol})$ show similar patterns. These can be seen in Figs. 3.5(i), (ii), (iii) and (iv). The H_m^E for benzene, toluene, *o*-, *m*-, *p*-xylene and mesitylene + methanol all have the same shape with a maximum value of H_m^E at a mole fraction of $0.6 < x < 0.7$. This is also true for the ethanol, 1-propanol and 2-propanol systems. The $H_m^E(x = 0.5)$ for the six methanol systems range between 610 and $730 \text{ J}\cdot\text{mol}^{-1}$ while for the six ethanol, six 1-propanol and six 2-propanol systems, $H_m^E(x = 0.5)$ ranges between 730 and $810 \text{ J}\cdot\text{mol}^{-1}$, 860 and $950 \text{ J}\cdot\text{mol}^{-1}$ and 1120 and $1230 \text{ J}\cdot\text{mol}^{-1}$ respectively.

3.4 Discussions

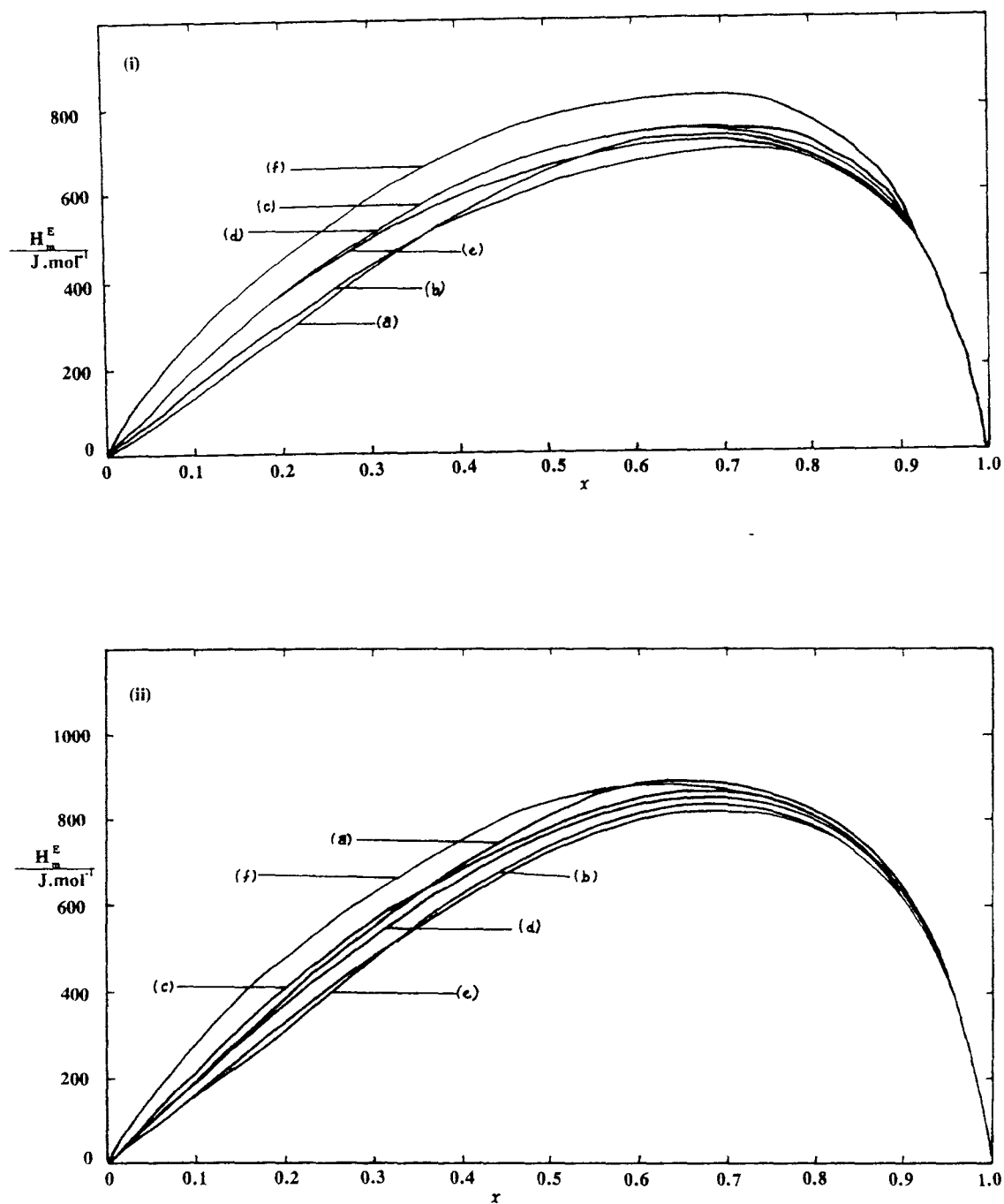


Fig. 3.5 : H_m^E for $\{x\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}$ at 298.2 K: (a) C_6H_6 ; (b) $\text{C}_6\text{H}_5\text{CH}_3$; (c) $o\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (d) $m\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (e) $p\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (f) $1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$ - in (i) methanol, or (ii) ethanol, taken from publication (8).

3.4 Discussions

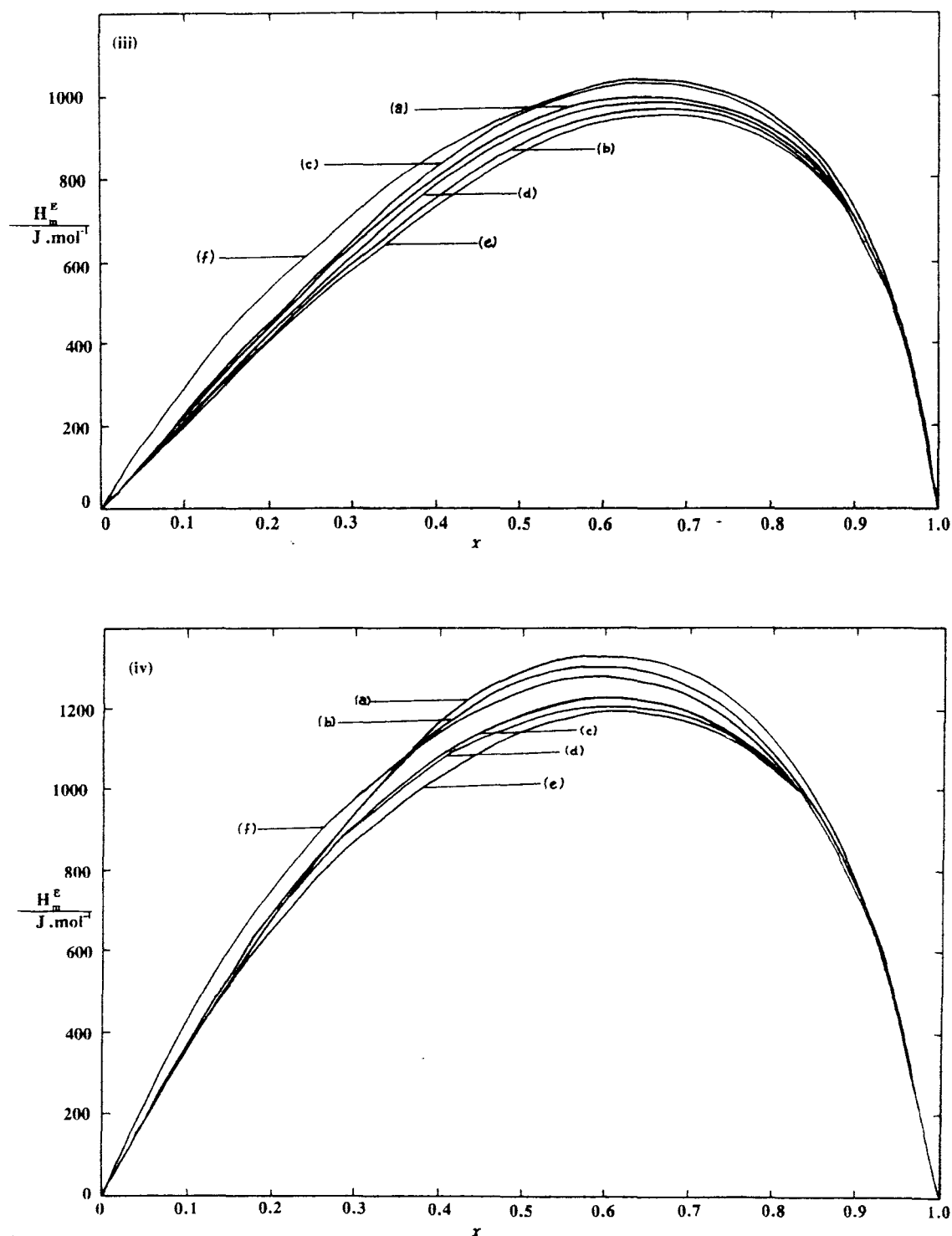


Fig. 3.5 : H_m^E for $\{x\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m + (1-x)\text{C}_3\text{H}_{7-1}(\text{OH})_1\}$ at 298.2 K: (a) C_6H_6 ; (b) $\text{C}_6\text{H}_5\text{CH}_3$; (c) $o\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (d) $m\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (e) $p\text{-C}_6\text{H}_4(\text{CH}_3)_2$; (f) $1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$ - in (iii) 1-propanol, or (iv) 2-propanol, taken from publication (8).

3.4 Discussions

The nature of these interactions are best discussed in terms of the partial molar excess enthalpies at infinite dilution, (see Chapter 2 for derivation of an excess partial molar property from partial molar data). In this work $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ (where 1 refers to an aromatic compound and 2 to an alkanol) have been calculated from the coefficients A_r (given in Tables 3.6 and 3.7) of the Redlich Kister eqn. 3.5.

The excess partial molar volume H_1^E at a mole fraction x_1 where $x_1 = n_1/(n_1 + n_2)$, is given by⁽⁸⁵⁾

$$H_1^E(x_1=0) = \sum_{r=0}^n A_r \quad 3.6$$

similarly

$$H_2^E(x_2=0) = \sum_{r=0}^n (\text{even}) A_r - \sum_{r=0}^n (\text{odd}) A_r \quad 3.7$$

The precision of $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ is dependent on the precision of the H_m^E data at low and high concentrations. The precision for $H_1^E(x_1 = 0)$ for the systems discussed in this work are estimated to be no better than 500 J.mol⁻¹. The calculated values of $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ are given in Table 3.12. In all cases $H_2^E(x_2 = 0) \gg H_1^E(x_1 = 0)$. Comparing the results of $H_m^E\{x(o-, m- \text{ or } p\text{-})\text{xylene} + (1-x)1\text{-C}_k\text{H}_{2k+1}\text{OH}\}$ for $k = 1, 2$ and 3 (considering only primary alkanols) with those of Rodriguez-Nunez *et al*^(96,146) and Nagata⁽¹⁴⁹⁾ for $H_m^E\{x(o-, m- \text{ or } p\text{-})\text{xylene} + (1-x)1\text{-C}_k\text{H}_{2k+1}\text{OH}\}$ where $k = 3, 4, 5, 6, 7$ and 8, (considering only primary alkanols) it appears that $H_m^E(\text{maximum})$ increases from $k = 1$ to $k = 4$ and decreases for $k > 4$.

An explanation for these results is possible if one assumes that the overall H_m^E for these mixtures is due to (i) a positive contribution due to the breakdown of π - π association between the aromatic species, (ii) a positive contribution due to the break-down of hydrogen bonding between alkanol molecules and (iii) a negative contribution as a result of π -OH group

3.4 Discussions

association between the aromatic and alkanol species. Furthermore it is reasonable to assume that (a) the positive hydrogen bond contribution ((ii) above) decreases as k increases, and (b) the magnitude of the negative contribution of the (π -OH) association, decreases by smaller amounts as k increases from 1 to 8. Assumption (a) is supported by the evidence of $H_m^E\{x \text{ cyclohexane} + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$ which show that $H_m^E(\text{maximum})$ decreases steadily as k increases for 2 to 4.⁽¹⁴⁹⁻¹⁵¹⁾ Methanol does not dissolve in cyclohexane in all proportions.

Assumption (b) is reasonable when one considers that the association between the aromatic group and the OH of the alkanol will decrease with increasing alkanol chain length because the longer the alkanol chain length the smaller is the contribution of the OH group to the overall property of the alkanol.

Thus, the large positive $H_2^E(x_2 = 0)$ is most probably primarily due^(41,97-99) to the endothermic dissociation of the hydrogen bonds linking the alkanol molecules as a result of adding a small amount of alkanol to a large amount of the aromatic component. The very much smaller $H_1^E(x_1 = 0)$ is, most probably, a result of (1) the smaller endothermic effect due to the breakdown of the association between the aromatic molecules and (2) the exothermic effect due to the association of the aromatic compound and the alkanol.

The results for $H_m^E\{x(o-, m- \text{ or } p\text{-})\text{xylene} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}$ and $H_m^E\{x(o-, m- \text{ or } p\text{-})\text{xylene} + (1-x)\text{C}_3\text{H}_7\text{OH}\}$ show that for each xylene isomer the two propanol isomers behave significantly differently. In all cases $H_m^E(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3) > H_m^E(\text{C}_3\text{H}_7\text{OH})$. This could be due to a weaker interaction of the aromatic component with the secondary alkanol than with the primary alkanol as a result of the steric effect of the methyl groups in the secondary alkanol which would tend to hide the OH group from the π -electron system of the aromatic component. This would have the effect of a smaller negative contribution to the overall H_m^E resulting in a larger positive H_m^E .

There is a close similarity between the shape and the magnitude of the H_m^E - x curve for

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mesitylene + an alkanol and the H_m^E -x curve for benzene + the same alkanol. This can be seen from the H_m^E (maximum) and x(maximum) data summarised in Table 3.11.

Table 3.11. The H_m^E (maximum) for $[x(C_9H_{12}) + (1-x)C_yH_{2y+1}OH]$ and for $[x(C_6H_6) + (1-x)C_yH_{2y+1}OH]$. The values of x(maximum) are given in parentheses. The results for the benzene mixtures have been obtained from the literature quoted in the text.⁽⁹⁻¹¹⁾

Alkanol	H_m^E (maximum) ^a	
	C_9H_{12}	C_6H_6
CH ₃ OH	813(0.71)	722(0.72)
C ₂ H ₅ OH	890(0.65)	890(0.65)
1-C ₃ H ₇ OH	1040(0.63)	1045(0.63)
2-C ₃ H ₇ OH	1270(0.60)	1322(0.60)

^aUnits : J.mol⁻¹

These results suggest that, as far as the H_m^E results are concerned, the three substituted methyl groups have little overall effect. The positive enthalpy contribution from the dissociation of the benzene molecules and the negative enthalpy contribution from the benzene-alkanol association is similar in magnitude to the enthalpy contribution resulting from the dissociation of the mesitylene molecules and the enthalpy from the association of mesitylene and alkanol molecules.

In work by Letcher *et al.*,^{(103(b))} the H_m^E data for a chloro-substituted benzene (C_6H_5Cl or 1,2- $C_6H_4Cl_2$ or 1,3- $C_6H_4Cl_2$ or 1,2,4- $C_6H_3Cl_3$) + an alkanol have been reported. These results are similar in magnitude and shape to the benzene or methyl-substituted benzene + an alkanol results. The position and number of the chloro-group on the benzene ring has less effect than the number of carbon atoms, or position of the OH-group, of the alkanol. The H_m^E (maximum) values are more positive for the chlorinated benzene + alkanol systems, than for the methyl-substituted benzene + alkanol systems. This could be due to a stronger

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association between the chlorinated benzenes than between the methyl-substituted benzenes. The association is thought to be most likely through H-Cl interactions. Furthermore,^{(103(b))} it appears that the electron-withdrawing effect of the chloro-group has more of an influence on alcohol interactions than the electron-releasing effect of the CH₃-group.

3.4.2 Mixtures of Alkenes and Alkynes

(a) 1-alkene + alkanol mixtures

At 298.15 K CH₃OH does not mix in all proportions with the n-alkanes, C₆H₁₄, C₇H₁₆ and C₈H₁₈, but does mix with the 1-alkenes, 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆. This could be considered as evidence for specific interactions between the double bond of the 1-alkene and the hydroxyl group of the alkanol. The H_m^E results for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + C₂H₅OH show skew curves with maxima (of 620, 660 and 700 J.mol⁻¹, respectively), at about 0.7 mole fraction 1-alkene. These H_m^E(maxima) are between 40 and 50 J.mol⁻¹ more positive than the H_m^E(maxima) for C₆H₁₄, C₇H₁₆ and C₈H₁₈ + C₂H₅OH.⁽¹⁵²⁻¹⁵⁴⁾

The self association between 1-alkene molecules is relatively weak as judged by the small positive H_m^E(maximum) for 1-C₆H₁₂ + n-C₆H₁₄,^{(155(a))} 1-C₇H₁₄ + n-C₇H₁₆,^{(155(a))} and 1-C₈H₁₆ + n-C₇H₁₆^{(155(b))} of between 40 and 55 J.mol⁻¹. The small positive enthalpy effect resulting from the dissociation of 1-alkene molecules is probably the cause of the H_m^E(maximum) for 1-alkene + C₂H₅OH mixtures being slightly more positive than the H_m^E(maximum) for n-alkane + C₂H₅OH mixtures. The fact that the H_m^E(maximum) results for the 1-alkene + C₂H₅OH mixtures are only slightly more positive than the H_m^E(maximum) results for the respective n-alkene + C₂H₅OH indicates that the association between 1-alkene and C₂H₅OH molecules is not strong. In both sets of data, the dominant feature is the dissociation of alkanol molecules resulting in relatively large positive H_m^E(maximum) values. The H_m^E(maximum) for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + C₂H₅OH at 298 K are between 50 and 70 J.mol⁻¹ more positive than the H_m^E(maximum) for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + CH₃OH.

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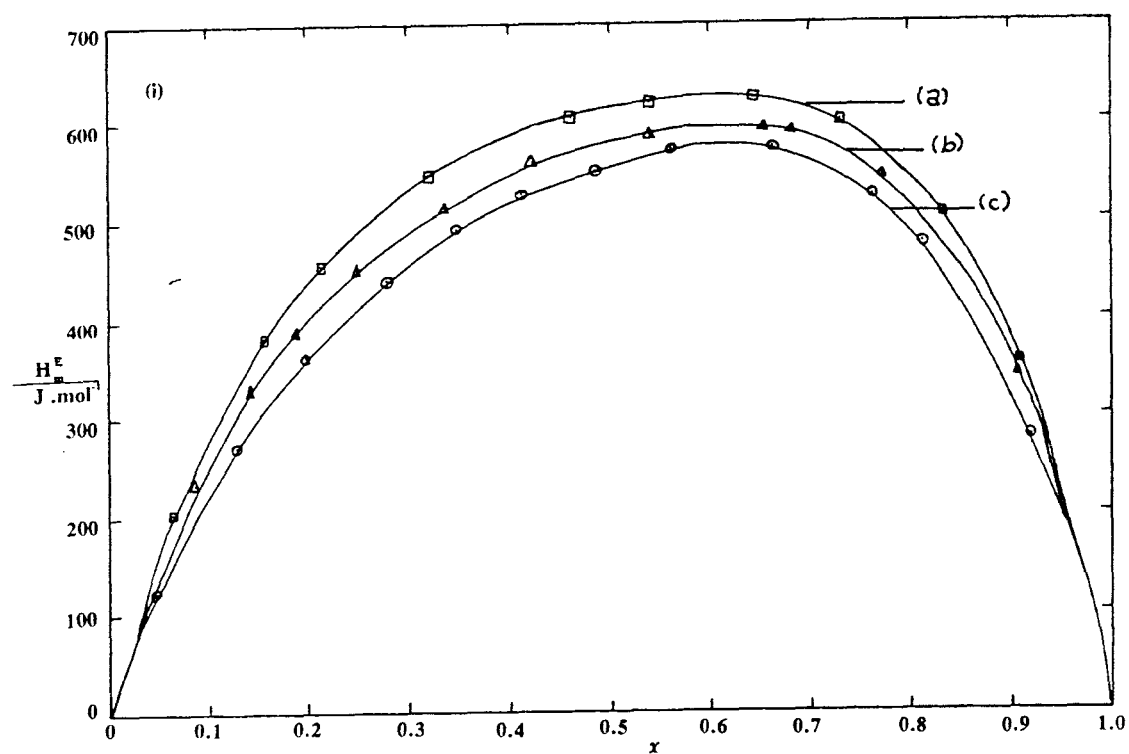


Fig. 3.6 : H_m^E for a 1-alkene + (i) methanol; (a) 1-octene, (b) 1-heptene, (c) 1-hexene.

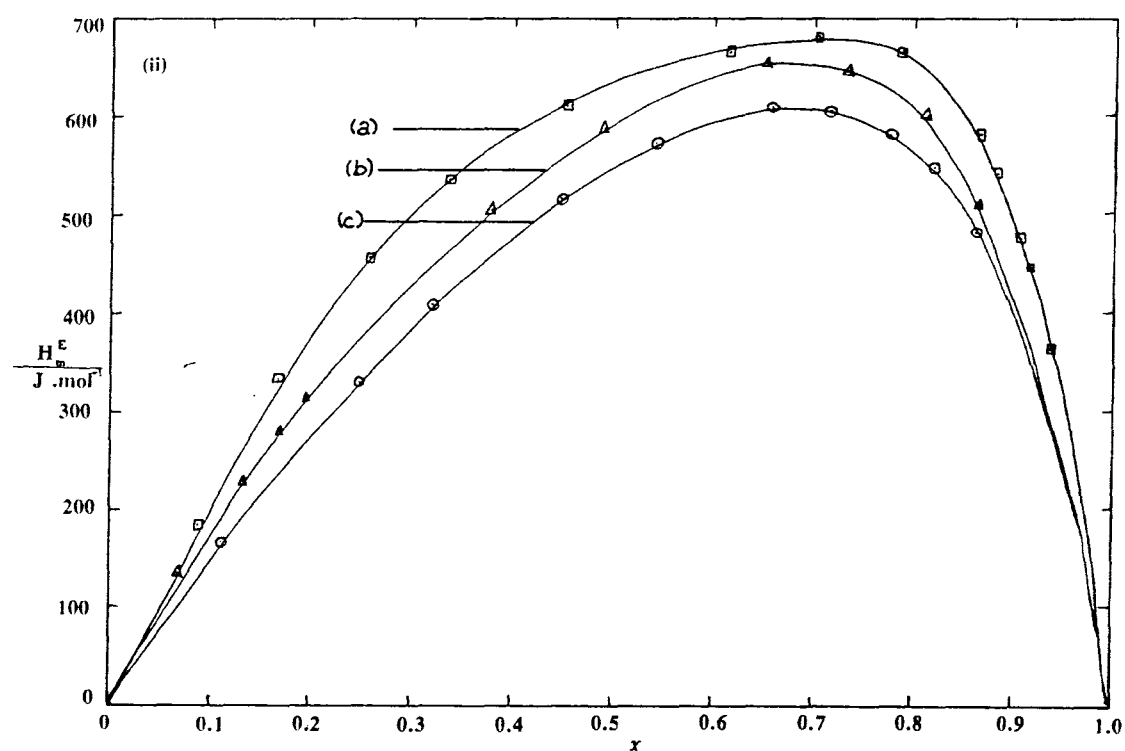


Fig. 3.6 : H_m^E for a 1-alkene + (ii) ethanol; (a) 1-octene, (b) 1-heptene, (c) 1-hexene.

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(b) 1-alkyne + alkanol mixtures

The H_m^E results for 1-C₆H₁₀, 1-C₇H₁₂ or 1-C₈H₁₄ + C₂H₅OH show markedly skew curves with maxima at about 0.7 mole fraction alkyne, of 770, 860 and 810 J.mol⁻¹ respectively. These H_m^E (maxima) are between 100 and 200 J.mol⁻¹ more positive than the H_m^E (maxima) for C₆H₁₄, C₇H₁₆ or C₈H₁₈ + C₂H₅OH as quoted in the literature.⁽¹⁵²⁻¹⁵⁴⁾ The results and those given in the literature are tabulated in Table 3.12.

Table 3.12. The H_m^E (maxima) for $[x(C_yH_{2y+2})$ and $x(C_yH_{2y-2}) + (1-x)C_zH_{2z+1}OH]$ at 298.2 K. The mole fractions relating to the H_m^E (maxima) are given in parentheses.

Compound	H_m^E (maxima) ^a	
	CH ₃ OH	C ₂ H ₅ OH
C ₆ H ₁₄	-	580(0.55)
1-C ₆ H ₁₀	650(0.72)	770(0.74)
C ₇ H ₁₆	-	620(0.55)
1-C ₇ H ₁₂	755(0.75)	860(0.74)
C ₈ H ₁₈	-	860(0.55)
1-C ₈ H ₁₄	682(0.73)	810(0.73)

^aUnits : J.mol⁻¹

The self association between alkyne molecules is relatively strong as judged by the positive H_m^E results reported by Woycicki and Rhensius,⁽¹⁵⁶⁾ Otsa *et al*⁽¹⁵⁷⁾ for 1-alkyne + n-alkane mixtures. Woycicki and Rhensius⁽¹⁵⁶⁾ determined H_m^E for the mixture (1-C₆H₁₀ + C₆H₁₄) (592 J.mol⁻¹) and the mixture (1-C₇H₁₂ + C₇H₁₆) (567 J.mol⁻¹). Otsa *et al* determined H_m^E for the mixture (1-C₇H₁₂ + C₇H₁₆) (557 J.mol⁻¹) and for the mixture (1-C₈H₁₄ + C₈H₁₈) (523 J.mol⁻¹).

A comparison of the n-alkane + alkanol with the H_m^E results reported here, show that the

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interactions between 1-alkyne molecules and ethanol molecules ($\pi \dots \text{H}$ and $\dots \text{O}$ bonding, resulting in a negative contribution to H_m^E) are probably weaker than either the dissociation of 1-alkyne molecules ($\pi \dots \pi$ bonding, resulting in a positive contribution to H_m^E) or the dissociation of ethanol molecules ($\text{H} \dots \text{O}$ bonding, producing a positive effect).

The H_m^E curves for the 1-alkyne + ethanol mixtures are very asymmetrical compared to the H_m^E curves for n-alkane + ethanol mixtures which are reasonably symmetrical. This can be seen in the concentrations related to $H_m^E(\text{maxima})$ given in Table 3.12. This skewness can be attributed to the different interactions present in the mixtures, eg. weak $\pi \dots \text{H}$ and $\pi \dots \pi$, and strong $\text{H} \dots \text{OH}$ interactions.

Once again, an insight into the different interactions can be gained from the partial molar excess enthalpies at infinite dilution, calculated from finite concentration data. In this work, $H_1^E(x_1=0)$ and $H_2^E(x_2=0)$ are only accurate to approximately $500 \text{ J} \cdot \text{mol}^{-1}$. The partial molar excess enthalpy for $\text{C}_2\text{H}_5\text{OH}$ at infinite dilution in $1\text{-C}_6\text{H}_{10}$, $1\text{-C}_7\text{H}_{12}$, and $1\text{-C}_8\text{H}_{14}$ is much greater than the partial molar enthalpy for $1\text{-C}_6\text{H}_{10}$, $1\text{-C}_7\text{H}_{12}$ or $1\text{-C}_8\text{H}_{14}$ at infinite dilution in $\text{C}_2\text{H}_5\text{OH}$. This is reflected in the data given in Table 3.13.

Table 3.13. The excess molar enthalpies at infinite dilution for $x_1 1\text{-C}_y\text{H}_{2y-2} + x_2 \text{C}_z\text{H}_{2z+1}\text{OH}$.

y	z	$H_1^E(x_1=0)^a$	$H_2^E(x_2=0)^a$
6	1	1200	5770
6	2	1130	8350
7	1	890	8480
7	2	820	9490
8	1	850	7810
8	2	1220	8520

^aUnits : $\text{J} \cdot \text{mol}^{-1}$

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The high positive values for the partial molar enthalpies for C_2H_5OH at infinite dilution suggest the complete dissociation of the C_2H_5OH molecules in the alkyne. On the other hand the smaller positive values of the partial molar enthalpies for an 1-alkyne at infinite dilution in C_2H_5OH are probably due to the weaker dissociation effect of 1-alkynes (positive effect) and also the interaction of the 1-alkynes with C_2H_5OH (negative effect).

Similar effects relating to the partial molar excess enthalpies are apparent with 1-alkyne + CH_3OH mixtures as can be seen from the results tabulated in Table 3.13. It is difficult to explain why some of the partial molar excess enthalpies at infinite dilution go through a maxima. The maximum is probably a reflection of the error in $H_2^E(x_2=0)$.

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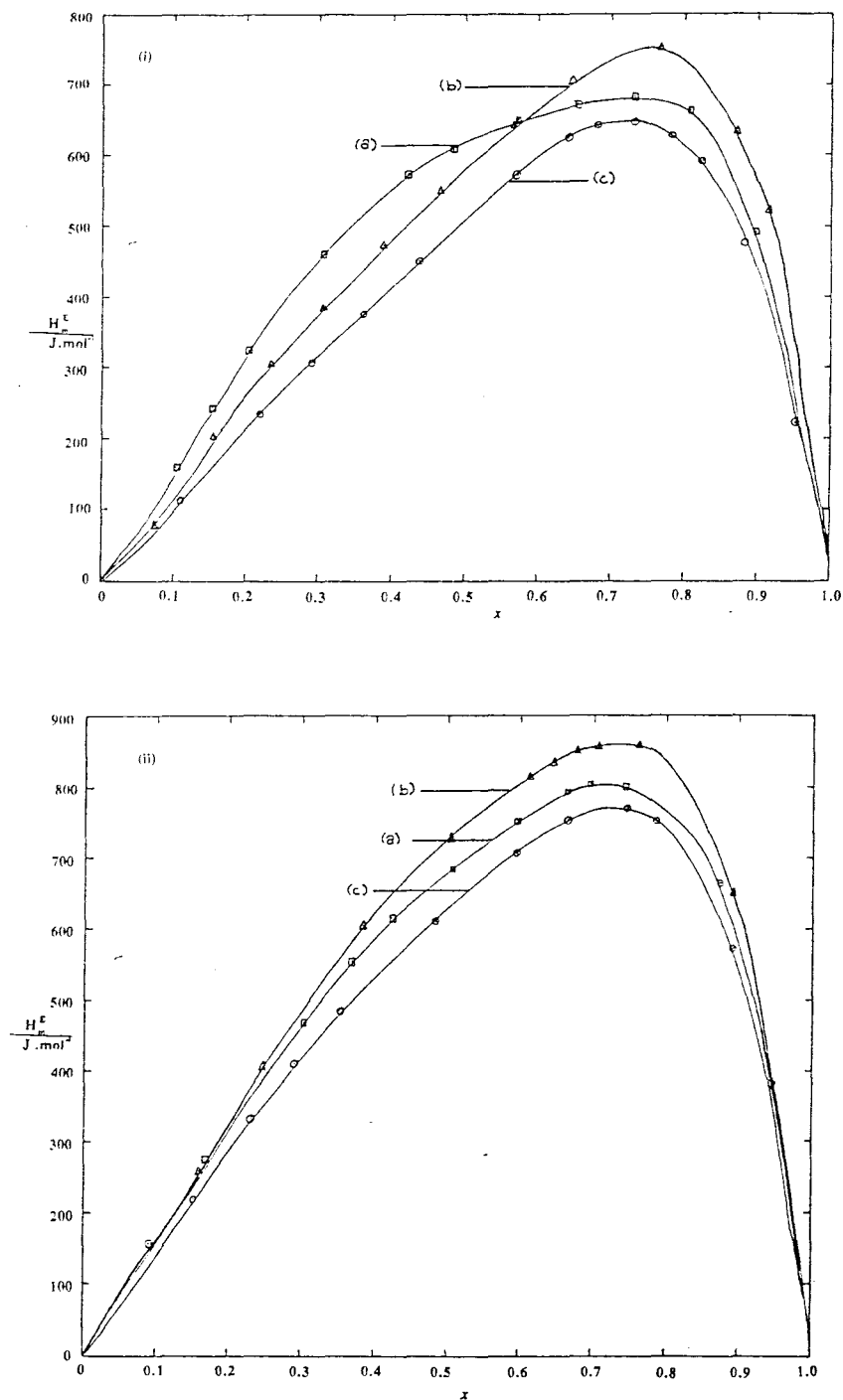


Fig. 3.7 : H_m^E for a 1-alkyne + (i) methanol, or (ii) ethanol; (a) 1-octyne, (b) 1-heptyne, (c) 1-hexyne.

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3.4.3 Mixtures of Cycloalkanes + alkanols

(a) Previous work

H_m^E for five of the sixteen systems investigated here, have been published previously. The results of Stokes and Burfitt⁽¹⁵²⁾ for cyclopentane + ethanol and cycloheptane + ethanol are within 5 J.mol^{-1} of the smoothing curves fitted to this work except at very low alkanol concentrations. For cyclohexane + ethanol, the results for this work are within 10 J.mol^{-1} in the worst case, of the results given by Nagata and Kazuma⁽¹⁴⁹⁾ and also by Stokes and Adamson.⁽¹⁵⁸⁾ The results of this work for cyclohexane + 2-propanol are within 10 J.mol^{-1} of the smoothing curves based on the data of Vesely *et al.*⁽¹⁵⁰⁾ and Nagata *et al.*⁽¹⁵⁹⁾

There are four sets of data in the literature for $H_m^E\{xC_6H_{12} + (1-x)C_3H_7OH\}$.^(149,151,160,161) The results reported here are within 5 J.mol^{-1} , in the worst case, of the smoothing curve for the data given by Nagata and Kazuma⁽¹⁴⁹⁾ but almost 30 J.mol^{-1} higher than the published data of Vesely and Pick^(151,160) and 80 J.mol^{-1} lower, than the published data of Belousov *et al.*⁽¹⁶¹⁾

(b) This work

The H_m^E values for all the sixteen systems discussed here are positive with $H_m^E(\text{maximum})$ ranging from 490 to 866 J.mol^{-1} . This reflects the breakdown of the hydrogen bonding between alkanol molecules on mixing with a cyclo compound. For each particular alkanol, the value of H_m^E (maximum) or $H_m^E(x=0.5)$ increases with increasing cycloalkane carbon number from $k=5$ to 7 and decreases from $k=7$ to 10 . This can be seen in Fig. 3.8 where $H_m^E(x=0.5)$ has been plotted against k .

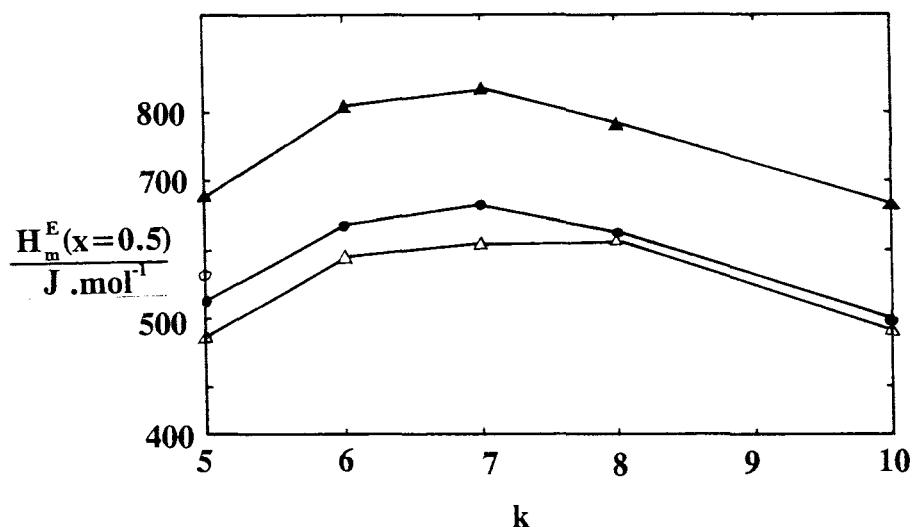


Fig. 3.8 : $H_m^E(x=0.5)$ for $(x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_l\text{H}_{2l+1}\text{OH})$ as a function of k : ○, CH_3OH ; ●, $\text{C}_2\text{H}_5\text{OH}$; △, $\text{C}_3\text{H}_7\text{OH}$; and ▲, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.

The concentration of the cycloalkane at which $H_m^E(\text{maximum})$ occurs for a particular alkanol, decreases with increasing cycloalkane carbon number. For example for ethanol systems $H_m^E(\text{maximum})$ occurs at $x=0.61$ for $k=5$, 0.56 for $k=6$, 0.54 for $k=7$, 0.51 for $k=8$ and 0.45 for $k=10$. In Fig. 3.8 $H_m^E(x=0.5)$ has been plotted against k . For cyclopentane systems, $H_m^E(x=0.5)$ decreases with increasing chain length of the 1-alkanols from $l=1$ to $l=3$. The same is true for each of the other cycloalkanes for $l=2$ and 3. This can be attributed to decreasing hydrogen bonding between alkanol molecules as l increases from 1 to 3.

The $H_m^E(x=0.5)$ for $\{x\text{-C}_k\text{H}_{2k} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}$ is larger than $H_m^E(x=0.5)$ for $\{x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_2\text{H}_5\text{OH}$ or $+ (1-x)\text{C}_3\text{H}_7\text{OH}\}$ for k between 5 and 10. This implies stronger hydrogen bonding between 2-propanol molecules than between ethanol molecules or between 1-propanol molecules. This could be due to the inductive effect of the methyl groups adjacent to the C-OH of 2-propanol.

CHAPTER 4

The Principle of Congruency

4.0 Introduction

The principle of congruence supplies researchers with one of the simplest correlations of the properties of mixtures of members of a homologous series. Properties which have been correlated and predicted by means of the principle include the activity coefficient,⁽²⁶⁾ solubility,⁽¹⁶²⁾ the excess Gibbs free energy of mixing,⁽²⁷⁾ excess enthalpy of mixing,⁽²⁸⁾ excess volume,⁽²⁹⁾ "excess" compressibility,⁽¹⁶³⁾ excess energy,⁽¹⁶⁴⁾ second virial coefficient,⁽¹⁶⁵⁾ liquid-vapour distribution ratio,⁽¹⁶⁶⁾ and viscosity.⁽¹⁶⁷⁾ The principle has also been used to extend a corresponding states treatment of chain-molecule liquids to their mixtures.^(168,169) A review by Cibulka and Holub⁽¹⁷⁰⁾ on the methods of calculation of the excess volume of binary liquid mixtures of non-electrolytes includes a discussion of the principle of congruence and its application to experimental data. A general review by Koh and Williamson⁽³⁰⁾ reports on the various applications of the congruence theory.

4.1 Theory of congruency

First proposed by Bronsted and Koefoed⁽²⁶⁾ in 1946, the principle of congruence states that a mixture of chain molecules from a given homologous series may be characterised by an index ν and that, at a given temperature and pressure, mixtures with the same index have the same values for certain of their properties. For mixtures of n -alkanes,⁽²⁶⁾ n -alcohols,⁽¹⁷¹⁾ perfluoro- n -alkanes,⁽¹⁷²⁾ 1-alkenes,⁽¹⁷³⁾ 1-chloroalkenes,⁽¹⁷⁴⁾ and methylalkanoates,⁽¹⁶²⁾ the index ν has usually been identified with n , the average number of the carbon atoms per molecule, defined by

4.1 Theory of congruency

$$n = \sum_i x_i n_i \quad 4.1$$

where x_i is the mole fraction of the member of the series containing n_i carbon atoms. Mixtures of the same average chain length n are said to be congruent.

The following relations for a mixture of members of a homologous series are fundamental to the theory of congruence⁽³⁰⁾:

$$X_m(T, P, x_1, \dots, x_c) = X_m(T, P, n; 1, \dots, c) \quad 4.2$$

$$X_m^E(T, P, x_1, \dots, x_c) = X_m^E(T, P, n; 1, \dots, c) \quad 4.3$$

where X_m and X_m^E represent a molar and an excess molar property, respectively.

The principle of congruence can be extended readily to mixtures with different indices by requiring X_m or X_m^E to be smooth and continuous functions of n . This is the form used by Koefoed⁽¹⁶²⁾ to correlate solubilities; by Hijmans⁽¹⁷⁵⁾ to correlate excess volumes and excess enthalpies; by Barker and Linton⁽¹⁶⁵⁾ to correlate the viscosities of gaseous n -alkanes.

The principle may be developed further by rewriting eqn. 4.3 in the form

$$X_m^E(T, P, n; 1, \dots, c) = X_m(T, P, x_1, \dots, x_c) - \sum_i x_i X_i^*(T, P) - \Delta X_m^{id}(T, P, x_1, \dots, x_c) \quad 4.4$$

where the superscripts id and $*$ refer to the ideal mixture and a pure substance, respectively. For enthalpy and volume, $\Delta X_m^{id} = 0$, and this suggests⁽³⁰⁾ that there may exist a single-valued function $f(n)$ such that

$$X_m^E(T, P, n; 1, \dots, c) = f(T, P, n; 1, \dots, c) - \sum_i x_i f(T, P, n_i) \quad 4.5$$

4.1 Theory of congruency

Various forms for $f(n)$ have been proposed by McGlashan,⁽¹⁷⁶⁾ Hijmans and Holleman,⁽¹⁷⁷⁾ Bellemans and Mat,⁽²⁷⁾ Diaz Pena and Fernandez-Martin,⁽³⁰⁾ and Fernandez-Garcia *et al.*⁽¹⁷⁸⁾

Eqn. 4.3 can also be written as

$$X_m^E = \phi(T, P, n) = \sum_j \alpha_j(T) \beta_j(P) \gamma_j(n)$$

where α , β and γ are some function of temperature, pressure, and the index, respectively. If the excess Gibbs energy is written as

$$G_m^E = \sum_j \alpha_j(T) \beta_j(P) \gamma_j(n) \quad 4.6$$

then the excess enthalpy and the excess volume are

$$H_m^E = \sum_j \alpha_j'(T) \beta_j(P) \gamma_j(n) \quad 4.7$$

$$V_m^E = \sum_j \alpha_j(T) \beta_j'(P) \gamma_j(n) \quad 4.8$$

where

$$\alpha_j' = \alpha_j - T(\partial \alpha_j / \partial T)$$

and

$$\beta_j' = \partial \beta_j / \partial P$$

These equations show the inter-relationship between the coefficients in the summation. Eqn. 4.2 may be factorised in a similar⁽³⁰⁾ way to yield

4.1 Theory of congruency

$$X_m = \theta(T, P, n) = \sum_j \delta_j(T) \epsilon_j(P) \zeta_j(n)$$

If, following Koefoed,⁽¹⁶²⁾ pure components are assumed to be congruent with a mixture of the same index, then

$$X_i^* = \sum_j \delta_j(T) \epsilon_j(P) \zeta_j(n_i)$$

For those properties for which $\Delta X_m^{id} = 0$,

$$X_m^E = \sum_j \delta_j(T) \epsilon_j(P) [\zeta_j(n) - \sum_i x_i \zeta_i(n_i)]$$

(where δ , ϵ and ζ are some function of temperature, pressure, and index, respectively), which is physically meaningful only when n is an integer. This also implies that

$$X_m^E = X_n^* - \sum_i x_i X_i^* \quad 4.9$$

which was used by Desmyter and van der Waals⁽²⁹⁾ to correlate the unsymmetrical excess volume *versus* mole fraction curves of binary n -alkane mixtures.

Extensions to the principle of congruence have also been made by modifying the definition of the index as given in eqn. 4.1. Different indices have been proposed by Brown *et al.*,⁽¹⁷⁹⁾ Williamson,⁽¹⁸⁰⁾ Brzostowski,⁽¹⁸¹⁾ and Diaz Pena and Trigueros.⁽¹⁸²⁾ Longuet-Higgins,⁽¹⁸³⁾ in his theoretical justification of the principle, expressed the index through the assertion that two mixtures of chain molecules are congruent if they are such that their molecules may be divided into identical sets of fragments by cutting the chains in suitable places.

Using the symmetrical expression of Bronsted and Koefoed,⁽²⁶⁾ van der Waals and Hermans^(28,184) were able to correlate the excess enthalpy at 293.15 K of the pairs of n -alkanes 6+12, 6+16, 7+16, 8+16, 10+16, within the experimental errors of the

4.1 Theory of congruency

observations. This was corroborated by McGlashan and Morcom⁽¹⁸⁵⁾ for the equimolar 6+16 mixture. With this value in eqn. 4.12, the excess enthalpy of six other pairs of *n*-alkanes is reproduced to an accuracy of $\pm 8 \text{ J.mol}^{-1}$. This is, however, outside the limits of the experimental error of their measurements.

The more precise measurements by McGlashan *et al*^(186,187) of the excess enthalpy and the excess Gibbs energy for an *n*-alkane + *n*-hexadecane at 293.15 K revealed that these two properties are not accurately parabolic in composition. The curves are skewed towards compositions rich in the shorter alkanes, as is consistent with the regular solution concept of Hildebrand⁽¹⁸⁸⁾. McGlashan and co-workers' prediction⁽¹⁸⁹⁾ that the excess enthalpy would change sign from positive to negative at higher temperature was later verified.^(190,191) The occurrence of a lower critical solution temperature in methane + *n*-hexane⁽¹⁹²⁾ at a relatively high *T* is also consistent with a negative excess enthalpy for the system.⁽¹⁹³⁾

The expression gave poorer correlation with the data of six other pairs of *n*-alkane than that obtained with the single parameter equation in every case⁽¹⁸⁵⁾.

Hijmans and Holleman⁽¹⁷⁷⁾ have, however, pointed out that, if an equation of the type given by McGlashan⁽¹⁷⁶⁾ is used for extrapolation, a result indicating a volume dilation can be obtained. This is contrary to the experimental evidence. According to these workers, the principle of congruence implies that the thermodynamic properties of the *n*-alkanes and of their mixtures are dominated by the concentrations of the methyl and methylene groups. As the concentration of the former tend to zero for the large values of *n*, all these liquids will ultimately behave as assemblies of methylene groups and hence their thermodynamic properties should become functions of *n*-2.

Holleman⁽¹⁹⁴⁾ has also demonstrated that an equation with two parameters can correlate, to within the experimental error, the excess volumes of *n*-alkane mixtures from 324.15 K to 399.15 K. A similar good fit with the excess volume of five mixtures of *n*-alkanes:-

4.1 Theory of congruency

10+12, 10+14, 10+16, 12+14, 12+16 - at 298.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K was obtained with an equation with two parameters by Harrison and co-workers.^(195,196)

Pope *et al* tested McGlashan's approach⁽¹⁷⁶⁾ against the excess enthalpy⁽¹⁹⁷⁾ and the excess volume⁽⁷²⁾ at 298.15 K of eleven binary *n*-alcohol mixtures. These workers concluded that three or four parameters are required for a good fit with data.

The activity coefficients of the volatile component at infinite dilution in solutions of *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane in *n*-tetracosane and *n*-dotriacontane at 308.15 K, 333.15 K and 343.15K were measured by Young⁽¹⁹⁸⁾ using gas-liquid chromatography.

Young found that predictions based on Bronsted and Koefoed's statement of the principle of congruence,⁽²⁶⁾ this equation gave poor agreement with his data. Similar disagreement has been observed by Kwantes and Rijnders⁽¹⁹⁹⁾. This finding was verified by Jadot⁽²⁰⁰⁾ for the activity coefficients of ethane, propane and *n*-butane in *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane at 298.15 K.

4.2 Ternary mixtures

The principle of congruence has been applied to ternary mixtures of members of a homologous series in two ways, the first of which is due to Coursey and Heric⁽¹⁶⁷⁾. They based their method on a Hijmans plot for binary mixtures. Let the total amounts of components 1,2 and 3 in the ternary mixture be *N* and let their mole fractions be x_1 , x_2 and x_3 , respectively. The ternary mixture is considered as being formed in two stages. The first step consists of the mixing of components 1 and 2 to form a binary mixture of index n' where

$$n' = x_1/(x_1+x_2)n_1 + x_2/(x_1+x_2)n_2$$

4.2 Ternary mixtures

For this step,

$$X^E(n';1,2) = N(x_1+x_2)[X_m^E(n';A,B)-\{(n_2-n')/(n_2-n_1)\}X_m^E(n_1;A,B)-\{(n'-n_1)/(n_2-n_1)\}X_m^E(n_2;A,B,)]$$

The second step consists of the mixing of the binary mixture of index n' with component 3 to form a ternary mixture of index n . For this step,

$$X^E(n;1+2,3)=N[X_m^E(n;A,B)-\{(n_3-n)/(n_3-n')\}X_m^E(n';A,B)-\{(n-n')/(n_3-n')\}X_m^E(n_3;A,B)]$$

The total excess property is thus

$$X_m^E(n;1,2,3) = [X^E(n';1,2) + X^E(n;1+2,3)]/N$$

In the ternary mixture,

$$x_1 + x_2 = (n_3-n)/(n_3-n')$$

Hence

$$X_m^E(n;1,2,3) = X_m^E(n;A,B) - x_1X_m^E(n_1;A,B,)- x_2X_m^E(n_2;A,B) - x_3X_m^E(n_3;A,B)$$

Ternary and quaternary mixtures of homologues may be most simply tested for conformity with the principle of congruence by considering them as being constituted from two components, one of which is a binary mixture and the other may be a single component or a binary mixture. Two kinds of experimental test may be used, a null test, (such as that reported by Weiguo *et al*⁽²⁰¹⁾) or a comparative test (such as those reported by Brady *et al*⁽²⁰²⁾ and Lim and Williamson⁽²⁰³⁾), various versions of which are listed in Table 4.1. A,B,C,D,E and F are homologues. In a null test, components 1 and 2 are congruent and should yield no

4.2 Ternary mixtures

observable change on mixing for properties such as volume and enthalpy.

In a comparative test, components 1 and 2 are not congruent, and the change observed on mixing is compared against a binary mixture with which it is congruent. These changes observed on mixing should be the same if the principle of congruence is valid. Looi *et al*⁽²⁵⁾ used test 2.1 on a ternary mixture consisting of an equimolar mixture of *n*-tridecane and *n*-nonadecane with an index of 16 and *n*-hexane. The results are compared with that of the system *n*-hexadecane + *n*-hexane. The excess volumes obtained at 298.15 K agreed with the results of Diaz Pena and de Soto⁽²⁰⁴⁾ and also with those of Gomez-Ibanez and Liu.⁽²⁰⁵⁾ A slightly poorer correlation was obtained between the excess enthalpies at 298.15 K and the results of Larkin *et al*⁽²⁰⁶⁾, and those interpolated from the data of McGlashan and Morcom⁽¹⁸⁶⁾.

Table 4.1. Summary of the various possible tests.⁽³⁰⁾

Test	Component 1	Component 2	Test type
1.1	(A + B), $n=n_c$	C	Null test
1.2	(A + B), $n=n_c$	(D + E), $n=n_c$	Null test
1.3	(A + B), $n=n_c$ C	D D	Comparative test
1.4	(A + B), $n=n_c$ C	(D + E), $n=n_F$ F	Comparative test

4.3 This work

In this work, a novel set of mixtures involving accurately made pseudo-*n*-alkanes⁽²⁵⁾ has been used to test the principle by means of H_m^E and V_m^E , using a null test, (test 1.1 above). The null test has never been used on these types of mixtures before. This work has been devised

4.2 Ternary mixtures

in consultation with Prof. R. Battino (Wright State University, USA). The principle implies that a pseudo-*n*-alkane ($0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}$) will behave like C_mH_{2m+2} , where $m=(k+l)/2$. Ten pseudo-*n*-alkanes were made up for the V_m^E , and five for the H_m^E .

Following this, the same principle was tested on a series of cycloalkanes and their pseudo-compounds. This work reports on V_m^E for $[x\{\text{pseudo-c-C}_8\text{H}_{16}(0.5\text{c-C}_6\text{H}_{12} + 0.5\text{c-C}_{10}\text{H}_{20})\} - (1-x)\text{c-C}_8\text{H}_{16}]$, and $[x\{\text{pseudo-c-C}_7\text{H}_{14}(0.5\text{c-C}_8\text{H}_{16} + 0.5\text{c-C}_6\text{H}_{12})\} + (1-x)\text{c-C}_7\text{H}_{14}]$, and H_m^E for the systems described above, as well as $\{x\{\text{pseudo-c-C}_6\text{H}_{12}(0.5\text{c-C}_5\text{H}_{10} + 0.5\text{c-C}_7\text{H}_{14})\} + (1-x)\text{c-C}_6\text{H}_{12}\}$ and $[x\{\text{pseudo-c-C}_7\text{H}_{14}(0.6\text{c-C}_5\text{H}_{10} + 0.4\text{c-C}_{10}\text{H}_{20})\} + (1-x)\text{c-C}_7\text{H}_{14}]$.

4.4 Experimental

4.4.1 Materials

A summary of the materials used their suppliers and their purity is given in Table 4.2. The liquids were all analyzed by g.l.c, after being fractionally distilled. Their purity was found to be >99 per cent mole fraction.

4.4 Experimental

Table 4.2. Materials used, their suppliers and their purity.

Compound	Supplier	Purity (mole %)
hexane	Aldrich	> 99.5
heptane	Aldrich	> 99.5
octane	Aldrich	> 99.5
nonane	Fluka A.G.	> 99.5
decane	Aldrich	> 99.5
dodecane	Aldrich	> 99.5
tridecane	Aldrich	> 99.5
tetradecane	Aldrich	> 99.5
hexadecane	Aldrich	> 99.5
cyclopentane	Fluka A.G.	> 99
cyclohexane	SARchem	> 99
cycloheptane	Aldrich	> 99
cyclooctane	Janssen	> 99
cyclodecane	Fluka	> 99

4.4.2 Preparation of mixtures

The pseudo-*n*-alkane mixtures and pseudo-cycloalkane mixtures were made to within 1×10^{-4} of $x=0.5$, in each case. The bottles were weighed on a Mettler AT 250 (precision ± 0.01 mg). The liquids were degassed by immersing the flask in a sonic bath for 10 to 15 minutes, before weighing and mixing. The mixtures were made up in 5 cm³ bottles (with a mass of approximately 4 g), and the vapour space was kept to a minimum. In all cases, the least volatile component was added to the bottle first.

4.4 Experimental

The V_m^E results for the (pseudo-*n*-alkane + *n*-alkane) mixtures are believed to be accurate to within $\pm 0.004 \text{ cm}^3 \cdot \text{mol}^{-1}$, and for the (pseudo-cycloalkane + cycloalkane) within $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$. The H_m^E results are believed to be within $1 \text{ J} \cdot \text{mol}^{-1}$.

4.5 Results

The V_m^E and H_m^E results for the (pseudo-*n*-alkane + *n*-alkane) mixtures are given in Tables 4.3 and 4.4, respectively. Attempts were made to prepare pseudo-*n*-alkane mixtures with pentane, but the results showed a scatter greater than $0.004 \text{ cm}^3 \cdot \text{mol}^{-1}$. This was thought to be due to evaporation, and thus the results are not recorded here. The V_m^E results for the (pseudo-cycloalkane + cycloalkane) mixtures are given in Table 4.5. The H_m^E results are given in Tables 4.5 and 4.6.

4.5 Results

Table 4.3. V_m^E results for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$ at 298.15 K.

1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$
k=6, l=8, m=7							
0.1422	-2.8	0.4553	-4.2	0.6135	-2.1	0.6953	-4.1
0.3869	-4.6	0.5615	-4.4				
k=7, l=9, m=8							
0.0399	0.3	0.2996	-0.6	0.5434	-2.0	0.7194	-0.8
0.1438	1.9	0.4551	0.4	0.6931	-0.4	0.8681	0.1
0.1876	0.4	0.5429	-0.9	0.7073	0.7	0.9457	-0.4
0.2983	0.3						
k=6, l=10, m=8							
0.1837	-0.9	0.5473	-4.5	0.7180	-4.3	0.8915	-2.0
0.4431	-4.7	0.6204	-4.2				
k=6, l=12, m=9							
0.1636	-0.9	0.3280	-1.9	0.4969	-3.0	0.7211	-1.1
0.2517	-1.6	0.4138	-2.8	0.5684	-1.8	0.8369	-0.5
k=8, l=10, m=9							
0.1614	-0.6	0.3955	-3.1	0.5541	-2.5	0.7057	-1.4
0.1714	-1.2	0.4483	-1.6	0.6234	-1.7	0.8123	-1.4
0.3020	-3.5	0.4599	-2.1	0.6245	-2.2	0.9016	-2.3
0.3817	-0.9	0.5509	-1.2	0.6903	-3.2	0.9352	-1.7

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

4.5 Results

Table 4.3 continued...

1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$	1-x	$10^3 \cdot V_m^{Ea}$
k=6, l=14, m=10							
0.2375	-1.4	0.4019	-2.8	0.5969	-2.0	0.8611	-1.2
0.3715	-1.9	0.5223	-2.9	0.8352	-1.5		
k=8, l=16, m=12							
0.1819	0.3	0.3997	-4.2	0.5176	-3.2	0.6851	-2.1
0.3165	1.9	0.4379	-5.3	0.5937	-3.0	0.9037	-1.4
k=10, l=14, m=12							
0.1236	-0.8	0.4995	-1.8	0.6180	-4.2	0.8010	-1.9
0.3715	-0.9	0.4998	-4.3	0.6513	-3.9		
k=10, l=16, m=13							
0.1827	-0.7	0.4877	-4.1	0.5604	-2.5	0.8596	-0.3
0.3457	-2.9	0.4948	-4.1	0.6933	-0.7		
k=12, l=16, m=14							
0.1228	-1.0	0.4545	-4.6	0.5580	-3.7	0.8659	-0.5
0.2697	-1.7	0.4877	-1.2	0.6561	-1.4		

^aUnits : cm³.mol⁻¹

4.5 Results

Table 4.4. H_m^E results for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$ at 298.2 K.

1-x	H_m^{Ea}	1-x	H_m^{Ea}	1-x	H_m^{Ea}	1-x	H_m^{Ea}
k=7,l=9,m=8							
0.2006	0.0	0.3639	0.5	0.4596	1.1	0.7067	0.03
0.2946	0.0	0.4026	0.0	0.5082	0.0	0.7974	0.02
k=8,l=10,m=9							
0.1907	0.0	0.3512	0.1	0.5191	0.1	0.7743	0.0
0.2401	0.0	0.4007	0.2	0.6309	0.2	0.8411	0.0
k=12,l=16,m=14							
0.1156	0.5	0.2895	0.5	0.4434	0.8	0.6869	0.7
0.2354	0.6	0.3692	0.4	0.5142	0.9	0.8410	0.5
k=10,l=16,m=13							
0.1211	0.0	0.3464	0.6	0.4796	1.1	0.6812	0.7
0.2592	0.2	0.3915	0.8	0.5432	0.7	0.8528	0.5

^aUnits : J.mol⁻¹

4.5 Results

Table 4.5. V_{Δ}^E for $[x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}]$ at 298.15 K.

x	$10^3 \cdot V_m^{Ea}$	x	$10^3 \cdot V_m^{Ea}$	x	$10^3 \cdot V_m^{Ea}$
k=8,l=6,m=7					
0.2191	-2.03	0.4706	-0.34	0.7337	-2.37
0.3631	-3.00	0.6263	-5.62	0.8569	-4.88
k=6,l=10,m=8					
0.0505	-1.81	0.5015	-24.92	0.8135	-14.38
0.2134	-7.36	0.6416	-17.56	0.8910	-10.73
0.3999	-22.37				

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$

4.5 Results

Table 4.6. H_m^E for $[x(0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}) + (1-x)c-C_mH_{2m}]$ at 298.2 K.

x	H_m^{Ea}	x	H_m^{Ea}	x	H_m^{Ea}
k=5,l=7,m=6					
0.1120	9.2	0.5609	21.6	0.8466	10.8
0.1638	12.7	0.6038	20.2	0.8787	8.6
0.3524	19.6	0.7204	17.5	0.9045	7.3
0.5408	20.7				
k=8,l=6,m=7					
0.0648	0.6	0.4833	2.2	0.7482	1.6
0.1526	1.3	0.6222	2.2	0.8191	1.3
0.1807	1.6	0.6605	2.9	0.8287	1.5
0.2708	2.2				
k=10,l=6,m=8					
0.1676	4.5	0.4881	8.6	0.8168	5.5
0.1984	6.1	0.5638	8.9	0.8758	4.2
0.3642	8.6	0.7796	8.3		

^aUnits : J.mol⁻¹

4.5 Results

Table 4.7. H_m^E for $[x(0.6c-C_5H_{10} + 0.4c-C_{10}H_{20}) + (1-x)c-C_7H_{14}]$ at 298.2 K.

x	H_m^{Ea}	x	H_m^{Ea}	x	H_m^{Ea}
k=5,l=10,m=7					
0.1625	26.3	0.4306	47.8	0.8395	23.1
0.2799	39.2	0.5307	44.2	0.8712	19.8
0.3991	44.9	0.6805	37.8		

^aUnits : J.mol⁻¹

4.6 Discussion

4.6.1 Pseudo-alkane mixtures

The (alkane + pseudo-*n*-alkane) results, given in Tables 4.3 and 4.4, confirm the application of the principle of congruence to the volumetric and enthalpic behaviour of mixtures containing a wide range of components of widely different chain lengths. The results show that V_m^E and H_m^E for (an *n*-alkane of carbon number *m* + a pseudo-*n*-alkane of the same carbon number), over the whole composition range, were within $\pm 0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $\pm 1.1 \text{ J} \cdot \text{mol}^{-1}$ respectively, for all the mixtures studied here. See Figs. 4.1 (i), (ii), (iii), and 4.2. As can be seen from the plots, no pattern or symmetry is observed in the plotted points.

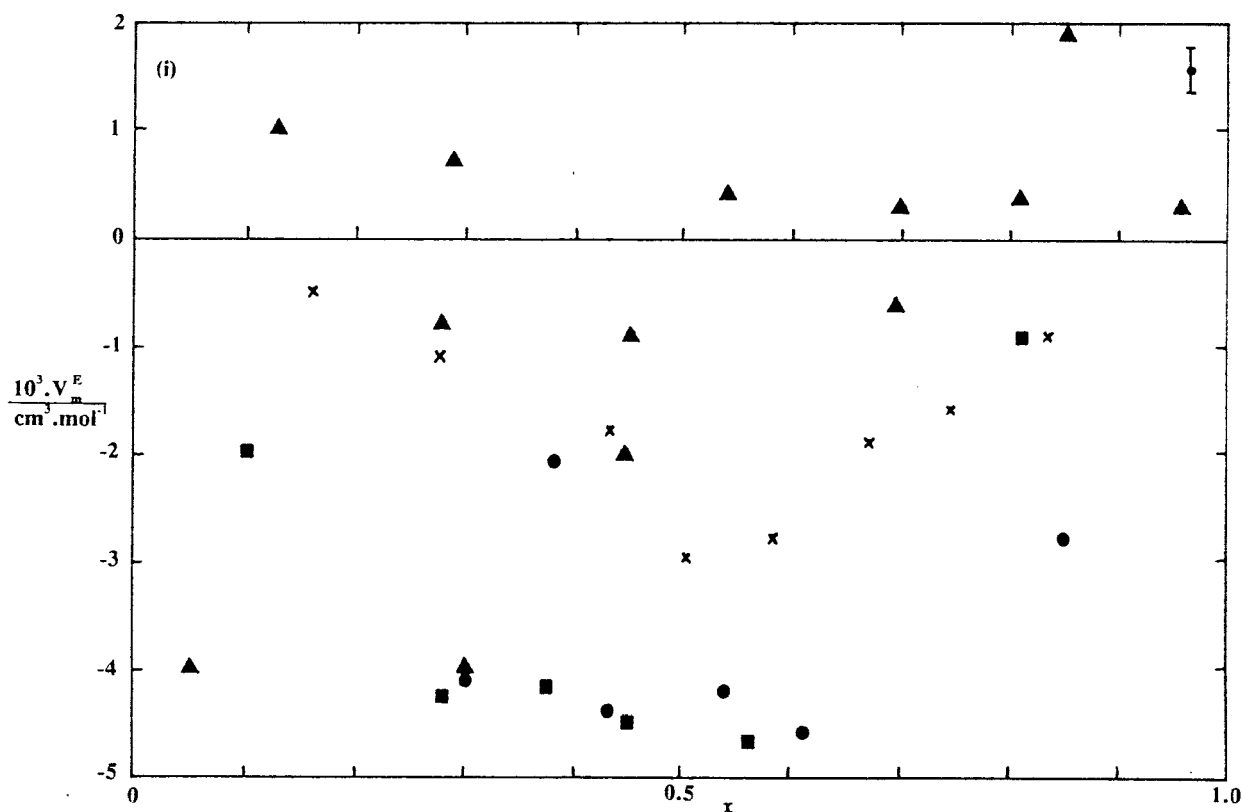


Fig. 4.1 (i) : V_m^E for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$: $\bullet$, $k=6, l=8, m=7$; $\blacktriangle$, $k=7, l=9, m=8$; $\blacksquare$, $k=6, l=10, m=8$; $\times$, $k=6, l=12, m=9$.

4.6 Discussion

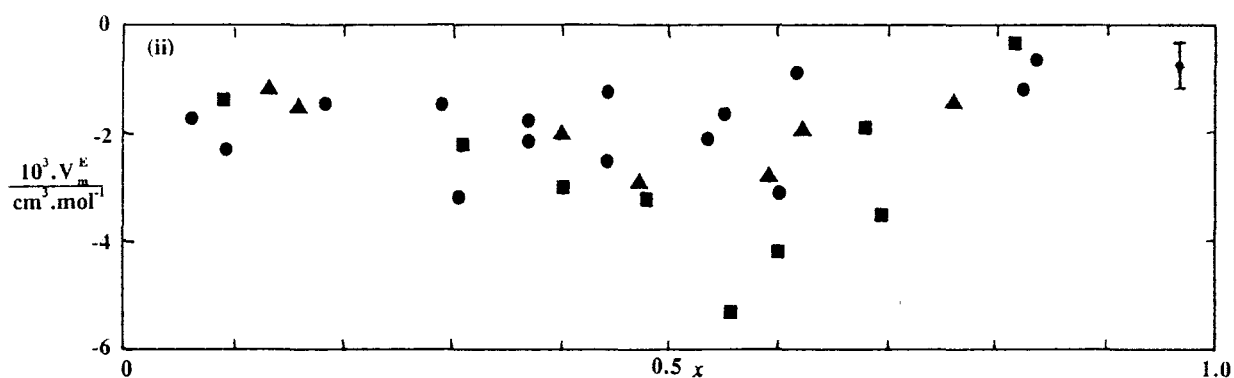


Fig. 4.1 (ii) : V_m^E for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$: $\bullet$, $k=8$, $l=10$, $m=9$; $\blacktriangle$, $k=6$, $l=14$, $m=10$; $\blacksquare$, $k=8$, $l=16$, $m=12$.

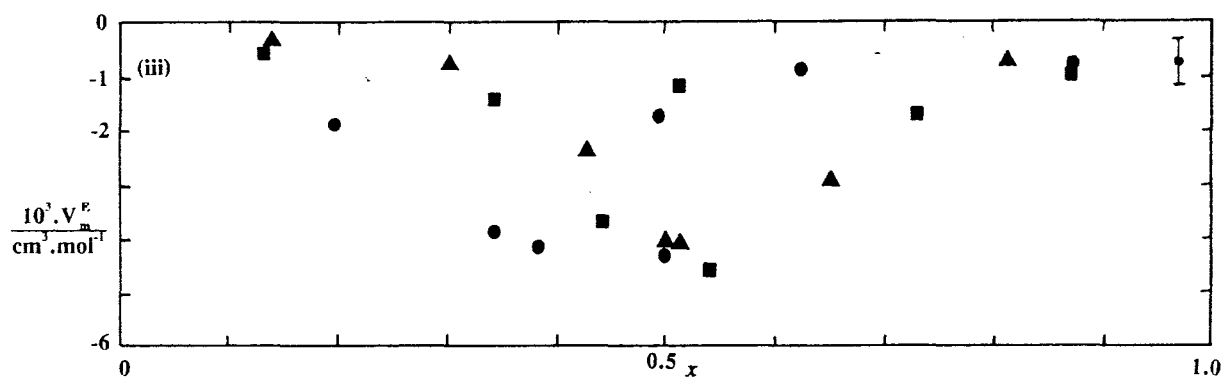


Fig. 4.1 (iii) : V_m^E for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$: $\bullet$, $k=10$, $l=14$, $m=12$; $\blacktriangle$, $k=10$, $l=16$, $m=13$; $\blacksquare$, $k=12$, $l=16$, $m=14$.

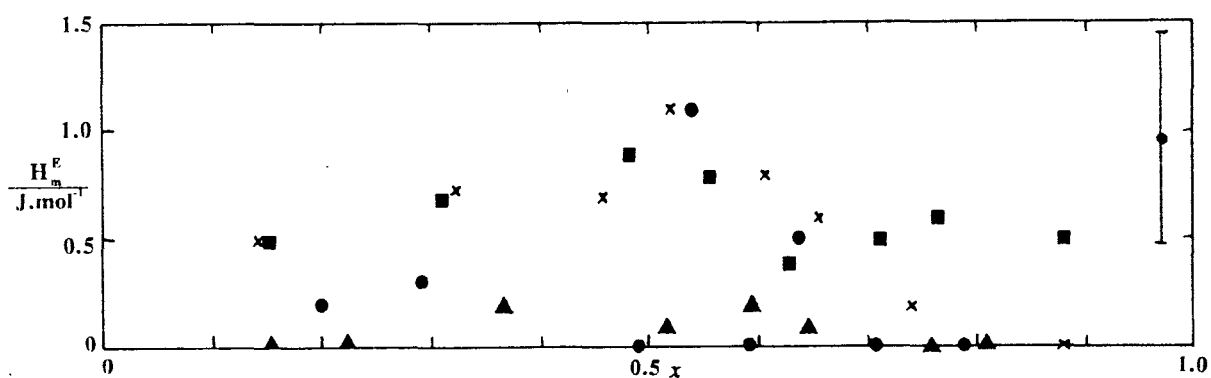


Fig. 4.2 : H_m^E for $[x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}]$: $\bullet$, $k=7$, $l=9$, $m=8$; $\blacktriangle$, $k=8$, $l=10$, $m=9$; $\blacksquare$, $k=12$, $l=16$, $m=14$; $\times$, $k=10$, $l=16$, $m=13$.

4.6.2 Pseudo-cycloalkane mixtures

The (pseudo-cycloalkane + cycloalkane) results show a small positive excess enthalpy (see Fig. 4.3) and a small negative excess volume (see Fig. 4.4) of mixing for all of the mixtures. Mixtures containing $c\text{-C}_5\text{H}_{10}$ appear to produce the greatest divergence from the congruence principle. This shows that the effect of adding a $-\text{CH}_2-$ group to $c\text{-C}_5\text{H}_{10}$ is not the same as the addition of a $-\text{CH}_2-$ group to $c\text{-C}_8\text{H}_{16}$ or $c\text{-C}_{10}\text{H}_{20}$. In general, the greater the disparity in carbon number, the greater is the divergence from the congruence principle. The cycloalkane mixtures do not satisfy the congruence principle as well as the n -alkane mixtures do.

This null method could perhaps be applied to mixtures of eg. alkanol, or alkynes, or alkenes, to test the theory of congruence further.

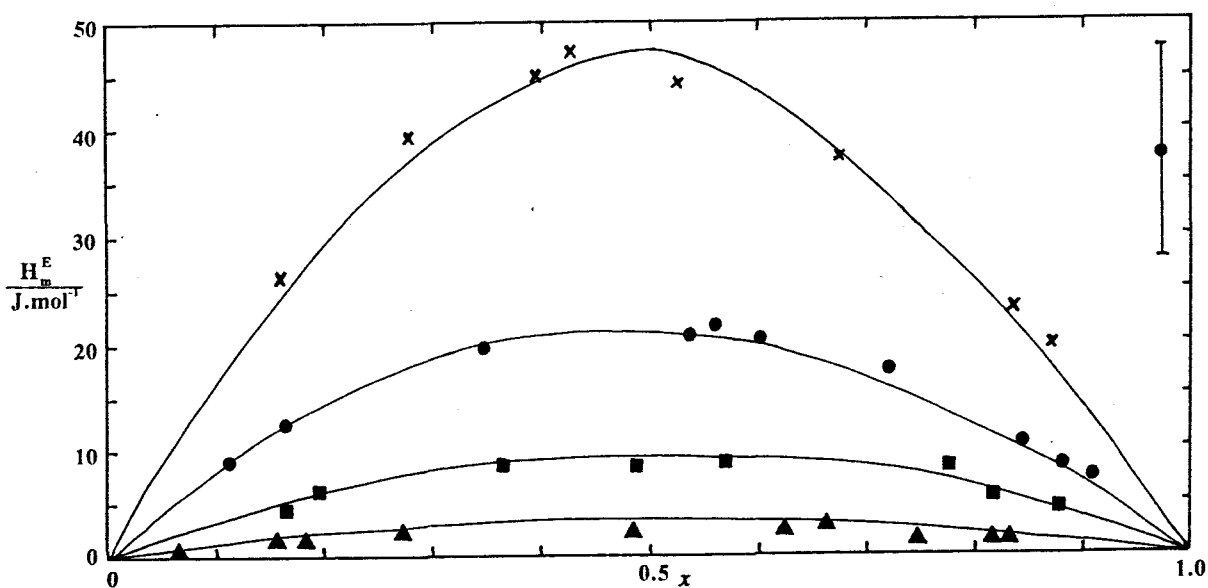


Fig. 4.3 : H_m^E for $[x(0.5c\text{-C}_k\text{H}_{2k} + 0.5c\text{-C}_l\text{H}_{2l}) + (1-x)c\text{-C}_m\text{H}_{2m}]$ and $[x(0.6c\text{-C}_5\text{H}_{10} + 0.4c\text{-C}_{10}\text{H}_{20}) + (1-x)c\text{-C}_7\text{H}_{14}]$ (the latter depicted by x on the plot) : ●, $k=5, l=7, m=6$; ▲, $k=8, l=6, m=7$; ■, $k=10, l=6, m=8$; x, $k=5, l=10, m=14$.

4.6 Discussion

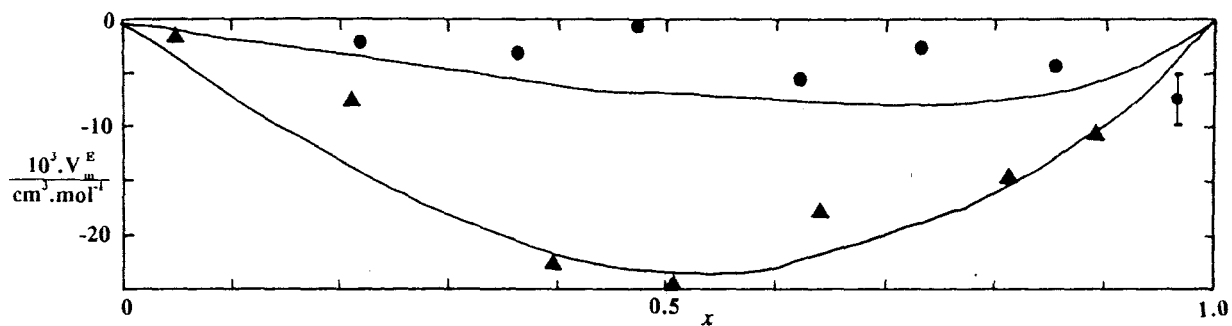


Fig. 4.4 : V_m^E for $[x(0.5c\text{-}C_kH_{2k} + 0.5c\text{-}C_lH_{2l}) + (1-x)c\text{-}C_mH_{2m}]$: ●, $k=8, l=6, m=7$; ▲, $k=6, l=10, m=8$.

CHAPTER 5

Theories of Non-Electrolytes - Flory Theory

5.0 Introduction

The prediction and interpretation of the thermodynamic properties of non-electrolyte mixtures from the properties of the individual pure components has long been the subject of research.⁽¹⁾ A number of theories to describe or predict such properties have been proposed and improved upon as experimental techniques improved and revealed more about the mixtures being investigated.^(4,15,40,207-209) A very thorough review of the development of the theories and their derivations has been reported by Baxter⁽²¹⁰⁾ in his PhD thesis.

Flory and co-workers^(15,17-20) have developed a theory which relates thermodynamic excess properties of liquid mixtures to measurable macroscopic properties of pure components. In their approach, they have included the concepts of degrees of freedom of the component molecules and the *r*-meric structural representation of linear molecules proposed by Prigogine and co-workers.^(209,211,212) The theory was initially derived to explain the thermodynamic properties of normal paraffin hydrocarbon mixtures,⁽¹⁵⁾ and was subsequently extended to encompass systems of non-polar molecules differing in size and shape.⁽¹⁷⁾ The theory has been applied with varying degrees of success to systems of simple liquids involving mixtures of benzene, a cycloalkane, and *n*-alkane with an *n*-alkane, an alkene, and an alkyne, a cycloalkane and bicyclic compounds.⁽²¹³⁻²¹⁸⁾

An improvement on this theory, the Prigogine-Flory theory, considers excess thermodynamic properties of binary mixtures to be the sum of three contributions.^(23,24,219) a combinatorial term, an interactional term arising from the difference in chemical nature of the two components, and a free volume contribution. More insight into the nature of these contributions has been given by Patterson and co-workers.⁽²²¹⁻²²³⁾ Their approximate equations lead to the separation of these

5.0 Introduction

contributions.

The excess molar volume can be expressed as: an interactional term which is proportional to the Flory χ_{12} parameter, a free volume contribution which originates from a difference in the degrees of thermal expansion between two components, and a P^* contribution which arises from the differences in the internal pressures and reduced volumes of the components. The approximate form of their excess molar enthalpy equation is divided into a free volume and an interactional contribution. Their theory has been applied successfully to predict excess thermodynamic properties for mixtures of a cycloalkane with an n -alkane, linear siloxane and decamethyltetrasiloxane with an n -alkane, and benzene, carbon tetrachloride with an n -alkane.⁽²¹⁹⁾ Work has been carried out with mixtures involving n -alkanes mixed with globular shaped molecules, and with highly branched isomers, with the aim of investigating the order effect which may occur on mixing.^(23,24,220-223)

In this work, the theory is applied to binary mixtures of a substituted benzene or a 1-alkene or a 1-alkyne or a cycloalkane + an alkanol. The predicted H_m^E and V_m^E have been compared to experimental values.

5.1 A short description of the Flory theory

In the Flory model,^(15,17,211) the excess molar volume is related to the reduced volume $\tilde{V}$, (where $\tilde{V} = V/V^{*(15)}$) the reduced temperature $\tilde{T}$, and the adjustable interactional parameter χ_{12} . The reduced volume of the pure substance i is defined in terms of the thermal expansion coefficients α_i

$$\tilde{V}_i = [1 + (4/3)\alpha_i T] / (1 + \alpha_i T)^3 \quad 5.1$$

At zero pressure, the reduced volume and temperature satisfy the reduced equation of state

$$\tilde{T}_i = (\tilde{V}_i^{1/3} - 1) / (\tilde{V}_i^{4/3}) \quad 5.2$$

5.1 Description of Flory theory

where the reduced temperature for a mixture is defined as

$$\tilde{T} = [(\phi P^* \tilde{T})_1 + (\phi P^* \tilde{T})_2] / [(\phi P^*)_1 + (\phi P^*)_2 - \phi_1 \theta_2 \chi_{12}] \quad 5.3$$

and the charactersitic pressure is defined as

$$P_i^* = (\alpha_i / \kappa_i) T (\tilde{V}_i)^2 \quad 5.4$$

The segment fraction ϕ_i and the site fraction θ_i are defined as

$$\phi_1 = (1 - \phi_2) = (xV^*)_1 / [(xV^*)_1 + (xV^*)_2] \quad 5.5$$

and

$$\theta_1 = (1 - \theta_2) = \phi_1 / [\phi_1 + (\phi s)_2 s_1] \quad 5.6$$

The ratio of the surface contact sites per segment for the respective components s_1/s_2 has been calculated from the approximation by Abe and Flory⁽¹⁸⁾

$$s_1/s_2 = (V_1^*/V_2^*)^{1/3} \quad 5.7$$

where V_i^* is the hard core volume.⁽¹⁷⁾

The excess molar volume V_m^E is given exactly by

$$V_m^E = [\{(xV^*)_1 + (xV^*)_2\} \{(\phi \tilde{V})_1 + (\phi \tilde{V})_2\}^{(7/3)} (\tilde{T} - \tilde{T}^o)] / [4/3 - \{(\phi \tilde{V})_1 + (\phi \tilde{V})_2\}^{1/3}] \quad 5.8$$

where $\tilde{T}^o$ is the "ideal" reduced temperature for the mixture and can be calculated exactly from Eqn. 5.2 using the "ideal" reduced volume for the mixture $\tilde{V}^o$

5.1 Description of Flory theory

$$\tilde{V}^o = (\phi \tilde{V})_1 + (\phi \tilde{V})_2 \quad 5.9$$

The formula for the excess molar enthalpy H_m^E is given by

$$H_m^E = (xP^*V^*)_1(\tilde{V}_1^I - \tilde{V}^I) + (xP^*V^*)_2(\tilde{V}_2^I - \tilde{V}^I) + x_1V_1^*\theta_2\chi_{12}/\tilde{V} \quad 5.10$$

where

$$\tilde{V} = \tilde{V}^o + \tilde{V}^E \quad 5.11$$

and

$$\tilde{V}^E = (\tilde{V}^o)^{7/3} [4/3 - (\tilde{V}^o)^{1/3}]^{-1} (\tilde{T} - \tilde{T}^o) \quad 5.12$$

Patterson and co-worker's⁽²⁴⁾ approximate expression for V_m^E , in terms of the three contributions is

$$\begin{aligned} V_m^E / [(xV^*)_1 + (xV^*)_2] &= [(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2\chi_{12}] / [(4/3)\tilde{V}^{-1/3} - 1]P_1^* \text{ (Interactional term)} \\ &- [(\tilde{V}_1 - \tilde{V}_2)^2(14/9\tilde{V}^{1/3} - 1)]\psi_1\psi_2 / [4/3(\tilde{V})^{-1/3} - 1]\tilde{V} \quad (\tilde{V} \text{ curvature}) \\ &+ [(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\psi_1\psi_2] / (P_2^*\psi_1 + P_1^*\psi_2) \quad (P^* \text{ effect}) \end{aligned} \quad 5.13$$

where the contact energy fraction ψ_1 is given by

$$\psi_1 = (1 - \psi_2) = (\phi P^*)_1 / [(\phi P^*)_1 + (\phi P^*)_2] \quad 5.14$$

In this approximation, $\tilde{V}$ has been equated to $\tilde{V}^o$. The remaining parameters are identical to those given by Flory.⁽¹⁷⁾

The corresponding approximate equation for the excess enthalpy given by Patterson and co-workers⁽²³⁾ can be separated into a free volume contribution and an interactional contribution.

5.1 Description of Flory theory

The free volume contribution is given by

$$H_m^E(f.v.)/(x_1U_1^*+x_2U_2^*) = \tilde{C}_p(\tilde{T}_u)[(\psi_1\tilde{T})_1+\psi_2\tilde{T}_2-\tilde{T}_u] \quad 5.15$$

where $\tilde{T}_u$ is an average reduced temperature for the solution, appropriate to the reduced configurational energy $\tilde{U}$ and is defined as

$$\tilde{U}(\tilde{T}_u) = \psi_1\tilde{U}_1(\tilde{T}_1) + \psi_2\tilde{U}_2(\tilde{T}_2) \quad 5.16$$

The reduced heat capacity $\tilde{C}_p$ for the pure components and for the mixture is given by

$$\tilde{C}_p^l = (4/3)\tilde{V}^{1/3}-1 \quad 5.17$$

In the van der Waals Model used by Flory and Patterson,⁽²³⁾

$$\tilde{U} = -\tilde{V}^l \quad 5.18$$

and the reduced parameter for the configurational energy, U_i^* is defined as

$$U_i^* = P_i^*V_i^* \quad 5.19$$

The interactional contribution as defined by Patterson⁽²³⁾ is given by

$$H_m^E(interac.)/(x_1U_1^*+x_2U_2^*) = [-\tilde{U}(\tilde{T}_u)+\tilde{T}_u\tilde{C}_p(\tilde{T}_u)]\chi_{12}\psi_1\theta_2/P_1^* \quad 5.20$$

5.2 Results

The Patterson equations 5.15 and 5.20 were used to fit the H_m^E data for 1-alkenes or 1-alkynes or cycloalkanes + an alkanol, and the value of $\chi_{12}(H_m^E)$ found, which minimized $\sigma(H_m^E)$ over the one hundred data points at 0.01 mole fraction intervals obtained from the Redlich-Kistner equation. This value of $\chi_{12}(H_m^E)$ was used in predicting V_m^E and the corresponding value of $\sigma^*(V_m^E)$ was calculated. The definitions of the calculated parameters given in this work are as follows:

$$\sigma^2(X_m^E) = \sum_{i=1}^{98} [X_m^E(\text{exp}) - X_m^E(\text{calc})]^2 / 97 \quad 5.21$$

where X_m^E refers to the excess molar property. $\chi_{12}(V_m^E)$ was determined from V_m^E data using eqn.5.13, the standard deviation $\sigma(V_m^E)$ was determined from eqn.5.21. The calculated H_m^E were then determined from $\chi_{12}(V_m^E)$ using eqn.5.10, and hence $\sigma^*(H_m^E)$ was determined from eqn.5.21 where X_m^E refers to the excess molar enthalpy.

The literature values for the thermal expansion coefficients α , the isothermal compressibilities κ , and the densities ρ , used in the application of the Flory and Patterson equations are given in Table 5.1. The best fit $\chi_{12}(H_m^E)$ values are given in Table 5.2, along with values for $\sigma^*(V_m^E)$ and $\sigma(H_m^E)$.

5.2 Results

Table 5.1. Physical properties of the pure liquids at 298.15 K.

Component	$10^{12}\kappa_T/(\text{Pa}^{-1})$	Ref.	$10^3\alpha_b/(\text{K}^{-1})$	Ref.	$\rho/(\text{g}\cdot\text{cm}^{-3})$	Ref.
1-hexene	1.414	236	1689	236	0.66805	234
1-heptene	1.267	230	1447	230	0.69297	234
1-octene	1.179	230	1297	230	0.71105	234
1-hexyne	1.371	236	1404	230	0.71034	234
1-heptyne	1.249	230	1256	230	0.72830	234
1-octyne	1.162	230	1148	230	0.74229	234

5.2 Results

Table 5.1 continued...

Component	$10^{12}\kappa_T/(\text{Pa}^{-1})$	Ref.	$10^3\alpha_b/(\text{K}^{-1})$	Ref.	$\rho/(\text{g.cm}^{-3})$	Ref.
MeOH	1263	224	0.965	231	0.7866	234
EtOH	1149	224	0.999	232	0.7851	234
1-PrOH	1026	224	1.019	232	0.7998	234
2-PrOH	1142	224	0.951	233	0.7808	234
Cyclo-5	1332	213	1.351	225	0.7374	234
Cyclo-6	1120	225	1.215	235	0.7739	234
Cyclo-7	967	226	1.000	226	0.8060	234
Cyclo-8	801	227	0.979	227	0.8315	234
Cyclo-10	455	228	0.610	228	0.8980	228

5.2 Results

Table 5.2. The H_m^E and V_m^E data at equilibrium concentrations and the best fit values using the Flory exact equation.

Mixture	$V_{\text{exp}}^E(0.5)^a$	$H_{\text{exp}}^E(0.5)^b$	$\chi_{12}10^{-8}^c$	$\sigma(H_m^E)^b$	$\sigma^*(V_m^E)^a$
1-hexene(1) + MeOH(2)	0.27	554.2	0.360	107.3	0.40
1-hexene(1) + EtOH(2)	0.20	550.6	0.310	144.1	0.30
1-heptene(1) + MeOH(2)	0.36	575.2	0.340	113.4	0.30
1-heptene(1) + EtOH(2)	0.29	591.6	0.310	154.6	0.30
1-octene(1) + MeOH(2)	0.38	603.8	0.340	123.9	0.20
1-octene(1) + EtOH(2)	0.34	614.3	0.300	172.9	0.20
1-hexyne(1) + MeOH(1)	-0.13	512.0	0.340	195.5	0.70
1-hexyne(1) + EtOH(2)	-0.09	622.1	0.380	211.2	0.70
1-heptyne(1) + MeOH(2)	-0.03	578.9	0.360	245.5	0.60
1-heptyne(1) + ETOH(2)	-0.14	723.1	0.380	245.5	0.60
1-octyne(1) + MeOH(2)	0.03	611.2	0.340	203.5	0.50
1-octyne(1) + EtOH(2)	0.05	614.3	0.310	169.9	0.50

^aUnits : $\text{cm}^3.\text{mol}^{-1}$; ^bUnits : $\text{J}.\text{mol}^{-1}$; ^cUnits : $\text{J}.\text{m}^{-3}$

5.2 Results

Table 5.2 continued...

Mixture	$V_{\text{exp}}^E(0.5)^a$	$H_{\text{exp}}^E(0.5)^b$	$\chi_{12}/10^{8c}$	$\sigma(H_m^E)^b$	$\sigma^*(V_m^E)^a$
Cyclo-5(1) + MeOH(2)	0.48	565.5	0.437	58.1	0.25
Cyclo-5(1) + EtOH(2)	0.40	419.4	0.348	98.6	0.20
Cyclo-5(1) + 1-PrOH(2)	0.21	469.0	0.291	125.8	0.20
Cyclo-5(1) + 2-PrOH(2)	0.39	674.9	0.404	124.9	0.40
Cyclo-6(1) + EtOH(2)	0.56	641.1	0.375	99.2	0.11
Cyclo-6(1) + 1-PrOH(2)	0.41	587.5	0.315	125.9	0.10
Cyclo-6(1) + 2-PrOH(2)	0.56	805.8	0.426	129.8	0.29
Cyclo-7(1) + EtOH(2)	0.53	663.9	0.360	106.0	0.06
Cyclo-7(1) + 1-PrOH(2)	0.35	606.2	0.300	127.2	0.10
Cyclo-7(1) + 2-PrOH(2)	0.47	831.0	0.399	113.4	0.20
Cyclo-8(1) + EtOH(2)	0.40	626.2	0.321	94.9	0.63
Cyclo-8(1) + 1-PrOH(2)	0.28	614.1	0.285	127.6	0.10
Cyclo-8(1) + 1-PrOH(2)	0.36	781.4	0.361	129.9	0.22

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$; ^bUnits : $\text{J} \cdot \text{mol}^{-1}$; ^cUnits : $\text{J} \cdot \text{m}^{-3}$

5.2 Results

Table 5.2 continued...

Mixture	$V_{\text{exp}}^E(0.5)^a$	$H_{\text{exp}}^E(0.5)^b$	$\chi 10^{-8}^c$	$\sigma(H_m^E)^b$	$\sigma^*(V_m^E)^a$
Cyclo-10(1) + EtOH(2)	0.23	497.1	0.229	33.8	0.43
Cyclo-10(1) + 1-PrOH(2)	0.17	485.2	0.211	76.9	0.32
Cyclo-10(1) + 2-PrOH(2)	0.14	665.3	0.275	102.4	0.35

^aUnits : $\text{cm}^3 \cdot \text{mol}^{-1}$; ^bUnits : $\text{J} \cdot \text{mol}^{-1}$; ^cUnits : $\text{J} \cdot \text{m}^{-3}$

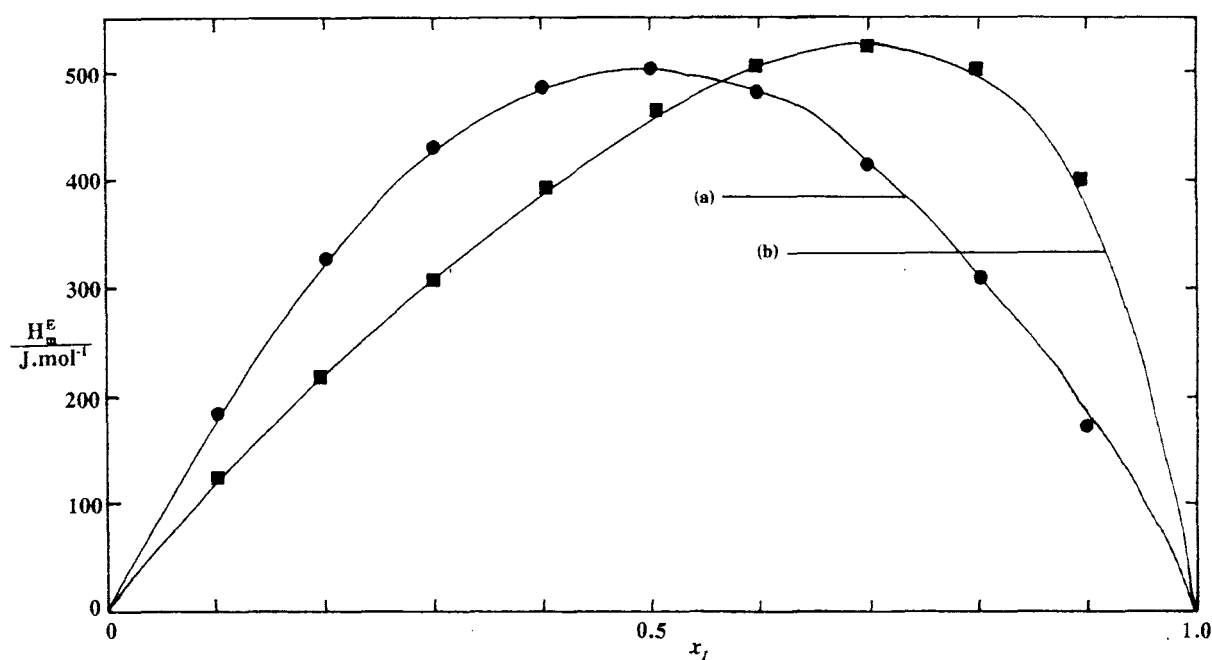


Fig. 5.1 : $H_m^E(\text{exp})$ and $H_m^E(\text{calc})$ plotted vs. mole fraction of cyclo-compound for cyclo-5(1) + 1-PrOH(2); (a) calculated, (b) experimental.

5.3 Discussions

As mentioned in the introduction to this chapter, the Flory theory was initially derived to explain the thermodynamic properties of normal paraffin hydrocarbon mixtures by Flory, Orwoll and Vrij,⁽¹⁵⁾ and was subsequently extended to encompass systems of non-polar molecules, differing in size and shape, by Flory.⁽¹⁷⁾ The theory has been applied with varying degrees of success to systems of simple liquids involving mixtures of benzene, a cycloalkane, and *n*-alkane with an *n*-alkane, an alkane, an alkyne, a cycloalkane and bicyclic compounds by Letcher and Perkins;⁽²¹³⁾ Letcher and Baxter;^(214,223) Jones, Weeks and Benson;⁽²¹⁵⁾ Benson, Murakami, Lam and Singh;⁽²¹⁶⁾ Letcher and Spiteri⁽²¹⁷⁾ and Fujihara, Kobayashi and Murakami.⁽²¹⁸⁾ For example, Letcher and Baxter⁽²²³⁾ use the theory to predict H_m^E from the V_m^E data, and compare $H_m^E(\text{Flory})$ and $H_m^E(\text{experimental})$. In their mixtures of {(benzene or cyclohexane or *n*-hexane) + an *n*-alkane}, the standard deviation of the predicted values never exceeds 6% or 16 J.mol⁻¹ of $H_m^E(\text{experimental})$.

In this work the same techniques as used by Baxter⁽²¹⁰⁾ were utilised. The systems investigated involved H_m^E and V_m^E data (discussed in Chapters 2 and 3), involving a 1-alkene or 1-alkyne or cycloalkane + an alkanol. The data was entered into a Fortran program designed to give results with which the Flory theory could be tested. Details of the program, along with data requirements, are given in *Appendix C*. The results obtained from fitting the Flory theory to the data is given in Table 5.2. From Table 5.2, it can be seen that the correlation results are poor. The calculated results *did*, however, predict the correct sign for H_m^E and V_m^E , in each case. The prediction obtained in this work is not as good as that obtained by Letcher and co-workers.^(213,217,223)

In this work, the standard deviation between $H_m^E(\text{calc})$ and $H_m^E(\text{exp})$ ranged from 10 to 35%. These results confirm that the theory is not suitable for use with a polar component.

CHAPTER 6

Introduction

In the second part of this thesis, the work concerns itself with the solution properties of binary solutions involving a solid solute (18-crown-6 ether,⁽²³⁷⁾ dibenzo-18-crown-6 ether, dicyclohexano-18-crown-6 ether, 15-crown-5 ether, or cryptand-222), represented by CE henceforth. The partial molar volumes at infinite dilution, $V_i(x_i=0)$, of the solute i (the crown ethers or cryptand), have been measured in several solvents, (ranging from water, to alkanols, to alkanes).

In Chapter 7, the partial molar volumes at infinite dilution of 18-crown-6 ether (CE6), and cryptand-222 (c-222) in various solvents are reported. These results are discussed in terms of solute-solute interactions,⁽²³⁸⁾ and in terms of solvent/solute packing. These results are compared with $V_i(x_i=0)$ results calculated⁽²³⁹⁾ from previously published excess molar volume data of cyclohexane⁽²⁴⁰⁾ or decahydronaphthalene⁽²⁴¹⁾ in n -alkane solvents. Observations were made as to the dependence of $V_i(x_i=0)$ on the solvent type. In the case of CE6, all the solvents are non-polar - whereas for c-222 polar solutes are included. Observations were made of the trends observed with the different solvent types in a plot of $V_i(x_i=0)$ versus the solvent molar volume, V_2^o .

The $V_i(x_i=0)$ information was made use of in investigating the complexation properties of the crown ethers or cryptand with a selection of metal halide salts (NaCl, NaI, KCl, KI, CsCl, or CsI), represented henceforth by MX. The volume changes upon complexation at infinite dilution, ΔV^∞ , were calculated⁽³¹⁾ for CE.MX complexes from V_ϕ determined over a concentration range of 0.1 to 0.11 cm³.mol⁻¹.

ΔV^∞ has been shown to be related to the electrostrictive effect.⁽³¹⁾ The results obtained in

Introduction

this thesis are compared with those obtained by Letcher *et al.*,⁽³¹⁾ and discussed in terms of solvent electrostriction,⁽²⁴²⁾ compressibilities,⁽³⁵⁾ pressure dependence of ΔV^∞ ⁽²⁴³⁾ and the significance of the equilibrium constant of complexation.^(38,244)

CHAPTER 7

Partial Molar Volumes at Infinite Dilution

7.0 Introduction

The partial molar volume at infinite dilution, $V_i(x_i=0)$, of a solute i in a solution is defined as the change in volume that takes place when one mole of the *solute* is added to an infinitely large amount of *solvent* (j), $(V_i(x_i=0) = (\partial V/\partial n_i)_{n_j, T, P})$. The partial molar volumes at infinite dilution are easier to interpret than the molar volumes at finite concentration because, at infinite dilution, the solute-solute interaction is absent.

7.1 Partial Molar Volume at Infinite Dilution

The partial molar volume, V_1 , of a solute, 1 , in a pure solvent, 2 , was represented (in Chapter 2) by

$$V_1 = (\partial V/\partial n_1)_{n_2, T, P} \quad 7.1$$

where n_2 represents the moles of pure solvent, and V is the total volume. The partial molar volume of a solute, V_1 , may be evaluated from density measurements.⁽²⁴⁵⁾ The graphical methods are described elsewhere;⁽²⁴⁶⁾ the use of the apparent molar volume, V_ϕ , is more convenient, particularly for binary solutions involving a solid solute. The apparent molar volume, V_ϕ , is defined by⁽²⁴⁷⁾

$$V_\phi = (V - n_2 V_2^0)/n_1 \quad [\text{constant } T, P] \quad 7.2$$

7.1 Partial molar volume at infinite dilution

where n_1 represents the moles of solute and V_2° is the molar volume of pure solvent. $V_2^\circ = M_2/d_o$, where M_2 is the molecular mass of the solvent and d_o is the density of the pure solvent. Since $V = n_1 V_\phi + n_2 V_2^\circ$, the partial molar volume of the solute, 1, and solvent, 2, are given by the equations

$$V_1 = (\partial V / \partial n_1) = V_\phi + n_1 (\partial V_\phi / \partial n_1) \quad [\text{constant } T, P, n_2] \quad 7.3$$

and

$$V_2 = (V - n_1 V_1) / n_2 = 1/n_2 [n_2 V_2^\circ - n_1^2 (\partial V_\phi / \partial n_1)] \quad [\text{constant } T, P, n_2] \quad 7.4$$

In terms of the experimentally measured density of the solution, d , the density of the pure solvent, d_o , the molar masses, M_1 and M_2 , of solute and solvent, and the molar concentration, C , the apparent molar volume may be defined in the following way:^(247,248)

$$V_\phi = 1/n_2 [(n_1 M_1 + n_2 M_2) d - n_1 V_1^\circ] \quad 7.5$$

If the volume V is 1000 cm³, then the above expression becomes

$$V_\phi = -1000(d - d_o)/Cd_o + M_1/d_o \quad 7.6$$

In this work, equation 7.6 is used to calculate V_ϕ .

Molarity is most frequently used to express the concentration dependence of V_1 and V_ϕ , since the theoretical limiting Debye-Hückel equation (used to extrapolate electrolyte solution results to infinite dilution)⁽³¹⁾ uses this scale.

7.1 Partial molar volume at infinite dilution

By definition,⁽²⁴⁷⁾ at infinite dilution, the partial molar volume and the apparent molar volume are equal [$V_\phi(x_I=0) = V_I(x_I=0)$].

For non-electrolytes,^(249,250) V_ϕ varies linearly with C and the degree of dissociation, respectively.

Estimation of errors

To obtain reliable $V_\phi(x_I=0)$, ie. $V_I(x_I=0)$, values, it is necessary to measure the density, d , or the density difference between the solution and pure solvent, $d - d_o$, with great precision. Errors in V_ϕ , ΔV_ϕ , were calculated using the following equation:⁽²⁵¹⁾

$$(\Delta V_\phi)^2 = (\partial V_\phi / \partial d_o)^2 (\Delta d_o)^2 + (\partial V_\phi / \partial d)^2 (\Delta d)^2 + (\partial V_\phi / \partial C)^2 (\Delta C)^2 \quad 7.7$$

Using this equation, an average error of $0.025 \text{ cm}^3 \cdot \text{mol}^{-1}$ in V_ϕ was calculated, over the concentration range of 0.01 to $0.11 \text{ mol} \cdot \text{L}^{-1}$, (see details in *Appendix C*).

7.2 Additivity of Partial Molar Volumes

In determining the partial molar volumes of electrolytes at infinite dilution, the results enable one to study ion-solvent interactions, eg. by means of the additivity principle.^(248,252-255) By additivity it is meant that the partial molar volume at infinite dilution of an electrolyte, V_{MX}^∞ , is equal to the sum of its ionic components, $V_{M+}^\infty + V_{X-}^\infty$. The concept of the effect of separate ions is made use of by Hepler,⁽²⁴²⁾ and is discussed in a later chapter (Chapter 8).

Partial molar volumes at infinite dilution of non-electrolytes have been investigated by numerous workers, some of whose work is discussed in the following paragraphs. Edward and co-workers^(256,257) measured a large number of compounds in various solvents. They concluded that the partial molar volume of alkanes at infinite dilution ($V_I(x_I=0)$) can be

7.1 Partial molar volume at infinite dilution

expressed by

$$V_1(x_1=0) = V_c + n^k I^k + Z_g^l \delta^l + C \quad 7.8$$

where V_c is a constant co-volume; n^k is the number of, and I^k the volume increment associated with, atomic groups of type k ; Z_g^l is the average number of *gauche* interactions of type l and δ^l the volume change associated with the interaction; C is a cyclization parameter, the magnitude of which depends on the number of skeletal atoms in the ring. Using Equation 7.8, they estimated the value of V_c and I^k by means of a least-squares fitting of their experimental data. Using Stillinger's theory,⁽²⁵⁸⁾ they concluded that the estimated V_c of 11.61 cm³.mol⁻¹ in CCl₄ at 25°C, is the volume increase that would result even for a point particle on account of its kinetic contribution.⁽²⁵⁹⁾ However, the kinetic contribution predicted by Stillinger on the basis of the scaled-particle theory is of the order of 2-3 cm³.mol⁻¹ for most solvents.

Terasawa *et al*⁽²⁶⁰⁾ showed that the partial molar volume of a series of homologous compounds can be related to their van der Waals volume, V_w :

$$V_1(x_1=0) = aV_w + b \quad 7.16$$

where a and b are constants for the series of interest at constant temperature and pressure.

Yoshimura and Nakahara⁽²⁶¹⁾ derived expressions for the volume change accompanying contact-complex formation in hard-sphere fluids. They pointed out that the volume change is composed of two terms related (i) molecular packing and (ii) thermal motion of molecules. They further developed the additivity rule of the partial molar volume.^(261,262) Based on the virial theorem, they have derived the following equation:

$$V_1(x_1=0) = V_{conf}^\infty + \kappa_T RT \quad 7.10$$

7.1 Partial molar volume at infinite dilution

where V_{conf}^∞ is the volume contribution due to the configurational interaction between solute and solvent molecules, and κ_T the isothermal compressibility of the solvent used. The second term arises from the translational motion of a solute in solution. This term is in agreement with the one derived by Stillinger.⁽²⁵⁸⁾ They have shown that the additivity rule for n -alkanes consisting of n methylene units can be expressed as

$$V_{conf}^\infty = \alpha n + \beta \quad 7.11$$

where α and β are parameters independent of n , and this equation is obeyed quite accurately.

Nishimura *et al*⁽²⁶³⁾ showed that the size as well as shape of the atomic groups are the important factors in determining what they called the a term, ($a = V_\phi/V_w$, where V_w = the van der Waals volumes for the atoms or molecules).

Edward and Farrell,⁽²⁶⁴⁾ using the assumption that the solute molecules are spherical, produced an expression for the partial molar volume of the solute molecule of effective van der Waals radius r_w .

$$V_l(x_l=0) = (4/3)\pi L(r_w + \Delta)^3 \quad 7.12$$

where L is the Avogadro number and Δ denotes a parameter adjusting for the void where solvent molecules are excluded. See Fig. 7.1.

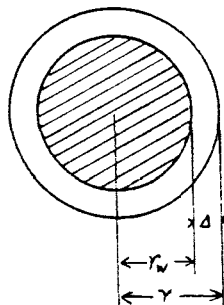


Fig. 7.1 : A sphere in continuum model proposed by Edward and Farrell, taken from ref. (264).

7.1 Partial molar volume at infinite dilution

By using the volume data of aliphatic and aromatic hydrocarbons in water, they examined (Equation 7.12), and found that the average separation of the molecules from the solvent as a continuum is 5.3 nm.

Lee⁽²⁶⁵⁾ developed a theory for the partial molar volume of the solute in infinitely dilute hard-sphere binary mixtures. The expression for $V_1(x_1=0)$ is formally the same as Equation 7.12. However, Δ is not constant but a slowly varying function of r_w and depends primarily on the size of solvent molecule and the packing density of the pure solvent.

Nishimura *et al*⁽²⁶³⁾ formulated the following model. If one considers a space enveloped by a spherical surface of radius R , centred by a solute molecule. The number of solvent molecules N within the sphere is given by

$$N = \int_0^R 4\pi r^2 \rho_o g(r) dr \quad 7.13$$

where ρ_o is the number density of the pure solvent molecule and $g(r)$ is the radial distribution function at the distance r from the solute molecule. In the absence of the solute molecule, the number of solvent molecule N_o is given by

$$N_o = \int_0^R 4\pi \rho_o r^2 dr \quad 7.14$$

If R is large enough compared with molecular dimensions, and the solution is sufficiently dilute, the partial molar volume of the solute in question at infinite dilution can be given by

$$\begin{aligned} V_1(x_1=0) &= (N_o - N)V_o \\ &= 4\pi L \int_0^R r^2 \{1 - g(r)\} dr \end{aligned} \quad 7.15$$

where V_o is the molar volume of the solvent. Therefore, $V_1(x_1=0)$ is interpreted as the

7.1 Partial molar volume at infinite dilution

number of "solvent" molecules excluded from the space, multiplied by the solvent molar volume, as depicted in Fig. 7.2.

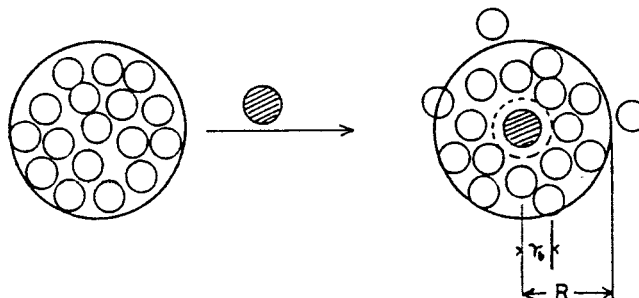


Fig. 7.2 : Schematic representation of the physical meaning of the partial molar volume at infinite dilution, taken from ref. (264).

In real solutions, it is difficult to estimate the radial distribution function. In the simplest case, one assumes that $g(r) = 0$ in the region $r < r_b$, $g(r) = 1$ in the region $r > r_b$. Then it follows from Equation 7.15,

$$V_1(x_1=0) = (4/3)\pi L r_b^3 \quad 7.16$$

If one sets $r_w + \Delta = r_b$, Equation 7.16 becomes identical to Equation 7.12. Therefore, this oversimplified model calculation is virtually the same as that of Edward and Farrell⁽²⁶⁴⁾ (Fig. 7.1), based on the sphere-in-continuum model. The success of their treatment for comparatively small molecules suggests that the proposed model is reasonable. Since the shapes of most of real molecules and atomic groups are far from spherical, more realistic models will be needed. Nishimura *et al*⁽²⁶³⁾ observed that the a term depended on the size and shape of the atomic groups concerned. As the simplest models, they regarded CH_3 -, CCl_3 -, H -, and Cl - as hemispherical, $-\text{CH}_2$ - and $-\text{CCl}_2$ - as cylindrical with a height of 12.6 nm (estimated from the C-C bond length and C-C-C bond angle). If Δ is defined as

$$\Delta = r - r_w \quad 7.17$$

as in the case of the sphere model,⁽²⁶⁵⁾ then Δ can be regarded as the thickness of the zone

7.1 Partial molar volume at infinite dilution

where the solvent molecules are excluded. If a liquid consists of hard spheres and has a randomly close packing structure,⁽²⁶⁶⁾ the radius of the sphere r could be calculated by using the following equation:

$$1.56(4/3)\pi r^3 L = V_2^0 - \kappa_T RT \quad 7.18$$

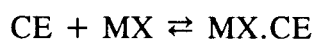
where V_2^0 is the molar volume of the liquid.

Yoshimura and Nakahara⁽²⁶¹⁾ have concluded that the solute to solvent ratio idea overwhelms the classical picture of sphere-in-continuum model. This is essentially the same picture as that of Lee.⁽²⁶⁵⁾ Nishimura *et al*⁽²⁶³⁾ have reported that the Δ value increases in the order of increasing curvature of the surface of solute molecules or moieties. These findings support the above predictions, at least on the CPK model level.

In this work crown ethers and the cryptand are used in order to attempt to isolate the effect of a single ion in the solution - based on predictions made by Hepler in 1957.⁽²⁴²⁾ (See Chapter 8 for detail).

7.3 This work

In this work, $V_l(x_l=0)$ was determined for crown ethers, a cryptand and electrolytes in order to investigate the volume changes at infinite dilution for the reaction type



Solvents (MeOH, AN, DMSO), were chosen to satisfy the condition that the equilibrium constant for complexation is large, so that the reactants are almost completely reacted. This work is described in Chapter 8.

7.3 This work

In determining $V_1(x_1=0)$ in of the three solvents, it was noted that V_ϕ seemed to be solvent dependent. As a result, further work was then done, using a range of solvents. This work is discussed in this chapter, together with details of the experimental procedure.

$V_1(x_1=0)$ of the following systems were determined: CE6 in MeOH, EtOH, 1-propanol (1-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), DMSO, butylmethylketone (BMK), chloroform (CHCl_3), carbontetrachloride (CCl_4), 1,4-dioxane, benzene, tetrahydrofuran (THF), cyclohexylbenzene (cHB), tetrahydronaphthalene (THN), water, AN, and of c-222 in water, MeOH, AN, EtOH, DMSO, 1-PrOH, 2-PrOH, CHCl_3 , benzene, 1-BuOH, cyclohexane (cyclo-6), BMK, hexane, THN, heptane, octane, cHB, and decane.

7.4 Experimental

7.4.1 Materials and Purification

A summary of materials used in this study, their suppliers and purity analyses are listed in Tables 7.1 and 7.2. Analyses on the liquids were carried out on a Hewlett-Packard 5890A gas chromatograph equipped with a 3393A integrator and a 25m carbowax 20M capillary column. Purification of the materials was carried out when necessary.⁽⁸⁹⁾

The crown ethers and cryptand were all used without further purification, the purities were furnished by the suppliers. The CE6 was supplied by Fluka A.G. with a purity of >98 mole percent; the c-222 by Merck with a purity of >99 mole percent. The solvents were refluxed and fractionally distilled where necessary,⁽⁸⁹⁾ (see Chapter 2, Experimental section for detailed description).

All the solvents were tested by Karl Fischer titration for water content, and at the time of use contained less than 0.02 mole percent of water.

7.3 Experimental

All the materials were stored in a drybox supplied with a double-door access and anhydrous silica gel that was replaced daily or twice daily whenever necessary.

Table 7.1. Suppliers and purities of solutes used in this study.

Compound*	Supplier	Purity (Mole %)
15CE5	Merck	> 98
18CE6	Fluka A.G.	> 98

* For structures and nomenclature, see page 170.

7.3 Experimental

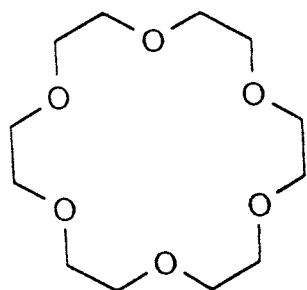
Table 7.2. Suppliers and purities of solvents used in this study.

Compound	Supplier	Purity (mole %)
MeOH	Merck	99.9
EtOH	Merck	99.9
1-PrOH	Riedel-de-Haen	99.9
1-BuOH	BDH	99.9
2-BuOH	Riedel-de-Haen	99
AN	Merck	99
DMSO	Merck	> 99
BMK	Fluka	> 99
CHCl ₃	Kleber	99
1,4-dioxane	Sarchem	98
benzene	BDH	> 99
THF	Carlo Erba	> 99
THN	BDH	99
cHB	Fluka A.G.	99
CCl ₄	Sarchem	98
Cyclo-6	Sarchem	99
hexane	Aldrich	97
heptane	Sarchem	> 99
octane	Sarchem	> 99
decane	Fluka	> 99

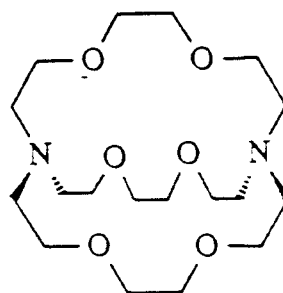
7.3 Experimental

7.4.2 Nomenclature and structures of solutes

The structures of the crown ethers and the cryptand used in this study are given here in Figs. 7.3-7.7 in order to facilitate the visualisation of the complexation reaction in solution. Crown ethers were named as such by Pedersen,⁽²³⁷⁾ due to their resemblance to a crown and their ability to "crown" the cations. The rules for their nomenclature were set out in the same publication. Jean-Marie Lehn is reputed to have named cryptands from the Latin *crypta*, which means "hidden or to hide".⁽²⁶⁷⁾



18-crown-6 ether



cryptand-222 (c-222)

7.3 Experimental

7.4.3 Experimental Procedure

In this work, volume changes were determined by density measurements using a commercially available Anton Paar DMA 601 vibrating tube densitometer. (Details in Chapter 2).

(i) Instrument description, operation, temperature control, sample injection

The laboratory arrangement of the density measurement apparatus is shown in Fig. 2. . The details of instrument operation are given in Chapter 2.

(ii) Preparation of the solutions

The metal halide and crown ether solutions were prepared by weighing the solutes into glass capsules, with a volume of 2 cm³, which were then introduced into flasks that had been oven dried and stored in a dry box. The flask contents were then swirled to aid dissolution and mixing. In some cases the solution had to be gently warmed in order to dissolve the solutes.

(iii) Degassing of liquids

The pure solvents and solutions were originally degassed by connecting the sample flask to a vacuum system. This method was found to be a little too vigorous for the volatile solvents, and thus the following method was applied. The flasks were immersed in a sonic bath for between 10 and 20 minutes. The solutions were weighed immediately before being injected into the densitometer cell.

7.4.4 Partial molar volume calculation

The density d of a solution was obtained from the density of pure solvent d_o and the periods

7.3 Experimental

of vibration of the tube when it contained the solution (τ) and the pure solvent (τ_o) using the relationship:

$$d = d_o + B(\tau^2 - \tau_o^2) \quad 7.21$$

where B is the densimeter constant. This constant was calculated using pure distilled and degassed solvents, water and air. The densities of the pure standards were obtained from the literature.⁽²³⁵⁾

The apparent molar volume, V_ϕ , of the solutions was calculated⁽²⁴⁸⁾ from eqn. 7.6, renumbered here

$$V_\phi = M_1/d_o - 1000(d - d_o)/d_o C \quad 7.22$$

where M_1 is the molar mass of the solute (1) and C the concentration in moles per litre. V_ϕ was determined for the solutes (1).

At infinite dilution, V_ϕ of the non-electrolyte solutes can be equated to the partial molar volume $V_1(x_1=0)$ and related through the following equation⁽²⁴⁷⁾

$$V_\phi = V_1(x_1=0) + mC \quad 7.23$$

For the metal halide (ionic) solutions, the extrapolation was based upon the observation that V_ϕ varies linearly with $C^{1/2}$ in dilute solution,^{(268,269(b))} or

$$V_\phi - S_v C^{1/2} = V_1(x_1=0) + bC \quad 7.24$$

where S_v is the Debye-Hückel limiting slope and has values of 14.19, 13.05 and

7.3 Experimental

7.55 cm.³L.^{1/2}mol^{-3/2} for the solvents MeOH,⁽²⁷⁰⁾ AN⁽²⁷¹⁾ and DMSO,⁽²⁷²⁾ respectively.

A computer programme was written to calculate the apparent molar volume, V_ϕ . Details of the computer programme are given in *Appendix C*.

7.5 Results

The V_ϕ results for the crown ethers and cryptand in the solvents are given in Tables 7.3 and 7.4, as a function of concentration. $V_I(x_I=0)$ and the slope of the plot of V_ϕ versus C , m , for each system are given in Table 7.5 and 7.6. The standard deviations, σ , of each fit calculated from

$$\sigma^2 = \Sigma(V_{\phi,exp} - V_{\phi,cal})^2/(n-2) \quad 7.25$$

where n is the number of observation, are also listed in Tables 7.5 and 7.6.

7.5 Results

Table 7.3. The apparent molar volumes, V_ϕ^a , at concentrations C_1^b resulting from fitting Equation (7.22) to the data, for CE6 + a solvent.

C_1	V_ϕ	C_1	V_ϕ	C_1	V_ϕ
1,4-dioxane					
0.01829	240.845	0.05117	240.068	0.06711	239.589
0.02868	240.339	0.05603	240.015	0.09911	240.187
0.03691	239.733				
chloroform					
0.01034	230.159	0.03186	229.363	0.06067	226.969
0.01166	229.691	0.03681	228.488	0.08018	227.319
0.01657	230.389	0.03832	227.319	0.09027	227.180
0.02749	229.959	0.05614	227.805		
carbontetrachloride					
0.01383	235.993	0.04610	236.328	0.08210	235.888
0.01880	235.521	0.04988	235.987	0.09547	235.517
0.02948	236.548	0.06412	235.635		
cyclohexylbenzene					
0.01993	242.601	0.05200	242.559	0.07664	242.036
0.03415	242.621	0.06979	242.388	0.09796	242.508
tetrahydronaphthalene					
0.04059	241.986	0.05535	242.490	0.08859	244.120
0.04883	243.998	0.07288	241.671	0.10318	245.323
0.05100	242.027	0.08135	241.861		

7.5 Results

Table 7.3. continued...

C_1	V_ϕ	C_1	V_ϕ	C_1	V_ϕ
ethanol					
0.02659	229.722	0.05447	232.204	0.08610	233.560
0.03487	230.031	0.07420	233.232	0.09529	233.832
0.04328	231.178				
acetonitrile					
0.02990	225.539	0.07638	225.178	0.09256	225.790
0.06770	225.399	0.08620	225.511	0.09773	225.855
0.07182	225.223				
tetrahydrofuran					
0.02395	236.178	0.04805	237.277	0.07765	237.668
0.03290	236.478	0.05062	236.786	0.09359	238.109
0.03425	236.372	0.05809	237.285	0.09591	238.275
benzene					
0.01453	236.575	0.05386	235.794	0.09123	235.353
0.03614	236.705	0.06494	237.730	0.09469	236.721
0.04908	234.841	0.07141	237.361		
methanol					
0.03769	228.985	0.05696	227.330	0.07309	228.295
0.04152	227.745	0.06019	227.961	0.08410	228.786
0.04805	227.511	0.07183	228.709	0.09042	228.880

7.5 Results

Table 7.3. continued...

C_1	V_ϕ	C_1	V_ϕ	C_1	V_ϕ
1-butanol					
0.02887	239.978	0.05675	240.343	0.08071	240.847
0.03037	239.856	0.07621	239.976	0.08521	240.042
0.05318	239.164				
2-butanol					
0.02489	238.146	0.04292	238.108	0.07420	240.497
0.02985	237.729	0.05087	238.522	0.07974	239.702
0.03237	238.192	0.06394	239.947	0.09363	240.847
0.04084	238.626				
butylmethylketone					
0.03732	238.133	0.06421	238.004	0.08229	238.089
0.05187	237.652	0.07563	237.653	0.09229	238.187
dimethylsulphoxide					
0.03099	232.554	0.05370	233.744	0.08758	232.766
0.04325	232.938	0.07143	232.410		
1-propanol					
0.03594	235.342	0.05868	236.324	0.08942	236.977
0.04655	234.981	0.06831	236.177	0.09139	237.600
0.05357	236.314	0.06988	235.644	0.09430	237.572
0.05581	235.398	0.08544	237.120		
water					
0.03536	222.981	0.04673	223.289	0.08004	223.962
0.04475	223.855	0.06447	223.815	0.09561	224.587

^aUnits: $\text{cm}^3 \cdot \text{mol}^{-1}$; ^bUnits: $\text{mol} \cdot \text{L}^{-1}$.

7.5 Results

Table 7.4. The apparent molar volumes, V_{ϕ}^a , at concentrations C_1^b resulting from the data being fitted to Equation (7.22), for c-222 + a solvent.

C_1^a	V_{ϕ}^b	C_1^a	V_{ϕ}^b	C_1^a	V_{ϕ}^b
water					
0.03606	316.008	0.05605	316.560	0.09497	316.166
0.04547	316.751	0.06961	316.320		
methanol					
0.01599	323.413	0.03787	322.875	0.05220	324.431
0.02373	323.023	0.04697	323.901		
acetonitrile					
0.02087	330.724	0.03279	330.893	0.06398	332.845
0.02802	330.723	0.03634	330.558	0.06739	330.610
0.02963	329.604	0.05304	329.135		
ethanol					
0.02127	325.379	0.04293	327.396	0.05666	328.887
0.02955	326.338	0.05070	328.503	0.06141	329.905
0.03751	326.988				
DMSO					
0.01919	342.110	0.03369	342.998	0.05831	344.962
0.02192	342.300	0.04557	343.881	0.05947	345.300
0.03232	342.991				

7.5 Results

Table 7.4. continued...

C_1^a	V_ϕ^b	C_1^a	V_ϕ^b	C_1^a	V_ϕ^b
1-propanol					
0.01742	323.775	0.03830	324.599	0.05627	327.159
0.02348	324.214	0.04329	325.973	0.05903	327.369
0.03135	324.932	0.04741	326.382		
2-propanol					
0.01835	325.673	0.04965	326.080	0.06365	326.546
0.02270	325.970	0.05077	326.132	0.06710	326.750
0.03928	326.026	0.05565	326.192		
CHCl_3					
0.02344	332.306	0.04174	331.358	0.05148	330.713
0.03822	331.428	0.04449	331.351	0.05458	330.321
benzene					
0.01575	343.844	0.03938	344.501	0.05187	344.187
0.02545	344.427	0.04079	344.529	0.07821	344.830
1-butanol					
0.02358	330.525	0.04216	333.616	0.06341	334.491
0.03793	332.804	0.05837	334.917	0.06546	334.174
cyclohexane					
0.01302	346.128	0.03681	346.363	0.05337	346.228
0.02156	346.473	0.05076	346.287	0.05616	346.199
0.03079	346.200				

7.5 Results

Table 7.4. continued...

C_1^a	V_ϕ^b	C_1^a	V_ϕ^b	C_1^a	V_ϕ^b
BMK					
0.02725	345.783	0.03875	345.383	0.06839	346.568
0.03674	345.623	0.04365	345.365	0.07934	345.996
tetrahydronaphthalene					
0.03463	341.581	0.04941	341.965	0.05523	342.860
0.04060	341.833	0.05176	342.714	0.08490	342.343
heptane					
0.01563	337.176	0.03814	337.745	0.04171	337.234
0.03283	336.077	0.03978	336.811	0.05943	337.735
octane					
0.02047	341.761	0.04742	342.993	0.07349	343.570
0.04691	342.715	0.05720	343.210		
cyclohexylbenzene					
0.02494	348.685	0.04510	347.020	0.05836	346.176
0.03850	347.569	0.05586	346.246	0.06966	345.094
0.03982	347.455				
decane					
0.02151	353.423	0.03765	354.065	0.05846	354.544
0.02924	353.699	0.04779	354.242	0.06446	354.618

^aUnits: cm³-mol⁻¹. ^bUnits: mol-L⁻¹

7.5 Results

Table 7.5. The partial molar volumes at infinite dilution, $V_1(x_1=0)$ for CE in various solvents, the solvent molar volumes V_2^0 , the slope m , and the standard errors σ , resulting from fitting the data to Equations 7.23 and 7.25.

Solvent	$V_1(x_1=0)^a$	σ	m	σ	V_2^{oa}
2-BuOH	236.6	5.8	44.6	0.41	91.8
DMSO	233.0	13.3	-2.6	0.59	70.9
BMK	237.8	5.8	2.1	0.26	123.8
CHCl_3	230.3	8.4	-42.6	0.72	80.0
1-PrOH	233.5	7.0	40.8	0.44	74.7
1-BuOH	239.5	9.0	8.6	0.51	91.5
EtOH	228.2	6.2	62.3	0.40	58.6
CCl_4	236.1	4.8	-4.6	0.37	96.5
1,4-Dioxane	240.4	6.1	-6.6	0.40	85.2
Benzene	236.3	14.8	0.2	1.06	89.3
THF	235.5	2.3	28.0	0.17	81.3
MeOH	227.2	11.4	15.5	0.59	40.5
cHB	242.7	2.8	-5.1	0.18	170.1
THN	240.6	21.0	33.4	1.23	136.7
Water	222.4	5.4	21.4	0.28	18.0
AN	225.1	4.7	4.1	0.26	52.6

^aUnits: $\text{cm}^3 \cdot \text{mol}^{-1}$.

7.5 Results

Table 7.6. The partial molar volumes at infinite dilution, $V_1(x_1=0)$ for c-222 in various solvents, the solvent molar volumes V_2^0 , and the slope m , resulting from Equation (7.23) being fitted to the data; and the standard deviations resulting from fitting Equation (7.25) to the data.

Solvent	$V_1(x_1=0)^a$	m	σ	V_2^{0a}
Water	316.5	-2.5	0.34	18.02
MeOH	322.5	27.8	0.56	40.55
AN	329.8	18.0	0.12	52.63
EtOH	323.0	107.0	0.21	58.69
DMSO	340.8	68.1	0.26	70.96
1-PrOH	322.0	88.6	0.37	74.75
2-PrOH	325.3	16.9	0.16	76.85
CHCl ₃	333.7	-60.1	0.16	80.01
Benzene	343.9	11.4	0.25	89.37
1-BuOH	329.1	87.6	0.73	91.51
Cyclo-6	346.2	-0.66	0.13	108.04
BMK	345.0	14.6	0.38	123.89
Hexane	326.9	-42.5	0.32	130.77
THN	341.4	14.5	0.49	136.72
Heptane	336.4	17.2	0.65	146.51
Octane	341.1	34.7	0.15	162.49
cHB	350.6	-78.1	0.08	170.13
Decane	352.8	27.8	0.08	194.92

^aUnits : cm³. mol⁻¹.

7.6 Discussions

7.6.1 V_ϕ vs C

The slope of the plot of the apparent molar volumes V_ϕ against concentration, have been generally regarded to reflect solute-solute interaction forces.⁽²³⁸⁾ In this work, most of the slopes were either very slightly positive or virtually horizontal. The only exceptions were those of CE6 + ethanol, CE6 + 2-butanol, and c-222 in MeOH, EtOH, 1-PrOH, 1-BuOH, and DMSO. This can be seen from the values of m in Tables 7.5 and 7.6. This suggests weak solute-solute interactions, as strong interactions would have resulted in a relatively large positive slope.⁽³⁵⁾

7.6.2 $V_1(x_1=0)$ vs. V_2°

(a) Solute systems involving non-polar solvents

Fig. 7.3 shows the partial molar volumes at infinite dilution $V_1(x_1=0)$ of CE6 plotted against the solvent molar volume, V_2° . The value of $V_1(x_1=0)$ varies as much as 10 per cent from 222 to 244 $\text{cm}^3\cdot\text{mol}^{-1}$ as the V_2° varies from 18 to 170 $\text{cm}^3\cdot\text{mol}^{-1}$, for CE6 + solute systems.

The results suggest that the dominant factor is attributable to the packing of the solvent molecules, (see Fig. 7.7) and that the addition of a solute disturbs the order in the solvent packing. The larger the solvent molecule, (as judged by the solvent molar volume), the larger the disruption in the packing of the solvent molecules. The same trend is also found in mixtures of cyclohexane⁽²⁴⁰⁾ or decahydronaphthalene⁽²⁴¹⁾ in n-alkane solvents. The partial molar volumes at infinite dilution for solutes cyclohexane or decahydronaphthalene in n-alkane solvents have been calculated from the excess molar volumes using the method described by Letcher et al⁽²³⁹⁾ and have been plotted in Figs. 7.4 and 7.5.

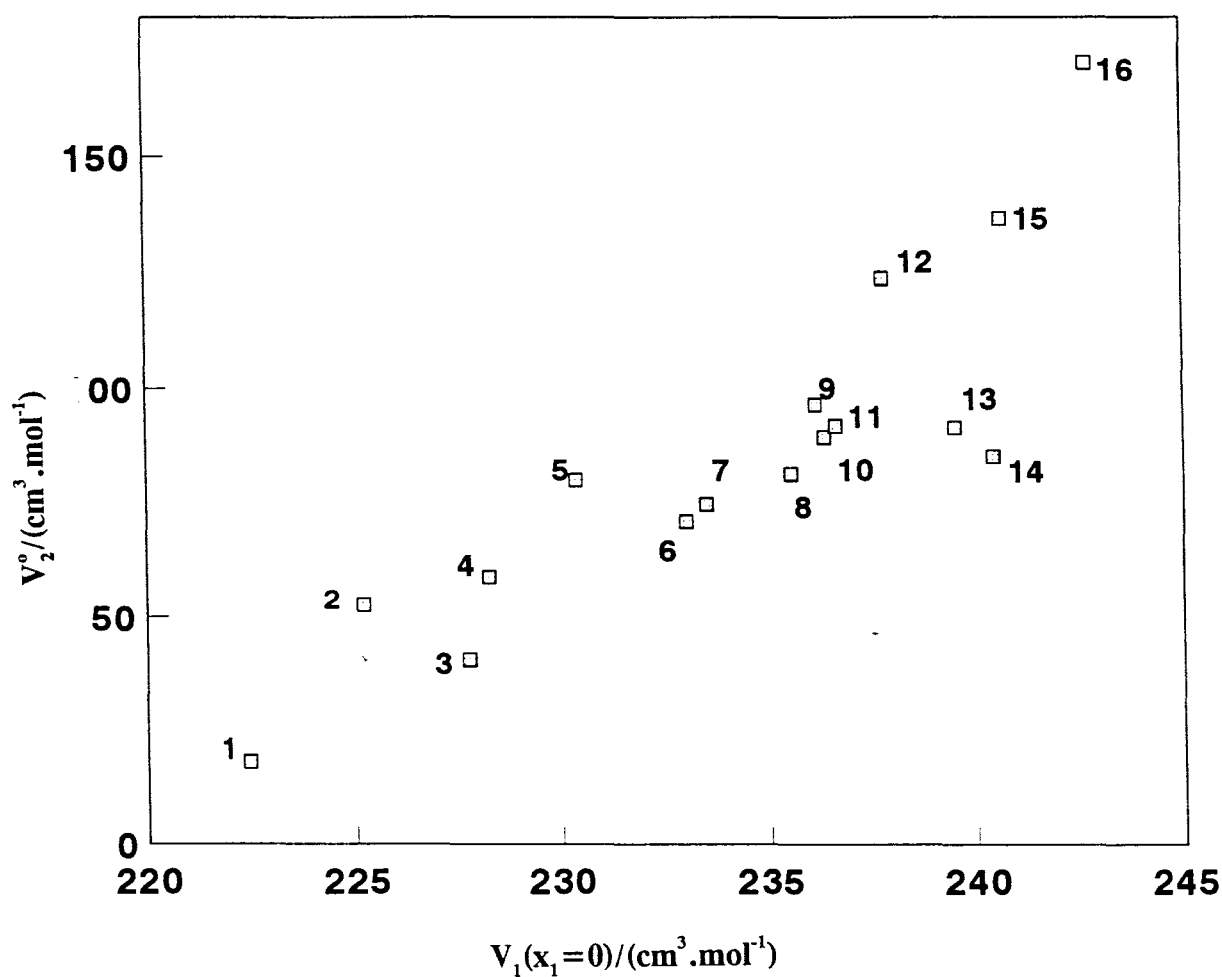


Fig. 7.3: Partial molar volumes at infinite dilution of CE6 in various solvents.

KEY:

1 = water; 2 = AN; 3 = MeOH; 4 = EtOH; 5 = CHCl_3 ; 6 = DMSO; 7 = 1-PrOH; 8 = THF; 9 = CCl_4 ; 10 = benzene; 11 = 2-BuOH; 12 = BMK; 13 = 1-BuOH; 14 = 1,4-dioxane; 15 = THN; 16 = CHB.

7.6 Discussion

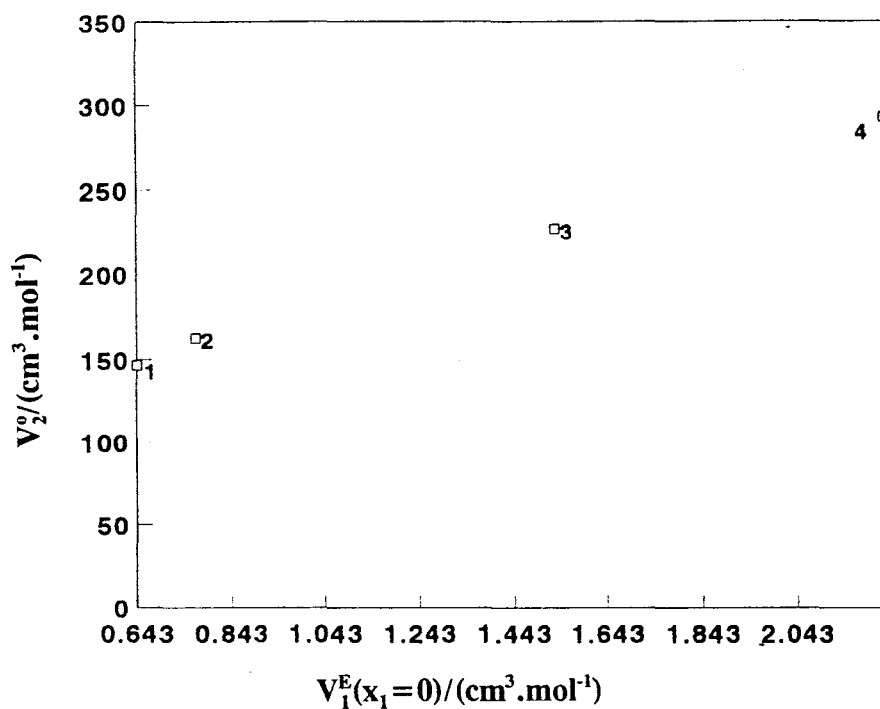


Fig. 7.4 : V_2^o vs. $V_1^E(x_1=0)$ for cyclohexane(1) + *n*-alkanes(2); 1=heptane, 2=octane, 3=dodecane, 4=hexadecane.

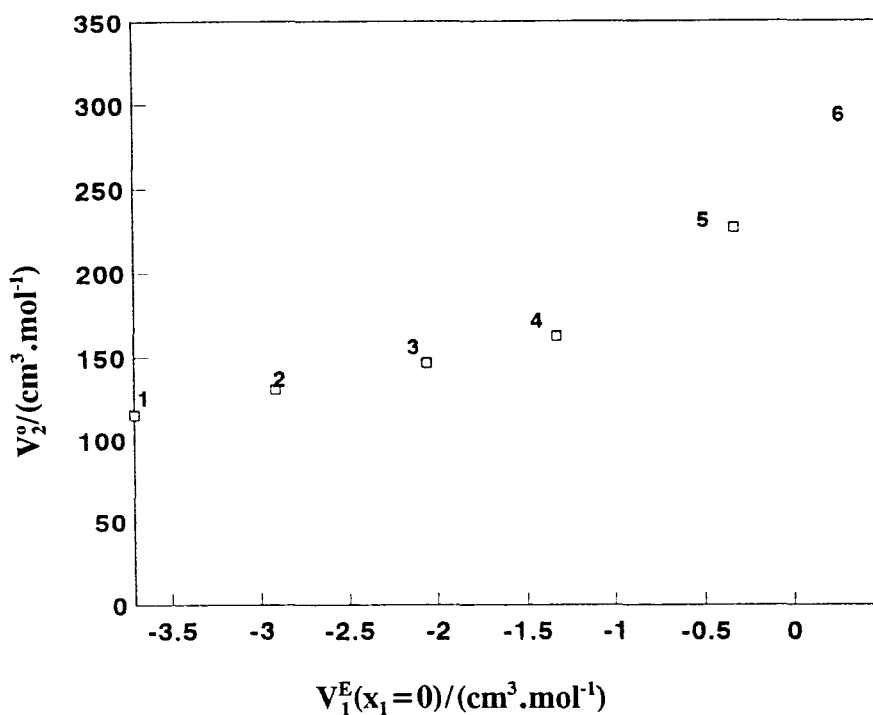


Fig. 7.5 : V_2^o vs. $V_1^E(x_1=0)$ for decalin(1) + *n*-alkanes(2); 1=pentane, 2=hexane, 3=heptane, 4=octane, 5=dodecane, 6=hexadecane.

7.6 Discussion

All the results presented in Figs. 7.3, 7.4 and 7.5, involve solute-solvent systems which can be described as "like-like" mixtures. Attempts to obtain results for CE6 in non-polar solvents have not been successful, as the CE6 is not soluble in solvents such as alkanes or cycloalkanes. The variation of $V_1(x_1=0)$ seems independent of the type of solvent, (ranging from hydrogen bonded solvents such as water, alkanols and chloroform, to polarizable aromatic solvents such as benzene and cyclohexylbenzene and ethers such as tetrahydrofuran and 1,4-dioxane).

(b) Solute systems involving polar solvents

Fig. 7.6 shows the partial molar volumes at infinite dilution ($V_1(x_1=0)$) of c-222 plotted against the solvent molar volume, V_2° . In this case, c-222 was found to be readily soluble in alkanes and these results are plotted in Fig. 7.6.

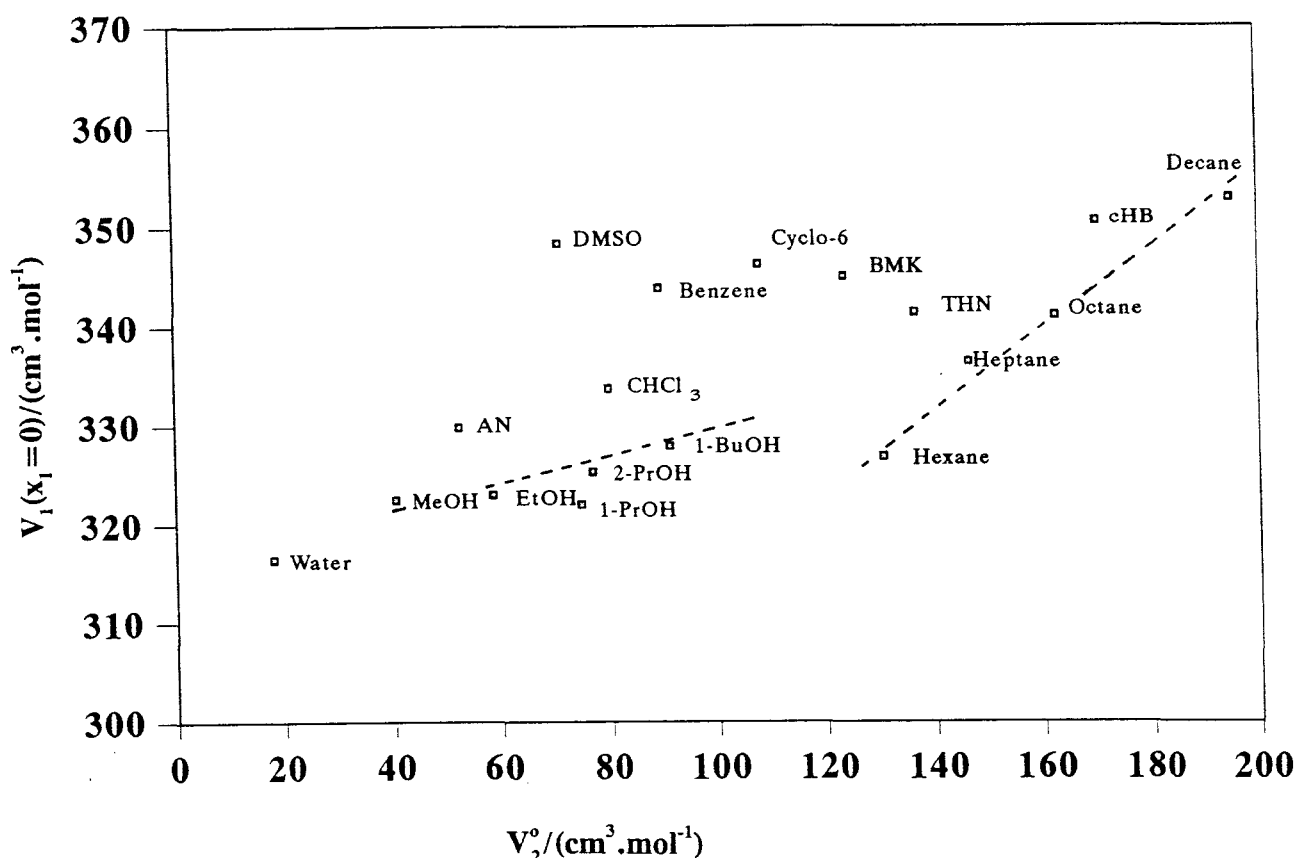


Fig. 7.6 : Partial molar volumes at infinite dilution of c-222 in various solvents.

7.6 Discussion

From Fig. 7.6, the slope of $V_1(x_1=0)$ vs V_2° for the alkanols is considerably less positive than the slope for the alkanes. This could once more be explained in terms of solvent-solute packing. The smaller the solvent molecules, the less is the distortion to the packed structure of the solvent as a result of the presence of the solute. The results show far more disorder in the packing of these solutions as the carbon-chain gets longer.

In conclusion, this work shows that the solute molar volume, $V_1(x_1=0)$, increases with the solvent molar volume, V_2° , in both polar and non-polar solvents and for both solutes, for $V_1(x_1=0) > V_2^\circ$.

It would be interesting to note $V_1(x_1=0)$ for $V_2^\circ > V_1(x_1=0)$, would the slope become negative?

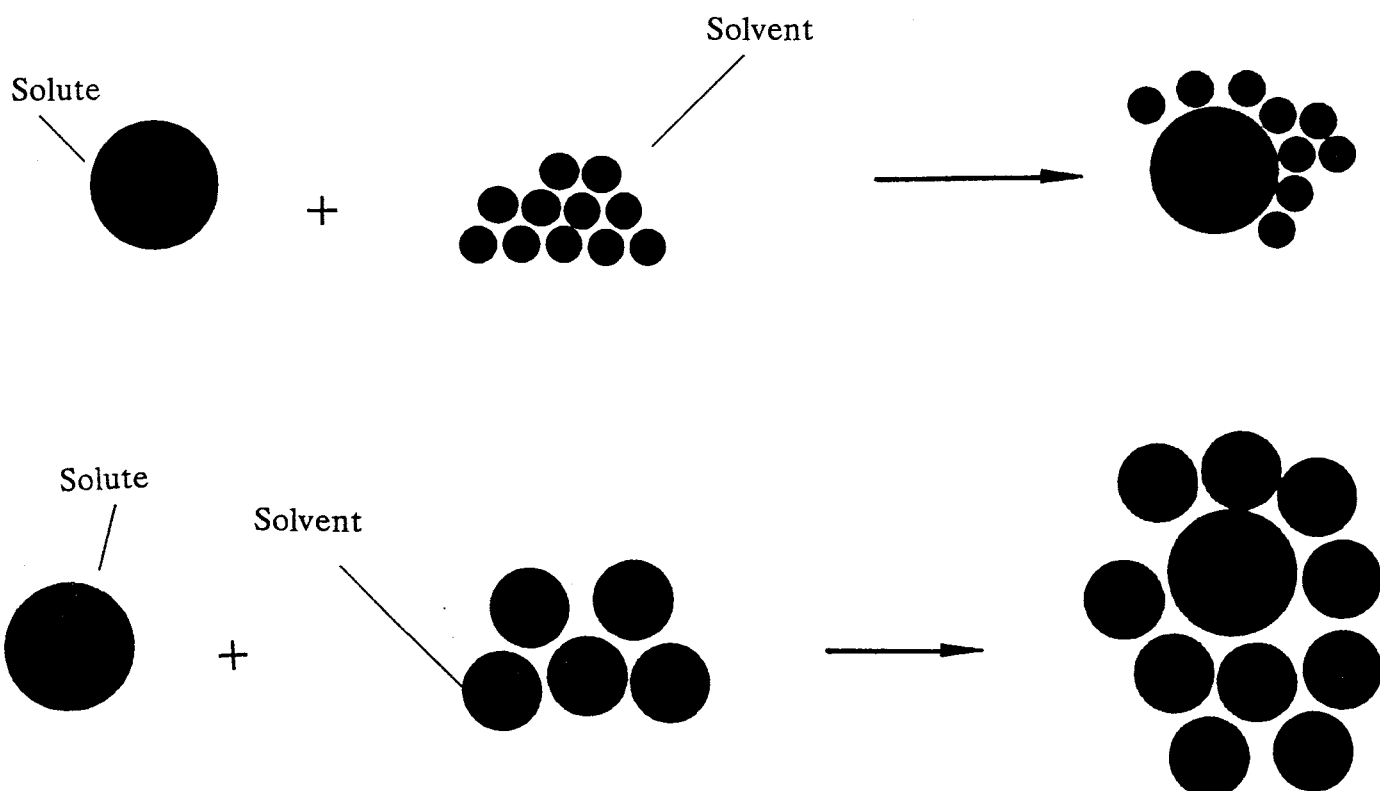


Fig. 7.7 : Representation of the solute-solvent packing, with solvent molecules of differing sizes.

CHAPTER 8

Volume Changes in Crown Ether or Cryptand and Metal Salt Reactions

8.0 Introduction

8.0.1 Related Work

The formation constants of alkali metal ion complexation by crown ethers⁽²³⁷⁾ has been investigated extensively by Izatt *et al*⁽³⁸⁾ in a variety of solvents and by various methods. However, the volume change upon complexation has been little studied. Høiland *et al*^(34,35) calculated the volume change of complexation, extrapolated to infinite dilution, (ΔV^∞), of alkali metal and alkali earth ions by 18-crown-6 ether (CE6), 15-crown-5 ether (CE5), and 12-crown-4 ether (CE4) from density measurements, in water. Studies were carried out by Morel-Desrosiers and Morel for the same ions complexed by cryptand[2.2.2](c222) in water.⁽³³⁾ They also investigated the complexation of mono- and divalent cations⁽³²⁾ in methanol (MeOH) by cryptands [2.2.2], [2.2.1], and [2.1.1]. More recently, Letcher, Paul and Kay⁽³¹⁾ published work on the ΔV^∞ s of CE6 and dibenzo-18-crown-6 ether (B₂CE6) in MeOH or acetonitrile (AN) or dimethylsulfoxide (DMSO).

8.0.2 Mechanism of Cation Complexation

In 1967 Pedersen,⁽²³⁷⁾ originally reporting on the nomenclature of the crowns, and the stoichiometry of the crown ether complexes with alkali and alkali earth salts - stated that the stoichiometry of these complexes was always one molecule of polyether per ion (regardless of its valence). In a later publication,⁽²⁷³⁾ he proposed a rough approximation of 2:1 and 3:2 polyether:ion complexes, which he named "sandwich" and "club-sandwich" complexes

8.0 Introduction

respectively. The formation of the complexes seemed to depend on the ion charge and the size of the polyether cavity. Due to lack of single-crystal X-ray analysis data, Pedersen was unable to confidently describe the geometry of these complexes. Truter,⁽²⁷⁴⁾ amongst others, later confirmed these structures by means of crystallographic studies. In the case of the 2:1 complex, he proposed that two relatively large flat molecules (the polyethers) were held together by a small sphere (the cation) particularly when the attractive forces were located on the sphere and toward the centre of the large molecules.

Infrared studies by Dale and Kristiansen⁽²⁷⁵⁾ have shown that the polyethers assume different conformations in the complexed and uncomplexed states. In this work, the model of cation-crown ether complex formation is based on that of H $\oplus$ iland *et al.*,⁽³⁴⁾ ie. 1:1 complexation. This model required compatibility in size between the diameter of the cations and the crown ether hole.

A crystallographic study by Truter,⁽²⁷⁶⁾ however, shows that the cation does not necessarily have to be in the centre of the crown ether hole in order to be complexed. It may be coordinated in a pentagonal pyramidal structure, as can be seen in Fig. 8.1.

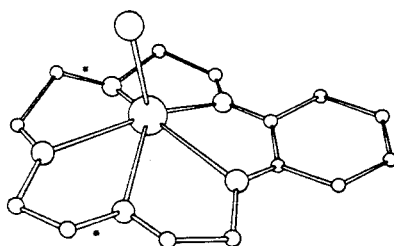


Fig. 8.1 : The sodium, water, benzo-15-crown-5 complex, taken from ref. (276).

This work by Truter also reports on the structures of, amongst others, the potassium(benzo-15-crown-5) complex that exhibits different torsional angles from the uncomplexed molecules,⁽²⁷⁶⁾ as can be seen in Fig. 8.2.

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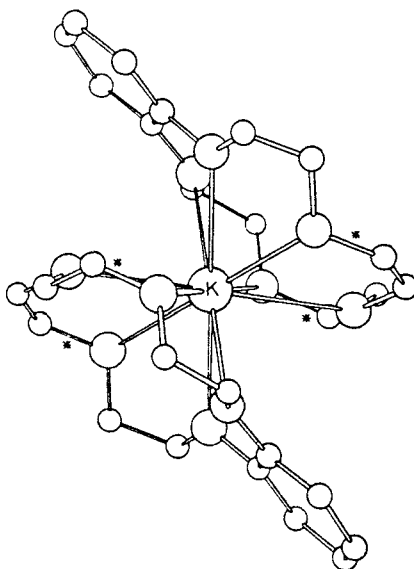


Fig. 8.2 : The potassium (benzo-15-crown-5)₂ complex. Asterisks show torsionally altered bonds, taken from ref. (264).

These observations are supported by later kinetic studies done by Liesegang *et al.*⁽²⁸¹⁾ and Rodriguez *et al.*⁽²⁷⁸⁾

8.0.3 The purpose of this work

Earlier workers have commented on the relationship, for CE.MX complexes, between ΔV^∞ s and the electrostrictive effect⁽³¹⁻³⁴⁾ - if this is indeed true, one would be able to obtain information on a property of a single ion, which is exceptional. In this thesis, work by Morel⁽³²⁾ on the volume changes of complexing at infinite dilution, ΔV^∞ , of c-222 complexes in MeOH, have been repeated and extended to include complexes in AN and DMSO. The measurement of ΔV^∞ for B₂CE6 with MX in these same solvents have been repeated and compared with those results obtained by Letcher *et al.*⁽³¹⁾ The investigation was extended to include measurements on the complexing of CE5 or dicyclohexano-18-crown-6 ether (Cy₂CE6) with the same salts in MeOH, AN and DMSO.

Observations were made with reference to the effect on the results of : the ring size, the different types of rings (ie. ranging from dibenzo-18-crown-6 ether to cryptand-222), the "flexibility" of the ring, as well as the effect of the type of solvent and spectator ion. The

8.0 Introduction

solvents were chosen such that both the crown and the metal salt were soluble in them, to a reasonable degree, (ie. concentrations of up to 0.1 mol.L⁻¹ were needed).

The general equation for the calculation of ΔV^∞ for the crown ether or cryptand complexes (CE.MX) is given by

$$\Delta V^\infty = V_{CE.MX}(x=0) - V_{MX}(x=0) - V_{CE}(x=0) \quad 8.1$$

which can be rewritten as

$$\Delta V^\infty = V_\phi(MX.CE, x_1=0) - V_\phi(MX, x_1=0) - V_\phi(CE, x_1=0) \quad 8.2$$

8.1 Experimental

(i) Materials and purification

Refer to section 7.1 in Chapter 7 on "Partial Molar Volumes...", for solvent suppliers, purification methods and purities.

A summary of the materials listed here, their purities and suppliers is given in Table 8.1. The crown ethers and cryptand were all used without further purification, the purities were furnished by the suppliers. CE5 was supplied by Merck with a purity of > 98 mole percent; the CE6 by Fluka A.G. with a purity of > 98 mole percent; the Cy₂CE6 by Janssen with a purity of 99 mole percent; the B₂CE6 by Aldrich with a purity of 99 mole percent; the c-222 by Merck with a purity of > 99 mole percent; the salts NaCl, NaI, KI, and CsI by Aldrich with a purity of 99.999 mole percent. All the materials were stored in a drybox supplied with anhydrous silica gel and double-door access.

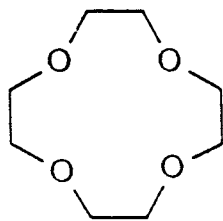
8.1 Experimental

Table 8.1. Suppliers and purities of solutes used in this study.

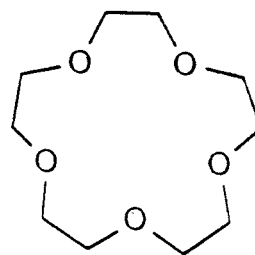
Compound	Supplier	Purity (Mole %)
15CE5	Merck	> 98
18CE6	Fluka A.G.	> 98
Cy ₂ CE6	Janssen	99
B ₂ CE6	Aldrich	98
c-222	Merck	> 99
NaCl	Aldrich	99.999
NaI	Aldrich	99.999
KI	Aldrich	99.999
CsI	Aldrich	99.999

(ii) Structures and nomenclature of the solutes

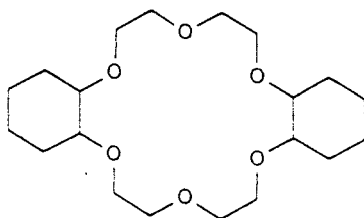
Also see Chapter 7 for more.



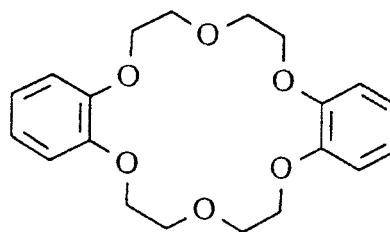
12-crown-4 ether



15-crown-5 ether



dicyclohexano-18-crown-6 ether



dibenzo-18-crown-6 ether

8.1 Experimental

(iii) Preparation of complexed solutions

The metal halide - crown ether complexes were prepared by weighing equimolar amounts of reactants (within $5 \times 10^{-5} \text{ mol.L}^{-1}$) into 2 cm^3 glass open capsules. These capsules were then introduced into flasks that had been oven dried and stored in a dry box. The flask contents were then swirled to aid dissolution and mixing. In some cases the solution had to be gently warmed in order to dissolve the solutes.

8.1.1 Extrapolation of V_ϕ to Infinite Dilution

The apparent molar volume at infinite dilution, $V_\phi(x_I=0)$ (defined in Equation 7.23), is related to the partial molar volume at infinite dilution of the crown ether or cryptand complexes, $V_I(x_I=0)$, where I represents the crown ether or cryptand, (see Equation 8.2). $V_I(x_I=0)$ was determined by extrapolation of V_ϕ to infinite dilution.

The extrapolation to infinite dilution of the apparent molar volume of electrolytes, and the expression of the concentration dependence of the apparent molar volume have been made by three major equations - the Masson equation,⁽²⁶⁸⁾ the Redlich-Meyer equation⁽²⁷⁹⁾ and the Owen-Brinkley equation.⁽²⁸⁰⁾ Masson⁽²⁶⁸⁾ reported that the apparent molar volumes of electrolytes, V_ϕ , vary with the square root of the molar concentration by the linear equation (a rearrangement of 7.24)

$$V_\phi = V_\phi(x_I=0) + S_v^* \sqrt{C} \quad 8.3$$

where S_v^* is the experimental slope (which varies with electrolyte type and charge), and C is the concentration. Scott⁽²⁸¹⁾ and Geffcken⁽²⁸²⁾ have also examined the V_ϕ s of electrolytes by this equation and found it to adequately represent the concentration dependence of V_ϕ over a wide temperature range (0 -100 °C).

8.1 Experimental

Redlich and Rosenfeld⁽²⁶⁹⁾ predicted that a constant limiting slope should be obtained for a given electrolyte charge type (at a constant temperature and pressure) if the Debye-Hückel limiting law is obeyed. By differentiating the Debye-Hückel limiting law for activity coefficients with respect to pressure, Redlich and Meyer⁽²⁷⁹⁾ have calculated the theoretical limiting law slope, S_v , using the equation

$$S_v = kw^{3/2} \quad 8.4$$

The two terms for the limiting-law slope are given by

$$k = N^2 e^3 (8\pi/1000D^3 RT)^{1/2} (\partial \ln D / \partial P - \beta/3) \quad 8.5$$

where e is the electronic charge, D the dielectric constant of the solvent, β the compressibility of the solvent, (the other symbols have their usual meaning),⁽²⁸³⁾ and

$$w = 0.5 \sum_i \gamma_i Z_i^2 \quad 8.6$$

where γ_i is the number of ions of species i and valency Z_i formed by one molecule of electrolyte. For electrolytes of a fixed valency (w is constant), the limiting slope depends only on temperature and the physical properties of the solvent (D , $\partial \ln D / \partial P$, and β).

Redlich and Meyer⁽²⁷⁹⁾ suggest the use of the following extrapolation equation:

$$V_\phi = V_\phi(x_I=0) + S_v \sqrt{C} + b_v C \quad 8.7$$

where S_v is the theoretical limiting slope and b_v is an empirical constant determined from the experimental results.

Results of a number of studies⁽²⁸⁴⁻³⁰³⁾ for various electrolytes in dilute solutions over a

8.1 Experimental

temperature range of 0 to 65°C have confirmed the predictions of Redlich and Rosenfeld,⁽²⁶⁹⁾ that S_v is independent of the nature of the electrolyte except for valency type.

The Owen-Brinkley⁽²⁸⁰⁾ equation, derived by including the ion-size parameter, a (in cm) is given by

$$V_\phi = V_\phi(x_I=0) + S_v\tau(\kappa a)\sqrt{C} + 1/2W_v\theta(\kappa a)C + 1/2K_vC \quad 8.8$$

where

$$W_v = -2.303\gamma RTS_f A 1/2(\partial \ln D / \partial P - \beta - 2\partial \ln a / \partial P) \quad 8.9$$

and

$$(\kappa a) = (\sum_i \gamma_i Z_i^2)^{1/2} (4\pi N e^2 / 1000 k D T)^{1/2} a \sqrt{C} = a' \sqrt{C} \quad 8.10$$

and K_v is an empirical constant. $\tau(X)$ and $\theta(X)$ (which approach unity as the concentration decreases) are given by

$$\tau(X) = 3/X^3 [X^2/2 - X + \ln(1-X)] \quad 8.11$$

and

$$\theta(X) = 4/X^4 [X^2/2 - 2X + 3\ln(1-X) + (1/(1-x))] \quad 8.12$$

The distance of closest approach, a , may be evaluated from the activity coefficient or conductivity data, and although W_v may in principle be calculated from theory, it must be evaluated from the data because of the appearance of the unknown derivative, $\partial \ln a / \partial P$.

8.1 Experimental

Summarising, the preferred method⁽³⁰⁴⁾ of obtaining $V_\phi(x_I=0)$ from V_ϕ data as a function of concentration is the use of the limiting slope, S_v , with the Redlich-Meyer⁽²⁷⁹⁾ or Owen-Brinkley⁽²⁸⁰⁾ equations. The ideal method is to make the measurements in very dilute solutions where the deviations from the limiting law are very small (i.e., b_v and the higher order terms of the Owen-Brinkley⁽²⁸⁰⁾ equation do not have to be considered).

8.1.2 Method of determination of V_ϕ and ΔV^∞ in this work

The volume change at infinite dilution for the reaction⁽³¹⁾ involving a crown ether or a cryptand (CE) and a metal ion (M^+)



were determined from $V_\phi(x_I=0)$, (see below).

The density d of a solution was obtained from the density of pure solvent d_o and the periods of vibration of the tube when it contained the solution (τ) and the pure solvent (τ_o) using the relationship in eqn. 7.21. The densities of the pure standards were obtained from the literature.⁽²³⁴⁾

The apparent molar volume, V_ϕ , of the solutions was calculated⁽²⁶⁷⁾ from eqn 7.22, rewritten here for convenience

$$V_\phi = M_1/d_o - 1000(d - d_o)/d_o C$$

where M_1 is the molar mass of the solute and C the concentration in moles per litre. V_ϕ was determined for the solutes MX, CE and MX.CE.

At infinite dilution, $V_\phi(x_I=0)$ of the non-polar solutes can be equated to the partial molar

8.1 Experimental

volume $V_I(x_I=0)$ ⁽²⁷⁴⁾ and related through the following eqn. 7.23 rewritten here

$$V_\phi = V_I(x_I=0) + mC$$

The V_ϕ data for the salts and complexes were extrapolated to infinite dilution and $V_I(x_I=0)$ was calculated using the limiting Debye-Hückel equation

$$V_\phi - S_v C^{1/2} = V_\phi(x_I=0) + bC \quad 8.14$$

where S_v is the Debye-Hückel limiting slope and has values of 14.19, 13.05 and 7.55 cm.³L.^{1/2}mol^{-3/2} for the solvents MeOH,⁽²⁷⁰⁾ AN⁽²⁷¹⁾ and DMSO⁽²⁷²⁾ respectively.

The volume change at infinite dilution, ΔV^∞ , for the formation of the complex MCl.CE (see Eq. 8.13), in the various solvents was calculated from eqn 8.2.

A computer programme was written to calculate the apparent molar volume, V_ϕ . Details of the computer programme are given in *Appendix C*.

8.2 Results

The V_ϕ results for the CE6 and the cryptand in the various solvents are given in Tables 7.3 and 7.4, as a function of concentration. V_ϕ for CE5, B₂CE6, and Cy₂CE6 are given in Tables 8.2-8.4, and $V_\phi(x_I=0)$ and m for these systems are given in Table 8.5. $V_\phi(x_I=0)$ and m for the CE6 and c-222 are given in Tables 7.5 and 7.6. The standard deviation, σ , of each fit calculated from

$$\sigma^2 = \Sigma(V_{\phi,exp} - V_{\phi,cal})^2/(n-2)$$

8.2 Results

where n is the number of observation, are also listed in Tables 7.5, 7.6 and 8.5.

The V_ϕ for the crown ether and cryptand complexes are given in Table 8.6. These data were extrapolated to infinite dilution using Eq. 8.14. The limiting apparent molar volumes, $V_1(x_1=0)$, of the crown ether and cryptand complexes are given in Table 8.7. The limiting apparent molar volumes of the alkali metal salts required to calculate ΔV^∞ (Eq. 8.2) are listed in Table 8.9. V_ϕ for the salts are given in Table 8.8. ΔV^∞ results are listed in Table 8.10.

8.2 Results

Table 8.2. The Apparent Molar Volumes, V_ϕ of the CE5 in MeOH, AN and DMSO.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
MeOH					
2.994	186.197	6.514	189.877	7.602	190.416
4.058	187.583	6.970	190.205	8.111	190.042
5.024	188.819				
AN					
2.215	186.591	6.233	189.452	8.516	192.168
3.338	187.835	6.292	189.548	8.772	190.769
4.701	189.169	6.437	189.		
DMSO					
1.718	194.108	3.953	197.691	6.216	197.982
1.966	194.134	4.984	197.465	7.969	199.750
3.241	195.532	5.448	197.501		

^aUnits : mol.L⁻¹; ^bUnits : cm³. mol⁻¹.

8.2 Results

Table 8.3 : The apparent molar volumes of Cy₂CE6 in MeOH, AN and DMSO.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
MeOH					
1.568	320.597	3.827	323.440	6.161	324.741
3.132	322.475	4.509	323.863	7.381	325.709
3.289	322.856	4.783	324.023		
AN					
1.766	325.936	3.934	326.944	5.588	327.353
3.144	326.488	4.160	327.066	6.976	328.313
3.274	326.744	4.954	327.191		
DMSO					
2.007	352.558	4.517	352.415	6.219	352.320
2.856	352.525	4.838	352.903	6.408	352.220
3.574	352.199	5.482	352.279		

^aUnits : mol.L⁻¹; ^bUnits : cm³.mol⁻¹.

8.2 Results

Table 8.4. The apparent molar volumes of B₂CE6 in AN and DMSO.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
AN					
1.479	271.168	3.394	271.356	4.280	271.191
2.215	271.182	4.278	271.842	4.979	271.936
DMSO					
1.743	288.614	3.235	288.592	4.189	288.866
2.219	288.865	3.929	288.026	4.729	288.819

^aUnits: mol-L⁻¹ ^bUnits: cm³-mol⁻¹

8.2 Results

Table 8.5. The Limiting Apparent Molar Volumes of the Crown Ethers, $V_{\phi}(x_1=0)$, in Various Solvents, calculated from the data in Tables 8.2-8.4 using Equation 7.23. The Molar Volumes of the Pure Solvents, V_2^o are included.

Solvent	$V_{\phi}(x_1=0)^a$	m	σ	V_2^{oa}
CE5				
MeOH	184.3	79.7	0.5	40.55
AN	185.3	69.9	0.5	52.63
DMSO	192.8	89.0	0.6	70.96
B ₂ CE6				
AN	270.8	19.1	0.3	52.63
DMSO	288.7	-1.8	0.4	70.96
Cy ₂ CE6				
MeOH	319.9	82.7	0.4	40.55
AN	325.2	42.2	0.1	52.63
DMSO	352.6	-4.8	0.2	70.96

^aUnits : cm³.mol⁻¹

8.2 Results

Table 8.6. The Apparent Molar Volumes, V_ϕ of the Crown Ether and Cryptand Complexes in MeOH, AN and DMSO at 25°C.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
CE5 + NaCl + MeOH		CE5 + NaI + MeOH		CE5 + KI + MeOH	
2.427	191.3	2.572	211.4	2.514	218.3
3.036	193.2	3.546	214.5	4.445	221.1
4.805	193.9	4.624	217.5	4.608	221.5
6.279	194.7	6.659	219.9	5.047	222.1
7.128	194.7	7.177	220.3	7.214	224.4
7.938	195.7	7.551	222.1	7.407	224.5
-	-	10.201	224.6	8.146	224.7
-	-	-	-	10.046	227.4
CE5 + CsI + MeOH		CE5 + NaI + AN		CE5 + KI + AN	
1.162	221.5	2.257	214.7	2.296	217.9
1.971	226.7	4.909	216.6	3.842	219.1
2.018	226.7	5.357	215.9	4.325	218.4
2.525	229.1	5.747	216.7	5.435	220.7
2.603	229.1	6.733	218.6	5.827	220.8
2.711	229.1	9.412	220.9	6.810	222.4
3.123	231.7	10.982	222.8	7.788	223.4
3.199	232.2	12.106	225.5	8.166	223.8

8.2 Results

Table 8.6. continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
CE5 + CsI + AN		B ₂ CE6 + KI + AN		B ₂ CE6 + CsI + DMSO	
1.676	200.4	1.964	308.5	1.078	338.6
1.780	199.6	2.216	308.2	2.351	339.2
1.862	200.7	2.630	308.4	2.871	339.1
2.223	200.5	3.809	307.8	3.652	339.3
2.275	200.5	4.133	307.8	3.844	339.3
2.484	200.9	4.779	307.5	4.373	339.2
2.761	200.6	5.990	307.6	5.345	338.3
Cy ₂ CE6 + NaI + AN		B ₂ CE6 + NaI + AN		B ₂ CE6 + NaI + DMSO	
2.963	357.9	1.749	299.6	1.719	326.6
2.972	357.7	2.297	299.3	2.591	325.9
3.632	357.8	2.776	299.8	3.037	326.3
4.999	358.4	3.145	299.1	3.132	325.9
5.046	358.6	3.524	298.9	3.736	326.1
5.529	358.0	4.219	298.7	4.191	326.1
5.913	361.0	5.512	298.2	4.588	326.3
-	-	6.164	297.9	5.081	326.0

8.2 Results

Table 8.6. continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
B ₂ CE6 + CsI + AN		B ₂ CE6 + KI + DMSO		Cy ₂ CE6 + NaI + MeOH	
1.672	315.2	1.631	330.2	2.471	349.5
2.242	314.1	2.228	330.7	2.759	349.7
2.492	314.7	2.547	330.5	2.956	349.8
2.527	314.8	3.042	329.9	3.213	349.9
3.725	314.3	3.149	330.1	3.607	350.0
4.509	313.7	3.167	330.2	4.079	350.6
4.585	313.8	3.879	330.1	5.148	351.3
-	-	4.427	329.5	6.078	351.8
Cy ₂ CE6 + KI + MeOH		Cy ₂ CE6 + CsI + MeOH		Cy ₂ CE6 + KI + AN	
2.029	354.4	2.655	359.5	2.114	360.4
2.181	354.5	2.723	360.6	2.751	360.9
3.006	354.8	3.743	359.8	3.055	361.2
4.069	355.2	4.129	360.2	4.166	361.4
4.656	355.3	5.016	361.1	4.899	363.8
6.364	355.8	5.526	361.4	5.402	363.9
7.338	356.5	6.926	361.8	6.459	366.3
-	-	7.097	362.2		

8.2 Results

Table 8.6. continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
Cy ₂ CE6 + CsI + AN		Cy ₂ CE6 + NaI + DMSO		Cy ₂ CE6 + KI + DMSO	
2.552	367.2	2.655	377.7	2.348	382.8
2.959	368.3	3.711	377.1	3.386	383.4
2.990	368.3	5.229	377.9	3.637	383.5
3.422	369.2	5.802	376.9	4.169	385.1
3.689	368.6	6.323	377.1	4.249	385.3
4.307	369.8	7.709	377.7	5.868	386.1
-	-	-	-	6.321	386.9

Cy₂CE6 + CsI + DMSO

1.811	396.4
3.355	396.5
3.671	394.7
4.586	394.9
6.473	394.9
6.885	395.9
9.335	396.7

8.2 Results

Table 8.6.continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
c-222 + NaCl + MeOH		c-222 + KCl + MeOH		c-222 + CsCl + MeOH	
3.326	335.85	1.149	329.35	2.042	346.36
5.750	335.57	2.671	328.16	3.926	345.99
6.897	334.58	5.123	327.47	6.467	345.13
7.997	335.77	7.833	327.40	9.825	342.81
12.237	333.46	8.667	325.92	10.463	342.63
c-222 + KI + MeOH		c-222 + NaI + MeOH		c-222 + CsI + MeOH	
3.184	355.00	2.312	347.17	3.296	362.47
3.793	354.60	3.969	346.29	3.746	362.92
6.082	353.30	6.768	345.63	5.467	361.77
7.744	353.30	8.212	345.79	6.126	361.74
9.020	353.60	9.152	345.49	7.721	361.13
10.191	353.30	10.139	345.30	9.736	360.84
C-222 + KI + AN		c-222 + NaI + AN		c-222 + CsI + AN	
1.529	362.52	2.054	353.05	1.091	368.59
2.058	362.21	4.036	352.59	1.949	367.81
3.597	361.42	5.046	351.91	1.966	368.58
6.520	360.85	6.106	351.59	2.249	368.42
9.294	360.95	6.712	352.05	2.346	367.83
10.856	360.50	10.061	351.25	2.392	367.70

8.2 Results

Table 8.6. continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
c-222 + NaI + DMSO		c-222 + KI + DMSO		c-222 + CsI + DMSO	
2.079	384.56	2.553	390.98	1.855	402.17
4.175	384.60	3.924	390.54	4.270	401.34
5.036	384.56	4.758	392.55	5.735	400.79
6.179	383.87	6.967	390.18	6.765	400.75
9.190	383.57	7.489	389.69	8.418	401.38
9.974	383.86	9.244	390.43	8.994	400.93

^aUnits: mol-L⁻¹; ^bUnits: cm³-mol⁻¹

8.2 Results

Table 8.7. The Limiting Apparent Molar Volumes, $V_\phi(x_1=0)$, of the Crown Ether Complexes in MeOH, AN and DMSO, calculated from the data in Table 8.6 using Equation (8.15).

Salt	$V_\phi(x_1=0)(\text{MeOH})^a$	$V_\phi(x_1=0)(\text{AN})^a$	$V_\phi(x_1=0)(\text{DMSO})^a$
CE5			
NaCl	190.7 ± 0.6	-	-
NaI	208.4 ± 0.9	211.1 ± 0.9	*
KI	215.9 ± 0.4	214.8 ± 0.6	*
CsI	216.2 ± 0.5	199.3 ± 0.4	*
B₂CE6			
NaI	-	300.4 ± 0.2	326.4 ± 0.2
KI	-	308.9 ± 0.2	331.0 ± 0.3
CsI	-	315.6 ± 0.3	339.1 ± 0.4
Cy₂CE6			
NaI	347.8 ± 0.1	355.6 ± 0.9	377.9 ± 0.4
KI	353.7 ± 0.1	357.1 ± 0.7	380.2 ± 0.5
CsI	358.4 ± 0.4	364.2 ± 0.4	395.5 ± 0.9

^aUnits: $\text{cm}^3\text{-mol}^{-1}$; *Equilibrium constant is of the order of 10.^(38,244)

Table 8.7. continued over the page with values for c-222.

8.2 Results

Table 8.7 continued...

Salt	$V_{\phi}(x_1=0)(\text{MeOH})^a$	$V_{\phi}(x_1=0)(\text{AN})^a$	$V_{\phi}(x_1=0)(\text{DMSO})^a$
c-222			
NaCl	336.9 ± 0.7	-	-
NaI	347.4 ± 0.3	353.3 ± 0.3	384.9 ± 0.3
KCl	329.5 ± 0.6	-	-
KI	355.4 ± 0.5	362.5 ± 0.4	391.8 ± 0.9
CsCl	347.7 ± 0.4	-	-
CsI	363.7 ± 0.3	369.3 ± 0.4	402.1 ± 0.4

^aUnits: $\text{cm}^3 \cdot \text{mol}^{-1}$; ^{*}Equilibrium constant is of the order of 10. ^(38,244)

8.2 Results

Table 8.8. The Apparent Molar Volumes of the Alkali Metal Salts in MeOH, AN and DMSO at 298.15 K.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
NaCl-MeOH		KCl-MeOH		CsI-MeOH	
4.025	-7.87	1.464	-7.17	2.943	14.34
5.736	-9.07	2.172	-7.53	3.968	13.92
6.721	-9.63	3.180	-7.79	4.167	13.58
8.821	-9.26	3.782	-8.55	4.302	14.06
11.354	-9.76	4.587	-8.62	5.715	13.25
29.844	-12.72	5.185	-9.11	7.075	12.34
				8.981	11.71
				10.090	12.17
NaI-MeOH		KI-MeOH		CsI-MeOH	
2.247	9.15	2.189	19.63	2.489	30.48
4.143	8.74	3.177	19.08	3.927	29.47
5.146	7.81	5.169	18.73	5.097	29.62
6.189	7.51	6.067	17.64	7.259	29.01
8.446	7.63	8.949	17.49	8.430	28.86
9.770	6.76	9.845	16.99	10.632	28.19

8.2 Results

Table 8.8. continued...

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
NaI-AN		KI-AN		CsI-AN	
2.361	5.14	2.116	15.69	0.929	28.38
3.721	5.29	3.112	16.55	1.682	27.22
5.300	6.41	4.642	17.13	2.208	28.23
6.146	6.00	5.900	16.93	2.319	29.98
7.705	6.31	7.654	16.98	2.356	29.16
9.055	6.68	9.373	16.80	2.403	28.08
NaI-DMSO		KI-DMSO		CsI-DMSO	
2.796	33.89	2.615	40.81	2.420	52.49
3.501	33.84	3.432	41.22	3.488	52.41
5.112	32.99	4.694	40.35	4.394	52.92
6.239	33.06	5.415	41.08	6.134	51.91
7.943	32.97	6.467	39.92	7.860	51.21
9.226	33.09	9.254	41.08	9.839	51.39

^aUnits: mol-L⁻¹ ; ^bUnits: cm³-mol⁻¹

8.2 Results

Table 8.9. Limiting Apparent Molar Volumes, $V_\phi(x_1=0)$, of the Metal Halide Salts at 25°C obtained from the literature. These values have been calculated from V_ϕ values given in Table 8.8.

Salt	$V_\phi(x_1=0)^a$		
	MeOH	AN	DMSO
NaCl	-7.9 (-5.5) ^a	-	-
NaI	9.2 (12.7) ^a	4.7 (4.7) ^c	34.1 (33.4) ^d
KI	20.2 (22.3) ^a	16.4 (15.6) ^c	40.8 (41.9) ^d
CsI	30.8 (33) ^b	27.7 (26) ^c	53.2 (53.5) ^d

^aValue from Ref. 272; ^bValue from Ref. 312; ^cValue from Ref. 31; ^dValue from Ref. 275.

8.2 Results

Table 8.10. ΔV^∞ for Complex Formation Between Alkali Metal Ions and the Crown Ethers or Cryptand, and a Comparison with Eq. (8.24).

Solvent	Ion	ΔV^∞ ^c				B/r ^{±a}
		CE5	B ₂ CE6	Cy ₂ CE6	c-222	
MeOH	Na ⁺ (NaCl)	18	(9) ^a	-	-	18±2
	Na ⁺ (NaI)	15	(9) ^a	19	16 (11) ^b	18±2
	K ⁺ (KI)	11	(11) ^a	14	13	13±2
	K ⁺ (KCl)	-	-	-	13 (16) ^b	13±2
	Cs ⁺ (CsI)	1	(4) ^a	8	10 (7) ^b	10±1
	Cs ⁺ (CsCl)	-	-	-	10	10±1
AN	Na ⁺	21	25	25	19	25±3
	K ⁺	13	22(21) ^a	16	12	18±2
	Cs ⁺	-13	17	11	16	14±2
DMSO	Na ⁺	*	4	-9	2	13±2
	K ⁺	*	2(0) ^a	-13	1	9±2
	Cs ⁺	*	-3(-2) ^a	-10	3	7±1

*The equilibrium constant is of the order of 10; ^aValue from Ref. 31; ^bValues from Refs. 32,33; ^cUnits : cm³.mol⁻¹.

8.3 Discussion

8.3.1 Electrostriction

(a) Hepler's hypothesis

Hepler⁽²⁴²⁾ has proposed a model to obtain the partial molar volume of an ion in a solvent due to compression of a solvent (electrostriction) - which he reported in the following manner.

The volume change due to compression (electrostriction) of a solvent about an ion may be obtained from equation 8.18

$$dV = -\beta dP \quad 8.18$$

where β represents the compressibility of the solvent and P the internal pressure due to the ion charge. The total volume decrease about an ion is obtained by integrating equation 8.18 with respect to the pressure and then integrating over the total volume of solvent outside the ion cavity as indicated by equation 8.19.

$$\Delta V = \int_r^\infty \int_0^P \beta dP 4\pi r^2 dr \quad 8.19$$

Following Latimer and Casper⁽³⁰⁵⁾ and Zwicky,^(306,307) Hepler took the pressure due to the ion charge to be proportional to z^2/r^4 , (where z represents the charge on the ion, and r the Pauling radius), and also used an average constant compressibility. The result of the integration of 8.19 is that the volume decrease due to compression of the solvent by the internal pressure set up by the ion charge is proportional to z^2/r . From the Born equation 8.20

8.3 Discussion

$$\Delta F = -z^2/2r(1 - 1/D) \quad 8.20$$

(where ΔF is the electrostatic free energy of solution and D is the dielectric constant), and the thermodynamic relation $(\partial\Delta F/\partial P)_T = \Delta V$, he deduced that the volume decrease due to compression of the dielectric medium is also proportional to z^2/r .

On the basis of the above, the total volume decrease due to ion-solvent interaction is taken as proportional to z^2/r and the volume of the ion cavity as proportional to r^3 . Equation 8.21 for the partial molar volumes of ions at infinite dilution, V_ϕ , as a function of z and r is written as follows

$$V_\phi = Ar^3 - Bz^2/r \quad 8.21$$

where Ar^3 is the positive contribution to the partial molar volume due to the space occupied by the ion, and Bz^2/r represents the decrease in volume due to compression of the solvent about the ions (electrostriction).

Fajans and Johnson⁽³⁰⁸⁾ have investigated the partial molar volumes of ions in aqueous solution and found evidence that the partial molar volume at infinite dilution of chloride ions is about $18.0 \text{ cm}^3 \cdot \text{mol}^{-1}$. Hepler based the partial molar volumes of ions on this value.

Equation 8.21 may be rearranged to give equations 8.22 and 8.23 that are suitable for testing graphically the predicted dependence of $V_\phi(\text{ion})$ on z and r .

$$[V_\phi(\text{ion})r]/z^2 = Ar^4/z^2 - B \quad 8.22$$

$$V_\phi(\text{ion})/r^3 = A - Bz^2/r^4 \quad 8.23$$

Plots of $V_\phi(\text{ion})r/z^2$ vs. r^4/z^2 and $V_\phi(\text{ion})/r^3$ vs. z^2/r^4 , taken from ref. (242), are shown in Figs.

8.3 Discussion

8.3 and 8.4 respectively.

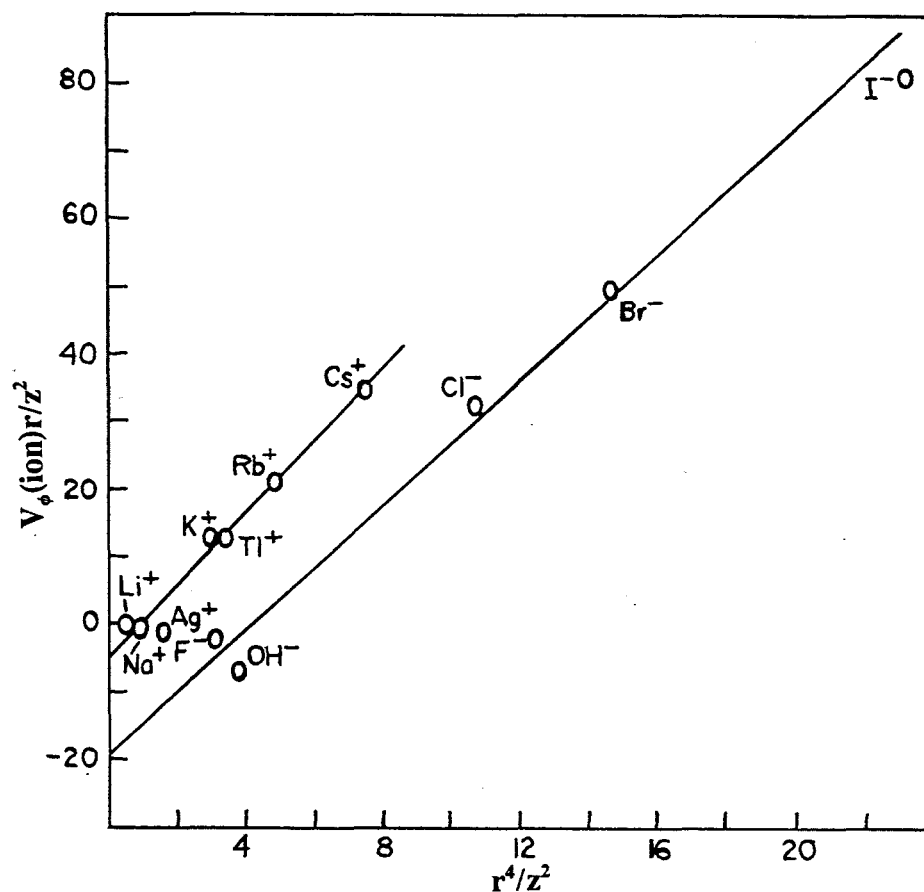


Fig. 8.3 : Plot of $V_{\phi}(\text{ion})r/z^2$ versus r^4/z^2

From the slopes and intercepts in the two plots, the constants A and B were evaluated as 5.3 and 4.7 respectively for cations; and 4.6 and 19 for anions.

Hepler⁽²⁴²⁾ also pointed out the fact that B is larger for anions than cations indicating that the ion-solvent interaction is greater for anions than for cations of the same size and charge.

8.3 Discussion

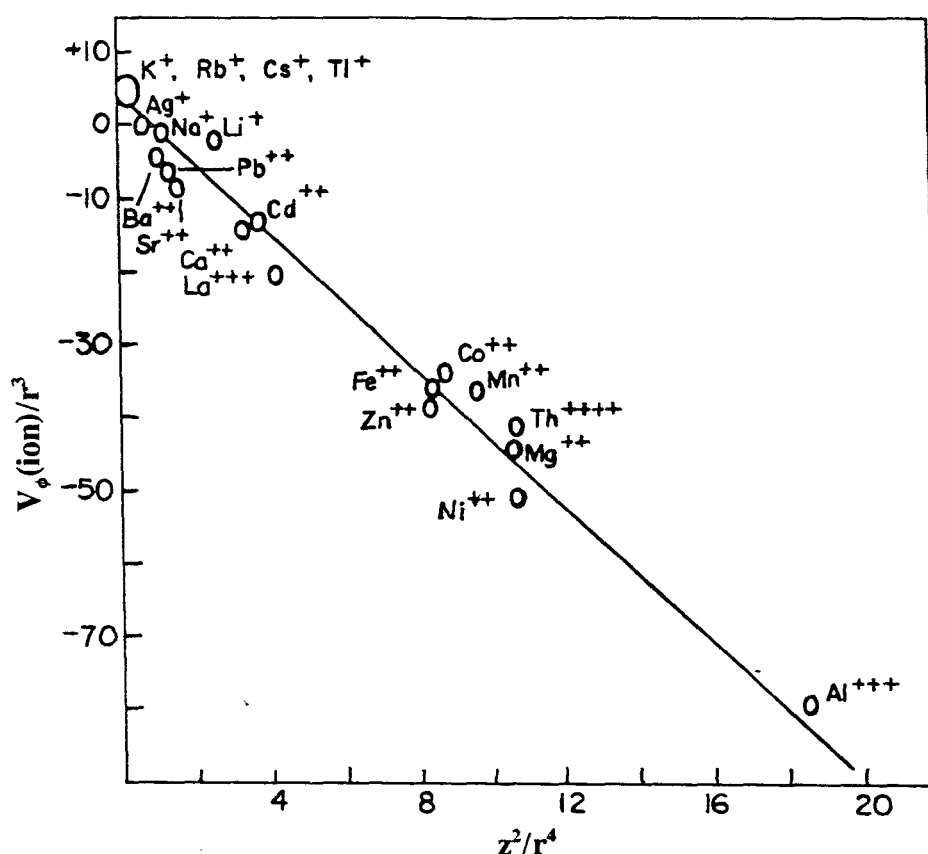


Fig. 8.4 : Plot of $V_\phi(\text{ion})/r^3$ versus z^2/r^4 .

(b) Previous work

Previous work on ΔV^∞ for the complexation of cryptand-222 with metal salts in water and methanol has been done by Morel *et al.*^(32,33) The results support the concept that c-222, like 18-crown-6 ether and dibenzo-18-crown-6 ether,⁽³¹⁾ has the capacity to envelop metal ions. c-222 was found to be considerably more soluble than the crown ethers in these solvents, and went quickly into solution without the solutions having to be warmed. In this work, we have extended the systems studied to include c-222 complexed with metal salts in AN and DMSO. The ΔV^∞ results presented here for c-222 in MeOH, DMSO and AN are reported in Table 8.6. It is interesting to note that Morel⁽³³⁾ working with cryptand 222 and MCl in water obtained 14.2 ± 0.2 and 17.4 ± 0.2 for NaCl and KCl respectively. They also determined ΔV^∞ for cryptand 222 with MCl in MeOH⁽³²⁾ and obtained 10.6 ± 0.6 , 15.9 ± 0.6 and 7.4

8.3 Discussion

± 1.2 for NaCl, KCl and CsCl, respectively. Their ΔV^∞ results included a correction factor, of $13 \text{ cm}^3\text{-mol}^{-1}$, for the chloride ion of the metal salt, obtained from work done by Kawaizumi and Zana.⁽³¹⁰⁾ This correction has not been included in the results in this work, and the calculations have been carried out in a similar manner to Letcher *et al.*⁽³¹⁾

(c) Comparison of this work with previous results

The results reported here for Bz₂CE6.MX in AN and DMSO are in good comparison with the results reported by Letcher *et al.*⁽³¹⁾ The results for c-222.MX have not been compared to Morel's results⁽³²⁾ in MeOH, due to their use of a different method of calculation of ΔV^∞ - however, Morel's⁽³²⁾ for $V_1(x_1=0)$ for c-222 in MeOH is in very good agreement with the result obtained in this work.

(d) This work

The standard volume changes upon complex formation, ΔV^∞ , are given in Table 8.10. These results are compared to values attributed to the electrostriction term of the Hepler equation⁽²⁴²⁾, rewritten here from eqn 8.23 for $z=1$

$$V_\phi^\infty(\text{cation}) = Ar^3 - B/r \quad 8.24$$

If it can be assumed that the charge on the cation in the complex is shielded from the complex, that the salt involved in the complex is not ion paired, that the effect of the c-222 on the solvent packing is the identical to the effect of the c-222.MX complex on the solvent, and that the formation constants are large enough to ensure no uncomplexed cryptand, then it is possible that these results can be explained in terms of a loss of the electrostrictive effect of the M^+ ion in forming a complex with the crown ether or the cryptand.

Support for the concept that ΔV^∞ represents the electrostriction effect of the metal ion in the

8.3 Discussion

solvent, is given by a reasonable correlation with the Hepler⁽²⁴²⁾ prediction of the effect. Similar results were obtained by Letcher *et al*⁽³¹⁾ with work on 18-crown-6 ether and dibenzo-18-crown-6 ether in various solvents.

The comparison of ΔV^∞ and B/r^+ , (compiled by Zana *et al*⁽²¹⁷⁾), given in Table 8.10, for the crown ether complexes in solvents MeOH or AN, does suggest that ΔV^∞ is largely due to the electrostriction of the solvent by the metal ion Na^+ or K^+ . This does support the idea that the Na^+ and K^+ ions fit into the cavity, or are completely enveloped by the crown ether - an observation supported by a similar finding in work done by Letcher, Kay and Paul.⁽³¹⁾ The Cs^+ ion quite clearly is too large to be enveloped by the cavity, and is thus not adequately shielded from the solvent.

The ΔV^∞ results in DMSO do not correlate with the Hepler predictions. It has been suggested^(31,309) that, since B is zero for anions in DMSO, the two methyl groups on DMSO sterically hinder anion-solvent interaction, and thus prevent electrostriction of the solvent by anions.

(e) Effect of the cavity size

The cavity radius of c-222 has been estimated as 1.40 nm⁽³¹¹⁾ and the ionic radii of Na^+ , K^+ and Cs^+ ions are 1.02, 1.38 and 1.67 nm respectively.⁽³¹²⁾ It would seem, from both the results and the ionic radii, that the Na^+ and K^+ slip into the c-222 cavity. The Cs^+ is significantly larger in volume and yet, from the ΔV^∞ results, it seems to fit into the cavities. This is possibly due to the flexibility of the c-222 ring. Morel *et al*^(33,313) have reported on the complexation of alkali chlorides by c-222 in both water and MeOH. They have pointed out the anomalous behaviour of Cs^+ - whose radius is larger than that of the c-222 cavity. Complexation does occur - but it is likely that there is distortion of the molecule. The ΔV^∞ for the Cs^+ complex was observed to be smaller than that for the complex of the (smaller) Rb^+ ion.⁽³³⁾ Morel *et al* speculate that this may be due to the formation of a partially

8.3 Discussion

exclusive complex with Cs^+ , evidence of which has been given by NMR studies.⁽³¹⁴⁾

It would be interesting to investigate the complexation by these same crown ethers and cryptand in the same solvents of cations with a double charge, eg. Ca^{++} . C-222 + divalent cation systems have been investigated by Morel⁽³⁶⁾- and an extension to this work would be of interest in investigating the complexation properties of these macrocyclic molecules.

8.3.2 Compressibilities

The isentropic apparent molar compressibility, κ_ϕ , is a useful function that gives information on, amongst others, structural effects in solution as well as giving a more complete picture of electrolyte solutions. While the isothermal compressibilities (κ_T) are more desirable, they are more difficult to obtain experimentally.

κ_ϕ may be calculated from⁽³⁵⁾

$$\kappa_\phi = 1000(\beta_s - \beta_{so})/Cd_o + \beta_s V_\phi \quad 8.25$$

where β_s and β_{so} are the isentropic coefficients of compressibility of the solution and the solvent respectively; V_ϕ is the apparent molar volume; and C is the solute concentration.

Høiland *et al*⁽³⁵⁾ reported on the ΔV^∞ and $\Delta\kappa_\phi$ of complexation of CE6 + MX in water. They found that ΔV^∞ and $\Delta\kappa_\phi$ values were comparable in magnitude to ion association processes - they concluded from these results that the positive charge of the cation became effectively screened by the CE.

Letcher *et al*⁽³¹⁾ made a similar study of complexes involving CE6 and c-222 of the K^+ ion in water, MeOH, AN, and DMSO (see Fig. 8.5). They reported that, contrary to an *expected* increase in ΔV^∞ with the compressibility of the solvent - they obtained *no*

8.3 Discussion

correlation at all. That is, the κ_T of water and MeOH⁽³¹⁵⁾ differ by a factor of three, but the ΔV^∞ s for K^+ complexation in water and MeOH are almost the same.

The same point has been made by Zana *et al*⁽²⁷¹⁾, who argue that the lack of correlation between ΔV^∞ and $\Delta\kappa_T$ is due to ΔV^∞ reflecting the specificity of ion-solvent interaction at molecular level - whereas compressibility is a macroscopic property.

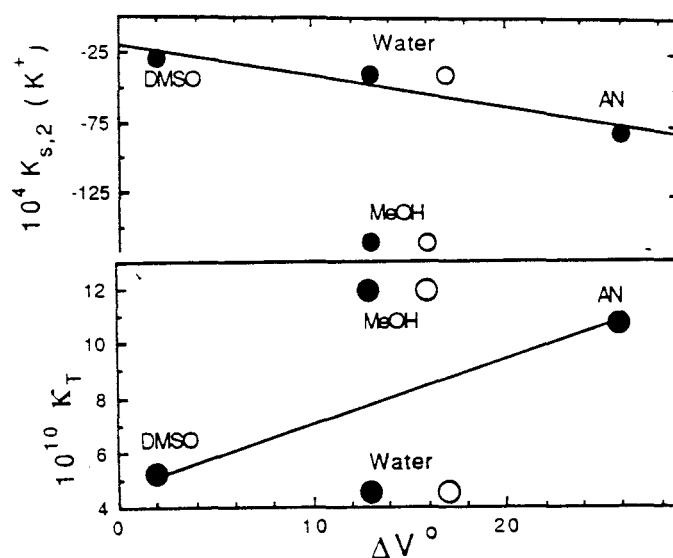


Fig. 8.5 : A correlation of the volume change, due to complexing of the K^+ ion by CE6 (filled symbols) and by c-222 (open symbols) in the various solvents, with the partial molar compressibilities of the potassium ion (top) and with the isothermal compressibilities of the solvent (bottom). The straight lines are arbitrary, taken from ref. (31).

8.3.3 Pressure dependence of ΔV^∞

The pressure dependence of ΔV^∞ may be calculated from⁽²⁴³⁾

$$(\partial \ln K / \partial P)_T = -\Delta V^\infty / RT \quad 8.26$$

where K is the equilibrium constant, and the rest have the usual meaning. These results would give support to the methods of measuring ΔV^∞ , reported in this thesis. As it is, the

8.3 Discussion

only available results are those of Dewey *et al*, reported in reference (31) - and they are unpublished. Dewey *et al* found that for both Na^+ and K^+ in $\text{B}_2\text{CE6-MeOH}$, the ΔV^∞ were found to be approximately $9 \text{ cm}^3.\text{mol}^{-1}$. This result was in good agreement with the density measurement results obtained by Letcher *et al*⁽³¹⁾ for ΔV^∞ of $10 \text{ cm}^3.\text{mol}^{-1}$ and $11 \text{ cm}^3.\text{mol}^{-1}$ for the Na^+ and K^+ complexes respectively.

8.3.4 Significance of the K of complexation

Stability constants, K ,^(38,244) of the order of 10^4 or better were desirable - in order to ensure that most of the crown ether was in the complexed state, thus no corrections would be necessary.⁽³¹⁾ For example, K for $\text{B}_2\text{CE6}$ in DMSO ⁽³⁸⁾ is of the order of 10^3 , which corresponds to as much as 15 per cent of the crown ether being uncomplexed.⁽³¹⁾

The stability constants^(38,244) of the CE6 complexes investigated here are of the order of 10^5 to 10^6 in MeOH and AN , and of the order of 10^3 for the DMSO complexes. The stability constants^(38,244) for the formation of most of the c-222 complexes are of the order of 10^4 (DMSO), 10^{10} (AN) and 10^5 (MeOH). This implies that at equilibrium, with equimolar concentrations of c-222 and metal salt, most of the material is in the complexed state, and thus no correction for the uncomplexed material has been made. This is not the case with the c-222- Cs^+ in DMSO , the stability constant (K) of which is of the order of 10^3 . This might explain why anomalous results were obtained for this system. The results are given in Table 8.10. This trend was also observed in work done by Letcher *et al*⁽⁴²⁾ in DMSO , where the K values were 10^3 or below.

In this work, the ΔV^∞ of $\text{CE5} + \text{MX}$ in DMSO were not reported as, with an equilibrium constant of complexation of the order of 10, a large percentage of the crown ether was uncomplexed. Thus, ΔV^∞ could not be correlated with B/r^+ values.

APPENDIX A

Error Analysis

Using the notation in the GWBASIC computer programme:

$$V^E = \{X_A \cdot M_A + (1-X_A)M_B\}/D_U - (X_A \cdot M_A)/D_A - \{(1-X_A)M_B\}/D_B$$

where V^E is the excess molar volume, X_A is the mole fraction of A, X_B is the mole fraction of B, M_A is the molar mass of A, M_B is the molar mass of B, D_U is the density of the mixture, D_A is the density of A, and D_B is the density of B.

$$X_A = \{(B_A - B_0)/M_A\} / \{(B_A - B_0)/M_A + (B_B - B_A)/M_B\}$$

where B_0 is the mass of the weighing bottle, B_A is the mass of $B_0 + A$, and B_B is the mass of $B_A + B$.

$$D_U = C(\tau_u^2 - \tau_w^2) + D_w$$

where C is the densimeter constant (0.542394), τ_u is the periodicity value obtained from the densitometer for the mixture, τ_w is the periodicity value for distilled and deionised water, and D_w is the density of the water.

$$D_A = C(\tau_A^2 - \tau_w^2) + D_w$$

where τ_A is the periodicity value obtained for A.

$$D_B = C(\tau_B^2 - \tau_w^2) + D_w$$

Appendix A

where τ_B is the periodicity value for B.

$$V_\phi = \{1000(d - d_o)\}/(C_1 d_o) + M_1/d_o$$

where V_ϕ is the apparent molar volume, d is the density of the solution, d_o is the density of the pure solvent, C_1 is the concentration of the solution, and M_1 is the molar mass of the solute.

Calculation of errors

Here Δ represents the error in the quantity, and an example of a typical (average value) calculation is given.

$$(\Delta X_A)^2 = (\partial X_A/\partial B_o)^2(\Delta B_o)^2 + (\partial X_A/\partial B_A)^2(\Delta B_A)^2 + (\partial X_A/\partial B_B)^2(\Delta B_B)^2$$

$$\begin{aligned}(\partial X_A/\partial B_o) &= -[M_A \cdot M_B(B_B - B_A)]/[M_B(B_A - B_o) + M_A(B_B - B_A)]^2 \\&= -[100.40(1.0)]/[40(1.0) + 100(1.0) + 100(1.0)]^2 \\&= -0.20408\end{aligned}$$

$$\begin{aligned}(\partial X_A/\partial B_A) &= [M_A \cdot M_B(B_B - B_o)]/[M_B(B_A - B_o) + M_A(B_B - B_A)]^2 \\&= [100.40(1.0)]/[40(1.0) + 100(1.0)]^2 \\&= 0.20408\end{aligned}$$

$$\begin{aligned}(\partial X_A/\partial B_B) &= -[M_A \cdot M_B(B_A - B_o)]/[M_B(B_A - B_o) + M_A(B_B - B_A)]^2 \\&= -[100.40(0.1)]/[40(1.0) + 100(1.0)]^2 \\&= -0.20408\end{aligned}$$

Thus, $\Delta X_A = 0.000004$ moles

Appendix A

$$(\Delta D_U)^2 = (\partial D_U / \partial \tau_u)^2 (\Delta \tau_u)^2 + (\partial D_U / \partial \tau_w)^2 (\Delta \tau_w)^2$$

$$(\partial D_U / \partial \tau_u) = 2\tau_u = 2(1.780000) = 3.56000$$

$$(\partial D_U / \partial \tau_w) = 2\tau_w = 2(1.739781) = 3.47956$$

$$(\Delta D_U)^2 = (3.56000)^2 (0.00002)^2 + (3.47956)^2 (0.00002)^2$$

$$\text{Thus, } \Delta D_U = 0.00001 \text{ g.cm}^{-3}$$

$$\text{Similarly, } \Delta D_A \text{ and } \Delta D_B \text{ are equal to } 0.00001 \text{ g.cm}^{-3}$$

$$(\Delta V^E)^2 = (\partial V^E / \partial X_A)^2 (\Delta X_A)^2 + (\partial V^E / \partial D_U)^2 (\Delta D_U)^2 + (\partial V^E / \partial D_A)^2 (\Delta D_A)^2 + (\partial V^E / \partial D_B)^2 (\Delta D_B)^2$$

$$(\partial V^E / \partial X_A) = (M_A - M_B) / D_U - M_A / D_A + M_B / D_B = 60 / 0.9 - 100 / 0.8 + 40 / 0.8 = -8.33333$$

$$(\partial V^E / \partial D_U) = -[X_A \cdot M_A - (1 - X_A) M_B \cdot D_U] / (D_U)^2 = -[0.5(100) - (0.5)40(0.9)] / (0.9)^2 = 39.50617$$

$$(\partial V^E / \partial D_A) = -M_A / (D_A)^2 \cdot (-D_A) = -[100 / (0.8)^2](-0.8) = 125$$

$$(\partial V^E / \partial D_B) = -[(1 - X_A) M_B] / (D_B)^2 \cdot (-D_B) = -[0.5 \cdot 40 \cdot (-0.8)] / (0.8)^2 = 25$$

$$\text{Thus, } \Delta V^E = 0.00132 \text{ cm}^3 \cdot \text{mol}^{-1}$$

$$(\Delta V_\phi)^2 = (\partial V_\phi / \partial d_o)^2 (\Delta d_o)^2 + (\partial V_\phi / \partial d)^2 (\Delta d)^2 + (\partial V_\phi / \partial C_1)^2 (\Delta C_1)^2$$

$$(\partial V_\phi / \partial d_o) = [-1000(d - d_o)(d_o)] / [C_1(d_o)^2] - (M_1 \cdot d_o) / (d_o)^2 = [-1000(0.9 - 0.8)(0.8)] / [0.05 \cdot (0.8)^2]$$

$$(\partial V_\phi / \partial d) = 1000 / (C_1 d_o) = 1000 / (0.05 \cdot 0.8)$$

$$(\partial V_\phi / \partial C_1) = -[1000(d - d_o)C_1] / (C_1^2 d_o) = [-1000(0.9 - 0.8)(0.05)] / [(0.05)^2 (0.8)]$$

$$\text{Thus, } \Delta V_\phi = 0.025 \text{ cm}^3 \cdot \text{mol}^{-1}$$

APPENDIX B

Calibration of the Hewlett-Packard 2804 A Quartz Thermometer

The Hewlett Packard quartz thermometer was used for all the accurate temperature measurements in this work, and was calibrated against a Tinsley platinum resistance thermometer, which had been previously calibrated by the CSIR-South Africa. The resistance of the platinum thermometer at any temperature, T , was measured with an FE Smith difference bridge. This is a modification of a Kelvin double bridge. This and other Wheatstone bridge type assemblies have been discussed by Hall and Barber.⁽³¹⁶⁾ The off-balance current was amplified using a PYE Galvanometer Photocell preamplifier, and was fed to a PYE Scalamp galvanometer. A 2V emf source was used to drive the circuit.

The heating effects could not be neglected for accurate readings. To a first approximation the heating effect at different temperatures is constant if the current in the thermometer bulb is kept constant. This is only true if the conditions of heat transfer between the bulb and its surroundings remain approximately the same. For this reason calibration was carried out in an environment closely resembling that in which later measurements would be made. The calibration of the quartz thermometer was carried out at 5 K intervals over the temperature range 273 K to 323 K in a thermostatted bath similar to the one described in Chapter 2.

To eliminate any stray emf's it was necessary to take resistance readings of both the platinum resistance thermometer and of the standard resistance with the current flowing in both directions in turn; that is four readings, x_i , for each temperature. The resistance, R_T , of the thermometer at the temperature, T , is given to a good approximation by:

$$R_T = [(x_3 + x_4)/2] - [x_1 + x_2]/2 \quad \text{B.1}$$

where the first term in equation B.1 corresponds to the average of the resistance of the

Appendix B

standard resistance, R , with the current flowing in both directions, and the second term is with respect to the platinum resistance thermometer at the temperature, T .

Resistance readings were converted to temperature values using the iterative relationship:

$$T^* = [(R_T - R_0)/\alpha R_0] + \delta[(T/100) - 1](T/100) \quad \text{B.2}$$

together with:

$$\dots\dots\dots t_{68} = T^* + 0.045(T^*/100)[(T^*/100) - 1][(T^*/630.74) - 1] \quad \text{B.3}$$

where α , δ and R_0 are the constants for the platinum resistance thermometer. In this case: $\alpha = 3.9214\text{E-}03$, $\delta = 1.4962$ and $R_0 = 24.9573\Omega$.

APPENDIX C

Computer programmes

The following are a brief guide to the computer programmes used in this work. The *Fortran* programmes were originally written for a dual processor Control Data Cyber 820 mainframe computer at Rhodes University, but have been subsequently adapted for use on an IBM AT compatible PC. The GWBASIC programmes were adapted from their original *Applesoft Basic* to the *Basic* language used on an IBM compatible PC.

Appendix C

Appendix C1. Computer programme to determine the excess molar volumes from density measurements.

```
10 REM *****
20 REM THE FOLLOWING PROGRAM IS WRITTEN IN GWBASIC FOR ANY IBM PC 100%
30 REM COMPATIBLE WITH IBM PERSONAL COMPUTERS.
40 REM THIS PROGRAM CALCULATES EXCESS VOLUMES FOR BINARY LIQUID MIXTURES
50 REM FROM DENSITY MEASUREMENT, BY THE FOLLOWING SIMPLE RELATIONSHIP :
60 REM
70 REM   VE = ((XA*MA + XB MB) / P.UNKNOWN) - (CA + CB)
80 REM
90 REM
100 REM WHERE : P.UNKNOWN IS THE DENSITY OF THE MIXTURE
110 REM C1 = ((XA*MA) / P.A)
120 REM C2 = ((XB*MB) / P.B)
130 REM
140 REM
150 REM (AN ANTON PAAR VIBRATING TUBE DENSITOMETER WAS USED IN THIS STUDY)
160 REM
170 REM ORIGINALLY WRITTEN FOR APPLE BY : R C BAXTER, RHODES UNIVERSITY
180 REM CONVERTED TO GWBASIC FOR IBM BY : B BEAN , RHODES UNIVERSITY
185 REM ADAPTED FOR EXP USE BY : J M-CHALMERS, RHODES UNIVERSITY
190 REM
200 CLS
210 PRINT "THE FOLLOWING PROGRAM CALCULATES EXCESS VOLUMES"
220 PRINT
230 PRINT "INPUT THE FOLLOWING CONSTANTS:"
240 PRINT "-----"
250 PRINT
260 REM *****
270 REM INPUT CONSTANTS
280 REM *****
290 PRINT"(MA AND MB - MOLAR MASSES, T-PERIODS FOR WATER(W), FOR STD(S), "
300 PRINT"AND FOR COMPOUNDS A AND B, "
310 PRINT"DW AND DS - THE DENSITIES OF WATER AND STD RESPECTIVELY, "
320 PRINT"B-MASSES OF SAMPLE CONTAINER(BO), CONTAINER+A(BA), CONTAINER+B(BB). "
330 PRINT"T-PERIOD FOR UNKNOWN(U) "
340 PRINT
350 PRINT" NOTE :- SEPARATE VALUES BY COMMAS" : PRINT
360 PRINT" INPUT YOUR VALUES FOR: MA,MB,TW,TS,TA,TB,DW,DS"
370 INPUT MA,MB,TW,TS,TA,TB,DW,DS
380 PRINT : PRINT" INPUT YOUR VALUES FOR: BO,BA,BB,TU"
390 INPUT BO,BA,BB,TU
393 REM
394 REM
395 GOTO 1500 : REM ***** CALCULATE ANSWERS *****
396 REM
397 REM
400 REM *****
401 REM
402 REM PRODUCE OUTPUT
403 REM
404 REM *****
420 CLS
430 LPRINT"THE CONSTANTS ARE : "
440 LPRINT"-----"
450 LPRINT""
460 LPRINT"MA : ",MA," MB : ",MB,"
470 LPRINT"TW : ",TW," TS : ",TS,"
480 LPRINT"TA : ",TA," TB : ",TB,"
490 LPRINT"DW : ",DW," DS : ",DS,"
500 LPRINT"BO : ",BO," BA : ",BA,"
510 LPRINT"BB : ",BB," TU : ",TU,"
520 LPRINT""
530 LPRINT"THE RESULTS ARE :-"
540 LPRINT"-----"
550 LPRINT""
560 LPRINT"DENSITY OF MIXTURE = ",DU
570 LPRINT"-----"
580 LPRINT"MOLE FRACTION OF COMPONENT A = ",XA
590 LPRINT"-----"
```

Appendix C

```
600 LPRINT"EXCESS VOLUME = ",VE
1000 INPUT "ENTER OUTPUT DATA FILENAME.[<ENTER> TO SKIP]";FLNMS
1010 IF FLNMS = "" GOTO 2000
1020 OPEN "O",#1,FLNMS
1030 PRINT#1,"THE CONSTANTS ARE : "
1040 PRINT#1,"-----"
1050 PRINT#1,""
1060 PRINT#1,"MA : ",MA," MB : ",MB
1070 PRINT#1,"TW : ",TW," TS : ",TS
1080 PRINT#1,"TA : ",TA," TB : ",TB
1090 PRINT#1,"DW : ",DW," DS : ",DS
1100 PRINT#1,"BO : ",BO," BA : ",BA
1110 PRINT#1,"BB : ",BB," TU : ",TU
1120 PRINT#1,""
1130 PRINT#1,"THE RESULTS ARE :-"
1140 PRINT#1,"-----"
1150 PRINT#1,""
1160 PRINT#1,"DENSITY OF MIXTURE = ",DU
1170 PRINT#1,"-----"
1180 PRINT#1,"MOLE FRACTION OF COMPONENT A = ",XA
1190 PRINT#1,"-----"
1200 PRINT#1,"EXCESS VOLUME = ",VE
1210 PRINT#1,"-----"
1220 CLOSE#1
1230 GOTO 2000
1400 REM
1410 REM
1420 REM
1500 REM *****
1510 REM
1520 REM PERFORM CALCULATIONS
1530 REM
1540 REM
1550 REM *****
1560 REM CALCULATE MOLE FRACTIONS
1570 REM *****
1580 XA = ((BA - BO) / MA) / ((BA - BO) / MA + (BB - BA) / MB)
1590 XB = 1 - XA
1600 REM *****
1610 REM CALCULATE EXCESS VOLUME
1620 REM *****
1630 C = (DW - DS) / (TW^2 - TS^2)
1640 DU = C * (TU^2 - TW^2) + DW
1650 DA = C * (TA^2 - TW^2) + DW
1660 DB = C * (TB^2 - TW^2) + DW
1670 VE = (XA * MA + XB * MB) / DU - XA * MA / DA - XB * MB / DB
1680 REM *****
1690 REM END OF CALCULATIONS
1700 REM *****
1710 REM RETURN TO PRODUCE OUTPUT
1720 REM *****
1730 GOTO 400
2000 PRINT
2010 INPUT "DO YOU WANT TO USE THE PROGRAM AGAIN ?>";YNS
2020 IF (YNS="YES") OR (YNS="Y") OR (YNS="yes") OR (YNS="y") GOTO 2040
2030 IF (YNS="NO") OR (YNS="N") OR (YNS="no") OR (YNS="n") GOTO 2200
2035 GOTO 2010
2040 PRINT
2050 PRINT "DO YOU WANT TO EMPLOY THE SAME CONSTANTS IN YOUR NEXT CALCULATION?"
2060 INPUT ">";YNS
2070 IF (YNS="YES") OR (YNS="Y") OR (YNS="yes") OR (YNS="y") GOTO 380
2080 IF (YNS="NO") OR (YNS="N") OR (YNS="no") OR (YNS="n") GOTO 360
2090 GOTO 2050
2200 END
```

Appendix C

Appendix C2. Fortran programme to determine Flory data.

The data has to be entered into a file in a word-processing package, eg. *Word Perfect*. The results must also be channeled to the word-processing package.

The data must be entered in the following way:

Temperature at which experiment is run (in K)

Density of A Density of B

Molar Mass of A Molar Mass of B

Thermal expansion coefficient of A Thermal expansion coefficient of B

Compressibility of A Compressibility of B

A_r values

B_r values

Appendix C

```
C      PROGRAM FLORY(INPUT,OUTPUT,DATA,RESULT,TAPES=DATA
C      *,TAPE7=RESULT)
C      #####
C
C      THE THERMODYNAMICS OF LIQUID MIXTURES
C
C      #####
C      #####
C      *****
C      THIS COMPUTER PROGRAM IS USED TO PROCESS MOLAR EXCESS VOLUME
C      AND MOLAR EXCESS ENTHALPY DATA OF BINARY NON-ELECTROLYTE SOLUTIONS.
C      SEVERAL THEORIES OF LIQUID MIXTURES ARE APPLIED. THE GENERAL APPROACH
C      BEING TO USE EITHER ONE OF THE TWO EXPERIMENTAL PROPERTIES MENTIONED
C      ABOVE TO PREDICT THE OTHER AND TO THEREAFTER COMPARE IT WITH ITS
C      EXPERIMENTAL VALUE.
C      THE FIRST OPERATION IS TO APPLY THE FLORY THEORY. THE FLORY
C      EQUATION OF STATE IS CALCULATED USING THE DENSITIES, MOLECULAR WEIGHTS
C      ,THERMAL EXPANSION COEFFICIENTS AND ISOTHERMAL COMPRESSIBILITIES FOR
C      THE TWO PURE LIQUIDS. THEN, USING A VALUE FOR THE INTERACTION
C      PARAMETER, CHI, WHICH HAS BEEN CALCULATED FROM BERTHELOT'S THEORETICAL
C      EQUATION, THE THEORETICAL MOLAR EXCESS VOLUMES AND ENTHALPIES ARE
C      OBTAINED. THESE ARE COMPARED TO THE EXPERIMENTAL VALUES.
C      THE SECOND OPERATION CALCULATES ADJUSTED CHI VALUES FROM THE
C      EXPERIMENTAL DATA (ONE FROM THE EXC.VOLUME & ONE FROM THE
C      EXC.ENTHALPY). THIS IS DONE THROUGH THE WHOLE RANGE OF COMPOSITIONS
C      AT MOLE FRACTION INTERVALS OF 0.1 . THE CHI VALUE WHICH GIVES THE
C      LEAST DIFFERENCE BETWEEN THE THEORETICAL AND EXPERIMENTAL VALUES
C      (SUMMED OVER ALL CONCENTRATIONS) IS CONSEQUENTLY FOUND. THIS IS DONE
C      BECAUSE CHI IS KNOWN TO VARY WITH COMPOSITION. THESE TWO CHI VALUES
C      ARE THEN USED TO FIRSTLY CALCULATE THE THEORETICAL PROPERTY FROM WHICH
C      THEY WERE OBTAINED INITIALLY AND THEN TO PREDICT THE ALTERNATE
C      PROPERTY. THESE COMPUTED FIGURES ARE THEN COMPARED TO THE EXPERIMENTAL
C      DATA.
C      THE EXPERIMENTAL EXC.VOLUMES AND EXC.ENTHALPIES ARE THEN USED TO
C      PREDICT THE MOLAR EXCESS GIBB'S FUNCTION USING AN EQUATION DERIVED BY
C      FLORY. THIS EQUATION IS, HOWEVER, KNOWN TO GIVE POOR RESULTS. AN
C      APPROXIMATE, YET SUPERIOR, EXPRESSION OBTAINED BY E.LIEBERMANN IS
C      ALSO CONSIDERED.
C      LIEBERMANN HAS FURTHERMORE DERIVED A MODIFIED FLORY THEORY IN
C      WHICH NO ADJUSTABLE PARAMETER IS NECESSARY. THIS THEORY IS TESTED
C      AS IS THE MODIFIED FLORY THEORY PRESENTED BY POLLIN & VRIED WHICH
C      TAKES INTO CONSIDERATION THE ENERGY/VOL. EXPONENT THAT FLORY EQUALLED
C      TO UNITY.
C
C      W.SPITERI          JUNE 1981
C      -----
C      MODIFIED B.BEAN    DECEMBER 1991
C      -----
C
C      *****
C      DATA INPUT AS FOLLOWS:
C      -----
C
C      /DATA
C      LABEL (60 SPACES) E.G. CYCLOPENTHANE + N-OCTANE ETC.
C      TEMPERATURE (K)
C      DENSITY OF LIQ.1    DENS.LIQ.2    (G/CC)
C      MOL.WT. OF LIQ.1    M.W.LIQ.2
C      THERMAL EXPANSION COEFFT. OF 1  THRM.EXP. COEFFT. OF 2  (PER DEGREE)
C      ISOTHERMAL COMPRESSIBILITY OF 1  ISOTHRML.COMPRS. OF 2  (/PA)
C      A0,A1,A2,A3,A4    (WHERE THESE ARE THE COEFFTS.
C      OF THE SMOOTHING CURVES OF THE EXPERIMENTAL
C      EXCESS VOLUME RESULTS (IN CC/MCL).)
```


Appendix C

```
C      NB. IF ONLY A0,A1 AND A2 ARE USED, THEN
C      DEFINE A3=0.000 & A4=0.000 .
C      THE CURVE MUST BE OF THE FORM:
C      VE=X1*X2*(A0+(A1*(X2-X1))+(A2*((X2-X1)**2))+(A3*((X2-X1)**3))
C      +(A4.....ETC.)))))
C
C      B0,B1,B2,B3,B4
C      (WHERE THESE ARE THE COEFFTS. FOR THE
C      EXPERIMENTAL EXC. ENTHALPY CURVES IN J/MCL.)
C      M1 AND M2.....(THE ENERGY/VOL. EXPONENTS FOR THE
C      PURE LIQS. I.E. POLLIN/VRIED THEORY.
CZ   C      IF M1&M2 ARE NOT KNOWN INPUT ZEROES.)
C      /END
C
C      DIMENSION X1(99),PSI1(99),PSI2(99),THETA1(99),THETA2(99
*) ,VDO(99),TDO(99),TD(99),VEXP(99),CHIEX(99),VDEX(99),VEX(99)
C      DIMENSION HEX(99),CHIHE(99),HET(99),VDE(99)
C      DOUBLE PRECISION T,RHO1,RHO2,MW1,MW2,ALPH1,ALPH2,BET1,BET2,X1,X2,V
*) ,V2,VD1,VD2
C      DOUBLE PRECISION VS1,VS2,GAM1,GAM2,P1,P2,TD1,TD2,RATR,RATS,VDEX,CH
*) IEX,PSI1,PSI2
C      DOUBLE PRECISION THETA1,THETA2,VDO,TDO,CHI,TD,VDE,VE,PP1,PP2,Q,VEX
*) P,DIFF
C      DOUBLE PRECISION VD,Z,W,HE,PHI1,PHI2,ALM,BETM,GS,GFH,GE,VEM,VSM,A0
*) ,A1,A2,A3,A4,SD
C      DOUBLE PRECISION DMIN,TDX,VDX,VEX,D,CHIMIN,R,VSN,TS1,TS2,GFL,DL1,D
*) L2,TENT
C      DOUBLE PRECISION B0,B1,B2,B3,B4,HEB,HEX,DIFFA,CHIHE,HET,CHIMH,HES,
*) SDH
C      DOUBLE PRECISION DET,AA,BB,CC,CH1,CH2,T1,TXD,VXD,AX,BX,CX,DX,EX,FX
*) ,GX,HX,XIX,XJX,XX,XLX,XX
C      DOUBLE PRECISION ZVS,ZVO,ZVDO,ZAO,ZAA,ZA,ZVD,ZV1,ZV2,ZC1,ZC2,ZC,
*) ZHE15,ZEPS1,ZEPS2,ZHE21,ZVE
C      DOUBLE PRECISION PM1,PM2,PVD1,PVD2,PPS1,PPS2,PVS1,PVS2,PTD1,PTD2
*) ,PTS1,PTS2,PV,MM,PGAM1,PGAM2
C      DOUBLE PRECISION MVD1,MVD2,MPS1,MPS2,MVS1,MVS2,MTD1,MTD2,MTS1,
*) MTS2,HAF1,HAF2,PHEX,R12,MSI2,MSI1,MVDM
C      CHARACTER*1 LABEL(60)
C      READ (5,12) (LABEL(I),I=1,60)
12   FORMAT (60A1)
C      WRITE (6,10) (LABEL(I),I=1,60)
10   FORMAT(/T10,60A1)
C      WRITE (6,9)
9     FORMAT(T8,60(' '*))
C      READ (5,*)T
C      READ (5,*) RHO1,RHO2,MW1,MW2,ALPH1,ALPH2,BET1,BET2
C      READ (5,*) A0,A1,A2,A3,A4
C      READ (5,*) B0,B1,B2,B3,B4
C      READ (5,*) PM1,PM2
C      WRITE(6,112)
112  FORMAT(/T5,'INPUT DATA:',/)
C      WRITE(6,121)T
C      WRITE(6,122)RHO1,RHO2
C      WRITE(6,123)MW1,MW2
C      WRITE(6,124)ALPH1,ALPH2
C      WRITE(6,125)BET1,BET2
C      WRITE(6,120)A0,A1,A2,A3,A4
C      WRITE(6,198)B0,B1,B2,B3,B4
C      WRITE (6,119) PM1,PM2
C      WRITE(6,812)
812  FORMAT (/T10,60(' '*))
119  FORMAT (/T8,'M1 =' ,F9.5,5X,'M2 =' ,F9.5,5X,'I.E. THE ENERGY/VOL.
*) EXP.(POLLIN & VRIED THEORY)')
120  FORMAT (/T5,'A0=' ,F10.5,3X,'A1=' ,F10.5,3X,'A2=' ,F10.5,3X,'A3=' ,
```

```

*F10.5,3X,'A4=',F9.5,'----- CC/MOL.---(VE).')
121  FORMAT (/T8,'TEMPERATURE=',F7.3,'K')
122  FORMAT (/T8,'DENSITY OF LIQ.1=',F9.7,'G/CC',3X,'DENSITY OF LIQ.2='
*,F9.7,'G/CC')
123  FORMAT (/T8,'MW1=',F7.3,5X,'MW2=',F7.3)
198  FORMAT (/T5,'B0=',F11.5,2X,'B1=',F11.5,2X,'B2=',F11.5,2X,'B3=',F11
*.5,2X,'B4=',F11.5,'.....J/MCL.---(HE).')
124  FORMAT (/T8,'THERM.EXP.COEFFT.1=',G13.6,'/K',3X,'THERM.EXP.COEFFT.
*2=',G13.6,'/K')
125  FORMAT (/T8,'COMPRESS.1=',G13.6,'/PA',3X,'COMPRESS.2=',G13.6,'/PA'
*)
V1=MW1/RHO1
V2=MW2/RHO2
VD1=((1+((4./3)*ALPH1*T))/(1+(ALPH1*T)))**3
VD2=((1+((4./3)*ALPH2*T))/(1+(ALPH2*T)))**3
VS1=V1/VD1
VS2=V2/VD2
GAM1=ALPH1/BET1
GAM2=ALPH2/BET2
P1=GAM1*T*(VD1**2)
P2=GAM2*T*(VD2**2)
TD1=((VD1**(1./3.))-1)/(VD1**(4./3.))
TD2=((VD2**(1./3.))-1)/(VD2**(4./3.))
TS1=T/TD1
TS2=T/TD2
RATR=VS1/VS2
RATS=(VS2/VS1)**(1./3.)
WRITE(6,38) V1,V2
WRITE(6,39) VD1,VD2
WRITE(6,40) VS1,VS2
WRITE(6,41) GAM1,GAM2
WRITE(6,42) P1,P2
WRITE(6,43) TD1,TD2
WRITE(6,772) TS1,TS2
772  FORMAT(/T2,'THE CHARACTERISTIC TEMPERATURES ARE...T*1=',F9.2,'K',
*3X,'AND T*2=',F9.2,'K')
WRITE(6,555)
555  FORMAT(/T2,'IN THE FLORY NOTATION THE RATIOS R1/R2 AND S1/S2 ARE :
*....')
WRITE(6,44) RATR
WRITE(6,45) RATS
38  FORMAT(/T2,'MOLAR VOLUME 1 =',F7.3,T35,'MOLAR VOLUME 2= ',F7.3,' -
*-----CC/MOL')
39  FORMAT(/T2,'RED.VOL.1(VD1)= ',F9.6,T35,'RED.VOL.2(VD2)= ',F9.6)
40  FORMAT(/T2,'V*1=',F7.3,T35,'V*2=',F7.3,' ---CC/MOL, ---WHERE V* IS
* THE HARD CORE MOLAR VOLUME')
41  FORMAT(/T2,'GAMMA 1 =',G12.5,T35,'GAMMA 2 =',G12.5,' ----PA/K---I.
*E. THE THERMAL PRESSURE COEFFTS.')
42  FORMAT(/T2,'CHARACTERISTIC PRESSURE 1 =',G13.6,T50,'CHARACT,PRESSU
*RE 2 =',G13.6,' --- PA')
43  FORMAT(/T2,'TD1 =',F11.9,T35,'TD2 =',F11.9,3X,'....I.E. THE REDUCE
*D TEMPERATURES.')
44  FORMAT(/T2,'R1/R2 = ',F5.3,3X,'...THE RATIO OF THE RESPECTIVE NO.
* OF SEGMENTS IN THE RESP. MOLECS.')
45  FORMAT(/T2,'S1/S2 = ',F5.3,3X,'...THE RATIO OF SURFACE SITES PER S
*EGMENT FOR RESPECTIVE MOLECS.')
CHI=P1*((1-(RATS**(1./2.))*((P2/P1)**(1./2.)))**2)
WRITE (6,46) CHI
46  FORMAT(/T2,'THE CHI VALUE OBTAINED USING THE BERTHELOT EQN. IS ',G
*12.5,'JOULES/CUBIC METRE *****.')
WRITE (6,47)
47  FORMAT(/T2,'IN WHAT FOLLOWS X1 REFERS TO THE MOLE FRACTION OF LIQ.
*1')
WRITE(6,666)

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666  FORMAT(T2,'(PSI IS THE SEGMENT FRACTION, AND THETA IS THE SITE FRA
*CTION.)')
DO 66 I=1,99
X1(I)=I*0.01
PSI2(I)=(1-X1(I))/((1-X1(I))+(X1(I)*RATR))
PSI1(I)=1-PSI2(I)
THETA2(I)=PSI2(I)/((RATS*PSI1(I))+PSI2(I))
THETA1(I)=1-THETA2(I)
VDO(I)=(PSI1(I)*VD1)+(PSI2(I)*VD2)
TDO(I)=((VDO(I)**(1./3.))-1)/(VDO(I)**(4./3.))
TD(I)=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P
*2)-(PSI1(I)*THETA2(I)*CHI))
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 1000
GOTO 66
1000 WRITE(6,48)X1(I),PSI1(I),THETA1(I)
48  FORMAT(T2,'X1=',F3.1,4X,'PSI1=',F5.4,4X,'THETA1=',F5.4)
66  CONTINUE
WRITE (6,30)
30  FORMAT(/T2,'THE REDUCED PARAMETERS FOR THE FLORY EQUATION OF STATE
* ARE --')
WRITE(6,31)
31  FORMAT(T2,'(WHERE D IMPLIES DASH(-) AND O IMPLIES SUPERScript O IN
* THE FLORY NOTATION.)')
I=10
DO 67 II=1,9
WRITE (6,49)X1(I),VDO(I),TDO(I),TD(I)
49  FORMAT(T2,'X1=',F3.1,3X,'VDO=',G13.6,3X,'TDO=',F11.9,3X,'TD(BERT.)
*=',F11.9)
I=I+10
67  CONTINUE
WRITE (6,50)
50  FORMAT(/T2,'USING THE BERTHELOT CHI VALUE ABOVE, THE FOLLOWING ARE
* CALCULATED:')
WRITE (6,2)
2  FORMAT(T2,'THE THEORETICAL REDUCED EXCESS VOLUME :-.....VDE')
WRITE (6,3)
3  FORMAT(T2,'THE THEORETICAL MOLAR EXCESS VOLUME:-...VE(FL)..I.E. US
*ING CHI FROM THE BERTHELOT EQN.')
WRITE (6,4)
4  FORMAT(T2,'VE(BERTHELOT) IS THEN COMPARED TO THE EXPERIMENTAL MOLA
*R EXCESS VOLUME (VEXP)')
D=0.00000
DO 68 I=1,99
VDE(I)=((VDO(I)**(7./3.))/((4./3.)-(VDO(I)**(1./3.))))*(TD(I)-TDO(
*I))
VE=((X1(I)*VS1)+((1-X1(I))*VS2))*VDE(I)
VEXP(I)=X1(I)*(1-X1(I))*(A0+(A1*(1-2*X1(I)))+(A2*((1-2*X1(I))**2))
*+(A3*((1-2*X1(I))**3)))+(A4*((1-2*X1(I))**4)))
DIFF=VEXP(I)-VE
D=D+(DIFF*DIFF)
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 1001
GOTO 68
1001 WRITE (6,51)X1(I),VDE(I),VE,VEXP(I),DIFF
51  FORMAT (T2,'X1=',F3.1,2X,'VDE=',F10.8,2X,'VE(BERT.)=',F8.6,'CC/MOL
*',2X,'VEXP=',F8.6,'CC/MOL',2X,'VEXP-VE(BERT.)=',F8.6,'CC/MOL')
68  CONTINUE
SD=(D/98.0)**0.5
WRITE (6,821)SD
821  FORMAT(/T2,'THE STD. DEVIATION HERE IS S=',G12.6)
WRITE (6,199)
199  FORMAT (/T2,'USING CHI(BERT.) THE EXC. ENTHALPY IS COMPUTED & COMP
*ARED TO THE EXPERIMENTAL VALUES.')

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193  WRITE (6,193)
      FORMAT(T2,60(' -'))
      D=0.000000
      VSM=VS1*1.0E-6
      VSN=VS2*1.0E-6
      DO 200 I=1,99
        VD=VDO(I)+VDE(I)
        HEB=(X1(I)*VSM*P1*((1./VD1)-(1./VD)))+(1-X1(I))*P2*VSN*((1./VD2)-
        *(1./VD)))+(X1(I)*VSM*THETA2(I)*CHI)/VD)
        HEX(I)=X1(I)*(1-X1(I))*(B0+(B1*(1-2*X1(I)))+(B2*((1-2*X1(I))**2))+
        *(B3*((1-2*X1(I))**3))+(B4*((1-2*X1(I))**4)))
        DIFFA=HEX(I)-HEB
        D=D+(DIFFA*DIFFA)
        X=FLOAT(I)
        IF ((X/10.0).EQ.(I/10)) GOTO 1002
        GOTO 200
1002  WRITE (6,201)X1(I),HEB,HEX(I),DIFFA
201   FORMAT(T2,'X1=',F3.1,2X,'HE(BERT.)=',G13.6,3X,'HE(EXP.)=',G13.6,3X
      *, 'HE(BERT.)-HE(EXP.)=',G13.6,'.....J/MOL.')
200   CONTINUE
      SD=(D/98.0)**0.5
      WRITE (6,202)SD
202   FORMAT(/T2,'THE STD.DEVIATION HERE IS : ',G13.6,'...J/MOL.')
      WRITE (6,195)
195   FORMAT(/T3,60('*'))
      WRITE (6,194)
194   FORMAT (/T3,'NB.-IN THE ABOVE CALCULATIONS OF HE(BERT.) & VE(BERT.
      *) NO ADJUSTABLE PARAMETERS WERE USED')
      WRITE (6,192)
192   FORMAT(/T3,60('*'))
      WRITE (6,74)
74    FORMAT(/T2,'THE FOLLOWING CHIEX VALUES ARE THE ADJUSTED INTERACTIO
      *N PARAMETERS (IN JOULES/CUBIC METRE) OBTAINED FROM VE(EXP.).')
      DO 69 I=1,99
        VDEX(I)=VEXP(I)/((X1(I)*VS1)+((1-X1(I))*VS2))
        PP1=PSI1(I)*P1
        PP2=PSI2(I)*P2
        Q=TDO(I)+(VDEX(I)*((4./3.)-(VDO(I)**(1./3.)))/(VDO(I)**(7./3.)))
        CHIEX(I)=(PP1+PP2-(PP1*TD1+PP2*TD2)/Q)/(PSI1(I)*THETA2(I))
        X=FLOAT(I)
        IF ((X/10.0).EQ.(I/10)) GOTO 1003
        GOTO 69
1003  WRITE(6,75)X1(I),CHIEX(I)
75    FORMAT(T2,'X1=',F3.1,5X,'CHIEX=',G12.5)
69    CONTINUE
      DMIN=1.0E10
      DO 72 M=1,99
        DO 70 I=1,99
          TDX=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P2)
          *- (PSI1(I)*THETA2(I)*CHIEX(M)))
          VDX=((VDO(I)**(7./3.))/((4./3.)-(VDO(I)**(1./3.))))*(TDX-TDO(I))
          VEX(I)=((X1(I)*VS1)+((1-X1(I))*VS2))*VDX
70    CONTINUE
          D=0.0000000
          DO 71 J=1,99
            D=D+((VEXP(J)-VEX(J))*(VEXP(J)-VEX(J)))
71    CONTINUE
            IF (D.GE.DMIN) GO TO 737
            CHIMIN=CHIEX(M)
            DMIN=D
737   CONTINUE
72    CONTINUE
          SD=(DMIN/98.0)**0.5
          WRITE (6,76)CHIMIN

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76  FORMAT(/T2,'THE MINIMIZING CHI VALUE, FROM VE(EXP.) , IS ',G12.5,'
* JOULES/CUBIC METRE*****')
WRITE(6,99)
99  FORMAT(/T2,'USING THIS CHI(MIN), OR CHI(VE), VALUE, THE THEORETICA
*L EXC.VOLS.,VE, ARE CALCULATED AGAIN')
DO 671 I=1,99
  TD(I)=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P
* 2)-(PSI1(I)*THETA2(I)*CHIMIN))
  VDE(I)=(VDO(I)**(7./3.))/(4./3.-(VDO(I)**(1./3.)))*(TD(I)-TDO(
* I))
  VE=((X1(I)*VS1)+((1-X1(I))*VS2))*VDE(I)
  D=VEXP(I)-VE
  X=FLOAT(I)
  IF ((X/10.0).EQ.(I/10)) GOTO 1004
  GOTO 671
1004 WRITE(6,77) X1(I),VDE(I),VE,VEXP(I),D
77  FORMAT(T2,'X1=',F3.1,3X,'VDE=',F10.8,3X,'VE(FLORY)=' ,F8.6,'CC/MOL'
* ,3X,'VEXP=' ,F8.6,'CC/MOL',3X,'VEXP-VE(FL.)=' ,G12.6,'CC/MOL')
671  CONTINUE
WRITE(6,823)SD
823  FORMAT(/T2,'THE STD. DEVIATION HERE IS S=' ,G12.6)
WRITE (6,203)
203  FORMAT(/T2,'THE FOLLOWING CHI(HE) VALUES ARE THE ADJUSTED INTERACT
*ION PARAMETERS (IN J/CUBIC METRES) OBTAINED FROM HE(EXP.).')
DO 204 I=1,99
  AX=X1(I)*P1*VSM
  BX=(1.-X1(I))*P2*VSN
  CX=X1(I)*VSM*THETA2(I)
  DX=(AX/VD1)+(BX/VD2)
  EX=AX+BX
  FX=HEX(I)-DX
  GX=(VDO(I)**(7./3.))/(4./3.-(VDO(I)**(1./3.)))
  HX=GX*TDO(I)
  XIX=(VDO(I)-HX)
  XJX=(PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2)
  XKX=(PSI1(I)*P1)+(PSI2(I)*P2)
  XLX=GX*XJX
  XMX=(XIX*XKX)+XLX
  AA=CX*PSI1(I)*THETA2(I)
  BB=(FX*XIX*PSI1(I)*THETA2(I))+(CX*XKX)+(EX*PSI1(I)*THETA2(I))
  CC=(EX*XKX)+(FX*XMX)
  DET=(BB**2.0)-(4.0*AA*CC)
  IF (DET.LT.1.E-20) GO TO 903
  CH1=(BB+(DET**0.5))/(2.0*AA)
  CH2=(BB-(DET**0.5))/(2.0*AA)
  T1=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P2)-
* (PSI1(I)*THETA2(I)*CH1))
  IF (T1.LT.1.E-20)GO TO 904
  CHIHE(I)=CH1
  GO TO 1111
904  CHIHE(I)=CH2
  GO TO 1111
903  WRITE (6,905)
905  FORMAT(T2,'THE SOLUTION FOR CHI(HE) HAS A NON-REAL VALUE.')
1111 X=FLOAT(I)
  IF ((X/10.0).EQ.(I/10)) GOTO 1010
  GOTO 204
1010 WRITE (6,205)X1(I),CHIHE(I)
205  FORMAT(T2,'X1=',F3.1,5X,'CHI(HE)=' ,G12.5)
204  CONTINUE
  DMIN=1.0E10
  DO 206 M=1,99
  DO 207 I=1,99
    TXD=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P2)
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* -(PSI1(I)*THETA2(I)*CHIE(M)))
VXD=VDO(I)+(((VDO(I)**(7./3.))* (TXD-TDO(I)))/((4./3.)-(VDO(I)**(1.
* /3.))))
HET(I)=(X1(I)*VSM*P1*((1./VD1)-(1./VXD))+((1-X1(I))*P2*VSN*((1./V
* D2)-(1./VXD)))+(X1(I)*VSM*THETA2(I)*CHIE(M))/VXD)
207 CONTINUE
D=0.000000
DO 208 J=1,99
D=D+((HEX(J)-HET(J))**2)
208 CONTINUE
IF (D.GE.DMIN) GO TO 209
CHIH=CHIE(M)
DMIN=D
209 CONTINUE
206 CONTINUE
SDH=(DMIN/98.0)**0.5
WRITE (6,210) CHIH
210 FORMAT (/T2,'THE MINIMIZING CHI(HE) VALUE IS ',G12.5,'JOULES/CUBIC
* METRE *****')
WRITE (6,211)
211 FORMAT(/T2,'USING THIS MINIMIZING CHI(HE) VALUE THE HE IS COMPUTED
* FROM THE FLORY THEORY')
DO 212 I=1,99
TXD=((PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2))/((PSI1(I)*P1)+(PSI2(I)*P2)
* -(PSI1(I)*THETA2(I)*CHIH))
VXD=VDO(I)+(((VDO(I)**(7./3.))* (TXD-TDO(I)))/((4./3.)-(VDO(I)**(1.
* /3.))))
HES=(X1(I)*VSM*P1*((1./VD1)-(1./VXD))+((1-X1(I))*P2*VSN*((1./VD2)
* -(1./VXD)))+(X1(I)*VSM*THETA2(I)*CHIH)/VXD)
D=HEX(I)-HES
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 1005
GOTO 212
1005 WRITE (6,213) X1(I),HES,HEX(I),D
213 FORMAT (T2,'X1=',F3.1,3X,'HE(FLORY)=' ,G13.6,3X,'HE(EXP.)=' ,G13.6,3
* X,'HE(EXP.)-HE(FLORY)=' ,G13.6,'....J/MOL')
212 CONTINUE
WRITE (6,214) SDH
214 FORMAT(/T2,'THE STD.DEVIATION HERE IS S=' ,G13.6,2X,'J/MOL')
WRITE (6,215)
215 FORMAT(/T2,'USING CHI(VE) AND VE(EXP) THE THEORETICAL FLORY EXCESS
* ENTHALPY IS PREDICTED')
D=0.00000
DO 216 I=1,99
VEM=VEXP(I)*1.0E-6
VD=VDO(I)+VDEX(I)
Z=X1(I)*VSM*PSI2(I)*((VD1-VD2)/VDO(I))*((P2/VD2)-(P1/VD1))
W=(VEM/(VDO(I)**2))* (PSI1(I)*P1+PSI2(I)*P2)
HE=((X1(I)*VSM*THETA2(I)*CHIMIN)/VD)+Z+W
DIFF=HEX(I)-HE
D=D+(DIFF*DIFF)
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 1006
GOTO 216
1006 WRITE (6,217) X1(I),HE,HEX(I),DIFF
217 FORMAT(T2,'X1=',F3.1,2X,'HE(PREDICTED)=' ,G13.6,3X,'HE(EXP.)=' ,G13.
* 6,3X,'DIFFERENCE =' ,G13.6,2X,'....J/MOL')
216 CONTINUE
SD=(D/98.0)**0.5
WRITE(6,218) SD
218 FORMAT(/T2,'THE STD.DEVIATION HERE IS S = ' ,G13.6)
WRITE (6,219)
219 FORMAT(/T2,'USING THE CHI(HE) VALUE THE THEORETICAL FLORY EXCESS V
*OLUME IS PREDICTED.')
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D=0.000000
DO 220 I=1,99
TD(I)=( (PSI1(I)*P1*TD1)+(PSI2(I)*P2*TD2)) / ((PSI1(I)*P1)+(PSI2(I)*P
* 2)-(PSI1(I)*THETA2(I)*CHIM))
VDE(I)=( (VDO(I)**(7./3.)) / ((4./3.)-(VDO(I)**(1./3.))) ) * (TD(I)-TDO(
* I))
VE=( (X1(I)*VS1)+((1-X1(I))*VS2)) * VDE(I)
DIFF=VEXP(I)-VE
D=D+(DIFF*DIFF)
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 1007
GOTO 220
1007 WRITE (6,221) X1(I),VE,VEXP(I),DIFF
221  FORMAT(T2,'X1=',F3.1,2X,'VE(PREDICTED) = ',G12.6,3X,'VE(EXP.) = ',
* F8.6,3X,'DIFFERENCE = ',G12.6,'...CC/MOL.')
220  CONTINUE
SD=(D/98.0)**0.5
WRITE (6,222) SD
222  FORMAT(/T2,'THE STD.DEVIATION HERE IS S = ',G12.6)
WRITE (6,901)
901  FORMAT(/T3,60(' '))
WRITE (6,223)
223  FORMAT(/T2,'USING THE EXPERIMENTAL VE AND HE A VALUE FOR THE EXCES
*S GIBBS FUNCTION IS PREDICTED.')
WRITE (6,224)
224  FORMAT(T2,'THIS IS CALCULATED USING TWO THEORIES :')
WRITE (6,225)
225  FORMAT(T2,' 1.- A FLORY EQN. GIVES THE EXC.ENTROPY, SE,THEN : GE=H
*E-TSE (NB. KNOWN TO GIVE POOR RESULTS.)')
WRITE (6,226)
226  FORMAT (T2,' 2.- AN EQN.DERIVED BY E.LIEBERMANN GIVES A BETTER APP
*ROXIMATION --....GE(LIE.)')
VEM=VEXP(50)*1.0E-6
VD=VDO(50)+VDEX(50)
DL1=(DLOG((VD1**(1./3.))-1)/((VD**(1./3.))-1))
DL2=(DLOG((VD2**(1./3.))-1)/((VD**(1./3.))-1))
TENT=(3*T*((X1(50)*P1*VSM)/TS1)*DL1+(((1-X1(50))*P2*VSN)
*/TS2)*DL2))*(-1.0)
GFL=(-1.0)*TENT)+HEX(50)
PHI1=X1(50)/(X1(50)+(1-X1(50))*(V2/V1))
PHI2=1-PHI1
ALM=ALPH1*PHI1+ALPH2*PHI2
BETM=BET1*PHI1+BET2*PHI2
R=8.3143
GS=((R*T*(BET1-BET2)*(PHI1-X1(50)))-VEM+((BETM*HEX(50))/(ALM
*T)))/((BETM*1.5)+(BETM/(ALM*T)))
GFH=(X1(50)*(DLOG(PHI1/X1(50)))+(1-X1(50))*(DLOG(PHI2/(1-X1(50)
*))))
GE=GS+(R*T*GFH)
WRITE (6,227)
227  FORMAT(/T2,'AT EQUIMOLAR CONCENTRATES THESE ARE THE RESPETIVE VALU
*ES : ')
WRITE (6,228) TENT,GFL,GE
228  FORMAT(/T2,'TSE = ',G13.6,5X,'GE(FLORY) = ',G13.6,5X,'GE(LIB.)
*= ',G13.6,'.....JOULES/MOLE.')
WRITE (6,902)
902  FORMAT(T2,60(' '))
WRITE (6,300)
300  FORMAT (/T2,60('#'))
WRITE (6,301)
301  FORMAT (/T2,'THE VARIATION OF THE FLORY EQN. DERIVED BY LIEBERMANN
* FOR HE & VE ARE NOW TESTED.')
WRITE (6,302)
302  FORMAT (T2,'THESE EQUATIONS ARE FREE OF EMPIRICAL PARAMETERS.')
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303  WRITE (6,303)
      FORMAT (/T2,'VALUES ARE CALCULATED AT EQUIMOLAR COMPOSITIONS.')
```

$$ZVS = (VS1 + VS2) / 2.0$$

$$ZVO = (V1 + V2) / 2.0$$

$$ZVDO = ZVO / ZVS$$

$$ZAO = (3. * ((ZVDO ** (1./3.)) - 1.)) / (T * (4. - (3. * (ZVDO ** (1./3.)))))$$

$$ZAA = ((ALPH1 * V1 / ZVO) + (ALPH2 * V2 / ZVO)) / 2.$$

$$ZA = (2. * ZAO) - ZAA$$

$$ZVD = ((3. + (4. * ZA * T)) / (3. * (1. + (ZA * T)))) ** 3.$$

$$ZV1 = V1 * 1.0E-6$$

$$ZV2 = V2 * 1.0E-6$$

$$ZC1 = (ALPH1 * T * GAM1 * ZV1 / R) / (3. + (4. * ALPH1 * T))$$

$$ZC2 = (ALPH2 * T * GAM2 * ZV2 / R) / (3. + (4. * ALPH2 * T))$$

$$ZC = (ZC1 + ZC2) / 2.$$

$$ZHE15 = T * (((GAM1 * ZV1) + (GAM2 * ZV2)) / 2.) - (R * ZC / (1. - (ZVD ** (-1./3. * .))))$$

$$ZEPS1 = ZC1 / (ZC1 + ZC2)$$

$$ZEPS2 = ZC2 / (ZC1 + ZC2)$$

$$ZHE21 = R * T * ((ZEPS1 / (1. - (VD1 ** (-1./3.)))) + (ZEPS2 / (1. - (VD2 ** (-1./3.))))) - (1. / (1. - (ZVD ** (-1./3.))))$$

$$ZVE = (ZVD * ZVS) - ZVO$$

```

      WRITE (6,304)
304  FORMAT (/T2,'THE CORRESPONDING DEGREE OF FREEDOM CONSTANTS ARE
      * :')
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```

      WRITE (6,305) ZC1,ZC2,ZC
305  FORMAT (T2,'C1=' ,G13.6,6X,'C2=' ,G13.6,6X,'C MIXT.=' ,G13.6)
      WRITE (6,306)
306  FORMAT (/T2,'THE CALCULATED EXCESS VOLUME IS : .....')
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```

      WRITE (6,307) ZVE,VEXP(50)
307  FORMAT (T2,'VE=' ,G12.6,6X,'VE (EXP.) =' ,G12.6,2X,' .....
      *CC/MOL.')
```

```

      WRITE (6,308)
308  FORMAT (/T2,'THE CALCULATED HE OBTAINED FROM EQNS. 15 & 21 RESP
      * . ARE : .....')
```

```

      WRITE (6,309) ZHE15,ZHE21,HEX(50)
309  FORMAT (T2,'HE(15) =' ,G13.6,6X,'HE(21) =' ,G13.6,6X,'HE (EXP.) =
      * ,G13.6,2X,' .....J/MOL.')
```

```

      WRITE (6,310)
310  FORMAT (/T2,60('#'))
      WRITE (6,1103)
1103  FORMAT (/T2,'THE THEORY OF POLLIN & VRIED IS NOW TESTED.')
```

```

      WRITE (6,1104)
1104  FORMAT (T2,'THIS THEORY PREDICTS HE FROM VE.')
```

```

      WRITE (6,1105)
1105  FORMAT (T2,'M IS THE VOLUME FRACTION AVERAGED MIXTURE ENERGY/VO
      *L. EXPONENT.')
```

$$IF (PM1.LE.0.0) GOTO 999$$

$$PVD1 = (((ALPH1 * T) / (3. * (1. + (PM1 * ALPH1 * T)))) + 1.) ** 3.0$$

$$PVD2 = (((ALPH2 * T) / (3. * (1. + (PM2 * ALPH2 * T)))) + 1.) ** 3.0$$

$$PGAM1 = GAM1 * 1.0E-6$$

$$PGAM2 = GAM2 * 1.0E-6$$

$$PPS1 = (PGAM1 * (PVD1 ** (PM1 + 1.)) * T) / PM1$$

$$PPS2 = (PGAM2 * (PVD2 ** (PM2 + 1.)) * T) / PM2$$

$$PVS1 = V1 / PVD1$$

$$PVS2 = V2 / PVD2$$

$$PTD1 = (((PVD1 ** (1./3.)) - 1.) / (PVD1 ** (PM1 + (1./3.)))) * PM1$$

$$PTD2 = (((PVD2 ** (1./3.)) - 1.) / (PVD2 ** (PM2 + (1./3.)))) * PM2$$

$$PTS1 = T / PTD1$$

$$PTS2 = T / PTD2$$

$$D = 0.0$$

```

      DO 1100 I=1,99
      PV = (X1(I) * V1) + ((1. - X1(I)) * V2) + VEXP(I)
      MM = ((X1(I) * PM1 * V1) + ((1. - X1(I)) * PM2 * V2)) / PV
      MVD1 = (((ALPH1 * T) / (3. * (1. + (MM * ALPH1 * T)))) + 1.) ** 3.0
```


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```
MVD2=(( (ALPH2*T) / (3.*(1.+(MM*ALPH2*T))) )+1.)**3.0
MPS1=(PGAM1*(MVD1**(MM+1.))*T)/MM
MPS2=(PGAM2*(MVD2**(MM+1.))*T)/MM
MVS1=V1/MVD1
MVS2=V2/MVD2
MTD1=(( (MVD1**(1./3.))-1.) / (MVD1**(MM+(1./3.))) ) *MM
MTD2=(( (MVD2**(1./3.))-1.) / (MVD2**(MM+(1./3.))) ) *MM
R12=MVS1/MVS2
MSI2=(1.-X1(I)) / ((1.-X1(I))+(X1(I)*R12))
MSI1=1.-MSI2
MVDM=((MSI1*MVD1)+(MSI2*MVD2))+(VEXP(I)/((X1(I)*MVS1)+((1.-X1(I)
*) *MVS2)))
MTS1=T/MTD1
MTS2=T/MTD2
HAF1=(( (X1(I)*PPS1*PVS1) / (PVD1**PM1)) + ((1.-X1(I))*PPS2*PVS2) / (
*PVD2**PM2))
HAF2=(( (T*(MVDM**(1./3.))) / (MM*((MVDM**(1./3.))-1.))) * ((X1(I)*M
*PS1*MVS1)/MTS1) + ((1.-X1(I))*MPS2*MVS2)/MTS2)
PHEX=HAF1-HAF2
DIFF=HEX(I)-PHEX
D=D+(DIFF*DIFF)
X=FLOAT(I)
IF ((X/10.0).EQ.(I/10)) GOTO 3333
GOTO 1100
3333 WRITE (6,1101) X1(I),MM,HEX(I),PHEX,DIFF
1101 FORMAT (T2,'X1=',F3.1,2X,'M=',F5.3,2X,'HE(EXP)=' ,G13.6,2X,'HE(C
*ALC.)=' ,G13.6,2X,'DIFF=' ,G13.6,'...J/MOL')
1100 CONTINUE
SD=(D/98.0)**0.5
WRITE (6,1102) SD
1102 FORMAT (/T2,'THE STD. DEVIATION IS S = ' ,G12.6,'.....J/MOL')
WRITE (6,1109)
1109 FORMAT (/T2,60('#'))
999 CONTINUE
STOP
END
```

Appendix C

Appendix C3. A GWBASIC programme to calculate the apparent molar volumes from density data.

```
1 REM *****
2 REM THE FOLLOWING PROGRAM IS WRITTEN IN GWBASIC FOR ANY IBM PC 100%
3 REM COMPATIBLE WITH IBM PERSONAL COMPUTERS.
4 REM THIS PROGRAM CALCULATES EXCESS VOLUMES OF SOLUTIONS
5 REM CONTAINING 1 SOLUTE AND 1 SOLVENT, FROM DENSITY
6 REM MEASUREMENTS, USING AN ANTON PAAR DENSITOMETER.
7 REM
8 REM WRITTEN BY J.D. MERCER-CHALMERS AND S.J. TAYLOR,
9 REM RHODES UNIVERSITY, GRAHAMSTOWN.
10 REM *****
19 CLS
20 PRINT "MAIN MENU "
30 PRINT
40 PRINT
50 PRINT "CHOOSE FROM ONE OF THE FOLLOWING :-"
60 PRINT
70 PRINT "A. INPUT THE DATA FOR A NEW RUN."
80 PRINT "B. EDIT THE OLD RUN"
90 PRINT "C. PRINT OUT THE RUN JUST COMPLETED"
100 PRINT "D. SAVE THE RUN"
110 PRINT "E. LOAD A PREVIOUS RUN"
120 PRINT "F. RUN THE RUN THAT IS IN MEMORY."
121 PRINT "G. PRINT A FILE FROM THE DISK."
130 PRINT "Q. QUIT"
140 INPUT ANSS$
150 IF ANSS$ = "A" THEN GOSUB 230
160 IF ANSS$ = "B" THEN GOSUB 900
170 IF ANSS$ = "C" THEN GOSUB 660
180 IF ANSS$ = "D" THEN GOSUB 1540
190 IF ANSS$ = "E" THEN GOSUB 3500
200 IF ANSS$ = "F" THEN GOSUB 370
201 IF ANSS$ = "G" THEN GOSUB 3000
210 IF ANSS$ = "Q" THEN END
220 GOTO 10
230 CLS
240 DAIR = .0011845
250 DWATER = .99707
251 REM *****
252 REM INPUT CONSTANTS
253 REM *****
260 INPUT "ENTER DATE OF RUN ";RDATES
270 INPUT "ENTER TIME OF RUN ";RTIME$
280 INPUT "INPUT TAU WATER VALUE AND TEMPERATURE";TWATER,TTWATER
290 INPUT "INPUT TAU AIR AND TEMP";TAIR,TTAIR
300 INPUT "INPUT TAU SOLUTION AND TEMP";TSOLUTION,TTOLUTION
310 INPUT "INPUT TAU SOLVENT AND TEMP ";TSOLVENT,TTOLVENT
320 INPUT "INPUT MOLECULAR MASS OF SOLUTE";MMSOLUTE
330 INPUT "INPUT MASS OF SOLUTE";MSOLUTE
340 INPUT "INPUT MASS OF SOLVENT";MSOLVENT
350 INPUT "ENTER LEFT AND RIGHT ROOM TEMPERATURES ";LROOMT,RROOMT
351 GOSUB 900
352 GOSUB 370
360 RETURN
361 REM *****
362 REM PERFORM CALCULATIONS
363 REM *****
370 IF (TWATER = 0 ) AND (TTWATER = 0) AND (TAIR = 0) AND (TSOLUTION = 0) AND
SOLVENT = 0) THEN GOTO 651
371 BCONST = ((DWATER - DAIR)/((TWATER * TWATER) - (TAIR * TAIR)))
380 DSOLVENT = BCONST * ((TSOLVENT * TSOLVENT) - (TWATER * TWATER)) + DWATER
390 DSOLUTION = BCONST * ((TSOLUTION * TSOLUTION) - (TSOLVENT * TSOLVENT)) +
OLVENT
400 CCONST = (MSOLUTE * DSOLUTION * 1000)/(MMSOLUTE * MSOLVENT)
```

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```
410 V = (MMSOLUTE/DSOLVENT) - ((1000 * (DSOLUTION - DSOLVENT))/(DSOLVENT * CCO
T))
420 CLS
430 PRINT "TAU AIR AND TEMPERATURE      ";TAIR,TTAIR
440 PRINT "TAU WATER AND TEMPERATURE   ";TWATER,TTWATER
450 PRINT "TAU SOLUTION AND TEMPERATURE ";TSOLUTION,TTSOLUTION
460 PRINT "TAU SOLVENT AND TEMPERATURE ";TSOLVENT,TTSOLVENT
470 PRINT
480 PRINT "DENSITY OF SOLVENT           ";DSOLVENT
490 PRINT "DENSITY OF WATER            ";DWATER
500 PRINT "DENSITY OF AIR              ";DAIR
510 PRINT "DENSITY OF SOLUTION         "; DSOLUTION
520 PRINT
530 PRINT "MASS OF SOLVENT               ";MSOLVENT
540 PRINT "MASS OF SOLUTE               ";MSOLUTE
550 PRINT "MOLECULAR MASS OF SOLUTE    "; MMSOLUTE
560 PRINT
570 PRINT "B      ";BCONST
580 PRINT "C      ";CCONST
590 PRINT "V      ";V
600 PRINT
610 PRINT "RIGHT AND LEFT HAND ROOM TEMPERATURES ";RROOMT,LROOMT
620 PRINT "TIME AND DATE OF RUN              ";RTIMES,RDATES
621 PRINT "NAME OF RUN                        ";RNAME$
630 PRINT
640 INPUT "PRESS RETURN TO CONTINUE";SS$
650 RETURN
651 PRINT "NO RUN IN MEMORY, PLEASE LOAD ONE ."
652 PRINT : PRINT : INPUT "PRESS RETURN TO CONTINUE";ZZ$
653 RETURN
655 REM *****
656 REM                      PRODUCE OUTPUT
657 REM *****
660 CLS
670 LPRINT "NAME OF RUN              ";RNAME$
690 LPRINT "DATE AND TIME OF RUN ";RDATES,RTIMES
700 LPRINT
710 LPRINT "TAU WATER AND TEMPERATURE   ";TWATER,TTWATER
720 LPRINT "TAU AIR AND TEMPERATURE    ";TAIR,TTAIR
730 LPRINT "TAU SOLUTION AND TEMPERATURE ";TSOLUTION,TTSOLUTION
740 LPRINT "TAU SOLVENT AND TEMPERATURE ";TSOLVENT,TTSOLVENT
750 LPRINT
760 LPRINT "B = ";BCONST
770 LPRINT "C = ";CCONST
780 LPRINT "V = ";V
790 LPRINT
800 LPRINT "DENSITY OF SOLVENT           ";DSOLVENT
810 LPRINT "DENSITY OF WATER            ";DWATER
820 LPRINT "DENSITY OF AIR              ";DAIR
830 LPRINT "DENSITY OF SOLUTION         ";DSOLUTION
840 LPRINT
850 LPRINT "MOLECULAR MASS OF SOLUTE    ";MMSOLUTE
860 LPRINT "MASS OF SOLVENT            ";MSOLVENT
870 LPRINT "MASS OF SOLUTE             ";MSOLUTE
871 LPRINT
880 LPRINT "LEFT AND RIGHT HAND ROOM TEMPERATURES (C) ";LROOMT,RROOMT
881 LPRINT : LPRINT : LPRINT
890 RETURN
900 CLS
910 PRINT "IF YOU WISH TO CHANGE ANY OF THE FOLLOWING TYPE IN THE CORRESPONDIN
LETTER."
920 PRINT
930 PRINT "A> DENSITY OF AIR              ";DAIR
940 PRINT "B> DENSITY OF WATER            ";DWATER
```

```

950 PRINT "C> TAU OF WATER AND TEMPERATURE ";TWATER,TTWATER
960 PRINT "D> TAU OF AIR AND TEMPERATURE ";TAIR,TTAIR
970 PRINT "E> TAU OF SOLUTION AND TEMPERATURE ";TSOLUTION,TTSOLUTION
980 PRINT "F> TAU OF SOLVENT AND TEMPERATURE ";TSOLVENT,TTSOLVENT
990 PRINT "G> MOLECULAR MASS OF SOLUTE ";MMSOLUTE
1000 PRINT "H> MASS OF SOLUTE ";MSOLUTE
1010 PRINT "I> MASS OF SOLVENT ";MSOLVENT
1020 PRINT "J> TIME AND DATE OF RUN ";RTIME$,RDATE$
1030 PRINT "K> LEFT AND RIGHT HAND ROOM TEMPERATURES ";LRROOMT,RRROOMT
1031 PRINT "L> RUN NAME ";RNAME$
1040 PRINT
1050 PRINT "Q> QUIT THIS EDITOR"
1060 PRINT
1070 INPUT "ENTER YOUR CHOICE ";CC$
1071 CLS
1080 IF CC$ = "A" THEN GOSUB 1270
1090 IF CC$ = "B" THEN GOSUB 1300
1100 IF CC$ = "C" THEN GOSUB 1330
1110 IF CC$ = "D" THEN GOSUB 1360
1120 IF CC$ = "E" THEN GOSUB 1390
1130 IF CC$ = "F" THEN GOSUB 1420
1140 IF CC$ = "G" THEN GOSUB 1450
1150 IF CC$ = "H" THEN GOSUB 1480
1160 IF CC$ = "I" THEN GOSUB 1510
1170 IF CC$ = "J" THEN GOSUB 1210
1180 IF CC$ = "K" THEN GOSUB 1240
1181 IF CC$ = "L" THEN GOSUB 1531
1190 IF CC$ = "Q" THEN RETURN
1200 GOTO 900
1210 INPUT "ENTER NEW DATE AND TIME ";RDATE$,RTIME$
1230 RETURN
1240 INPUT "ENTER NEW LEFT AND RIGHT HAND ROOM TEMPERATURES ";LRROOMT,RRROOMT
1260 CLEAR
1270 INPUT "NEW VALUE OF DENSITY OF AIR";DAIR
1290 RETURN
1300 INPUT "ENTER NEW VALUE FOR DENSITY OF WATER ";DWATER
1320 RETURN
1330 INPUT "ENTER NEW VALUE FOR TAU WATER AND TEMP ";TWATER,TTWATER
1350 RETURN
1360 INPUT "ENTER NEW VALUE FOR THE TAU AIR AND TEMP ";TAIR,TTAIR
1380 RETURN
1390 INPUT "ENTER NEW VALUE FOR TAU SOLUTION AND TEMP ";TSOLUTION,TTSOLUTION
1410 RETURN
1420 INPUT "ENTER NEW VALUE FOR TAU SOLVENT AND TEMP ";TSOLVENT,TTSOLVENT
1440 RETURN
1450 INPUT "ENTER NEW VALUE FOR THE MOLECULAR MASS OF SOLUTE ";MMSOLUTE
1470 RETURN
1480 INPUT "ENTER NEW VALUE FOR THE MASS OF SOLUTE ";MSOLUTE
1500 RETURN
1510 INPUT "ENTER THE NEW VALUE FOR THE MASS OF SOLVENT ";MSOLVENT
1520 RETURN
1531 INPUT "ENTER NEW RUN NAME ";RNAME$
1532 RETURN
1540 CLS
1541 INPUT "ENTER NAME OF FILE DATA IS TO BE STORED IN ";HBS$
1550 OPEN "O",#1,HBS$
1560 PRINT#1, RNAME$
1570 PRINT#1, RDATE$
1580 PRINT#1, RTIME$
1590 PRINT#1, TAIR,TTAIR
1600 PRINT#1, TWATER,TTWATER
1610 PRINT#1, TSOLUTION,TTSOLUTION
1620 PRINT#1, TSOLVENT,TTSOLVENT
1630 PRINT#1, DSOLVENT

```

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```
1640 PRINT#1, DWATER
1650 PRINT#1, DAIR
1660 PRINT#1, DSOLUTION
1670 PRINT#1, MMSOLUTE
1680 PRINT#1, MSOLVENT
1690 PRINT#1, MSOLUTE
1700 PRINT#1, BCONST
1710 PRINT#1, CCONST
1720 PRINT#1, V
1730 PRINT#1, LROOMT, RROOMT
1740 CLOSE #1
1750 RETURN
1760 CLS
1770 INPUT "ENTER THE NAME OF FILE TO BE ACCESSED ";HF$
1780 OPEN "I",#1,HF$
1790 INPUT#1,RNAMES$
1800 INPUT#1,RDATES$
1810 INPUT#1,RTIMES$
1820 INPUT#1,TAIR,TTAIR
1830 INPUT#1,TWATER,TTWATER
1840 INPUT#1,TSOLUTION,TTSOLUTION
1850 INPUT#1,TSOLVENT,TTSOLVENT
1860 INPUT#1,DSOLVENT
1870 INPUT#1,DWATER
1880 INPUT#1,DAIR
1890 INPUT#1,DSOLUTION
1900 INPUT#1,MMSOLUTE
1910 INPUT#1,MSOLVENT
1920 INPUT#1,MSOLUTE
1930 INPUT#1,BCONST
1940 INPUT#1,CCONST
1950 INPUT#1,V
1960 INPUT#1,LROOMT,RROOMT
1970 CLOSE #1
1971 RETURN
1980 CLS
1990 PRINT "FILE NAME           ";HF$
2000 PRINT "RUN NAME             ";RNAMES$
2010 PRINT "DATE AND TIME OF RUN ";RDATES$,RTIMES$
2020 PRINT
2030 PRINT "TAU WATER AND TEMPERATURE ";TWATER,TTWATER
2040 PRINT "TAU AIR AND TEMPERATURE  ";TAIR,TTAIR
2050 PRINT "TAU SOLUTION AND TEMPERATURE ";TSOLUTION,TTSOLUTION
2060 PRINT "TAU SOLVENT AND TEMPERATURE ";TSOLVENT,TTSOLVENT
2070 PRINT
2080 PRINT "DENSITY OF SOLVENT ";DSOLVENT
2090 PRINT "DENSITY OF WATER   ";DWATER
2100 PRINT "DENSITY OF AIR     ";DAIR
2110 PRINT "DENSITY OF SOLUTION ";DSOLUTION
2120 PRINT
2130 PRINT "MOLECULAR MASS OF SOLUTE ";MMSOLUTE
2140 PRINT "MASS SOLVENT            ";MSOLVENT
2150 PRINT "MASS OF SOLUTE         ";MSOLUTE
2160 PRINT
2170 PRINT "B ";BCONST
2180 PRINT "C ";CCONST
2190 PRINT "V ";V
2200 PRINT : PRINT
2210 INPUT "PRESS RETURN TO CONTINUE";AAS
2220 RETURN
3000 CLS
3010 GOSUB 1760
3020 GOSUB 660
3030 RETURN
```

APPENDIX D

Future work

(a) Chloro-substituted benzene + alkanol mixtures

The V_m^E results for these systems could give valuable insight into the Cl-H interaction observed in the H_m^E results reported by Letcher *et al.*^{(103 (b))} Furthermore, the results would serve as a useful comparison for the methyl-substituted benzene + alkanol systems.

(b) Further tests of the Principle of Congruency

Further null tests could be done on any homologous series of mixtures, eg. (a 1-alkene + a pseudo-1-alkene), (a 1-alkyne + a pseudo-1-alkyne) or (an alkanol + a pseudo-alkanol), to further test the theory of congruency. The effect of the double and triple bonds on the null test could be interesting to compare with the results for the (*n*-alkane + a pseudo-*n*-alkane) mixtures.

(c) Further use of crown ethers and cryptands

Complexes involving a crown ether with a smaller cavity, eg. 12-crown-4 ether, should bring further clarity to the relationship between ΔV^∞ and B/r^+ , (discussed in Chapter 8), ie. with the constraints of cavity size. Further insight into interactions of solvent and solute could also be gained with use of different cryptands and crown ethers, and possibly different substituents on the macrocycles.

Work with larger solvent molecules, as well as a solvent molecule with a larger molar volume than the solute (macrocycle), should confirm the trend observed so far. Could the slope of the plot of solvent molar volume *versus* partial molar volume at infinite dilution

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become negative, if the solvent molar volume is larger than that of the solute?

Interactions between the macrocycle and a doubly-charged cation should show interesting interactions - as well as further investigating the electrostrictive effect, and the shielding properties of the macrocycle.

Most interesting would be the investigation of the complexation of ions by an anion complexer, such as work done by Hoiland *et al*⁽³¹⁷⁾ on the complex formation of anions by cyclodextrins in aqueous solution. Confirmation of the assumptions made by Hepler⁽²⁴²⁾ could be gained by such data.

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Fluid Phase Equilibria, 61 (1990) 81–87
Elsevier Science Publishers B.V., Amsterdam

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EXCESS ENTHALPIES AND VOLUMES OF MIXING FOR MESITYLENE + ALCOHOLS AT 298.15 K

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(Received April 6, 1990; accepted in final form June 27, 1990)

ABSTRACT

Letcher, T.M., Schoonbaert, F.E.Z., Prasad, K.A., Mercer-Chalmers, J. and Prasad, V.R.,
1990. Excess enthalpies and volumes of mixing for mesitylene + alcohols at 298.15 K.
Fluid Phase Equilibria, 61: 81–87.

Direct measurements have been made at 298.15 K of the enthalpy changes and volume changes on mixing mesitylene with each of the following alcohols: methanol, ethanol, 1-propanol and 2-propanol.

The H_m^E value for mesitylene + an alcohol is similar in magnitude to H_m^E for benzene + the same alcohol. The V_m^E for mesitylene + an alcohol, however, is significantly more positive than the V_m^E for benzene + the same alcohol.

INTRODUCTION

The excess enthalpies and volumes (H_m^E and V_m^E , respectively) of mixing benzene with C_1 , C_2 and C_3 alcohols have been reported in the literature by Veselý et al. (1974), Mrazek and Van Ness (1961) and Brown and Smith (1962). No measurements, however, have been reported for 1,3,5-trimethylbenzene (mesitylene) with the C_1 , C_2 and C_3 alcohols.

The purpose of this work is to compare H_m^E and also V_m^E for benzene + each of the C_1 , C_2 and C_3 alcohols with H_m^E and V_m^E for mesitylene + each of the C_1 , C_2 and C_3 alcohols. The comparison will show the influence of the substituted methyl groups on these mixing properties.

EXPERIMENTAL

Materials

Mesitylene was obtained from Merck and was vacuum distilled before use. Analysis by GLC showed that the total impurity content was less than 0.35 mol%.

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The alcohols were obtained from Merck (methanol and 1-propanol), Aldrich (2-propanol) and N.C.P. (South Africa) (ethanol) and were dried and purified as previously described by Letcher et al. (1986). The water concentration was determined before use and in all cases was found to be less than 0.01 mol%. The total organic impurity content in each of the alcohols was found by GLC to be less than 0.1 mol%.

Procedure

The excess enthalpies were measured using an LKB 2107 calorimeter as previously described by Letcher and Scoones (1982).

The excess volumes were measured by a vibrating tube densitometer (Paar DMA 601) method, which has been fully described by Letcher and Lucas (1982).

TABLE 1

Molar excess enthalpies H_m^E at 298.15 K for $x\text{C}_9\text{H}_{12} + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}$ and the deviations δH_m^E calculated from eqn. (1) and the coefficients from Table 3

x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)
CH₃OH								
0.0494	141.1	1.2	0.2885	569.4	-2.9	0.7039	812.9	-3.4
0.0882	235.0	-1.4	0.3992	682.4	5.1	0.8211	719.2	-2.8
0.1332	333.5	-0.7	0.4706	732.9	3.6	0.8915	550.4	-2.4
0.2159	475.8	-2.1	0.5686	788.6	2.4	0.9021	520.3	3.6
C₂H₅OH								
0.0738	222.4	1.8	0.4200	757.8	7.4	0.7350	883.1	-6.6
0.1532	402.5	-4.7	0.5255	830.8	3.7	0.8303	785.1	-2.2
0.2345	548.2	-1.2	0.6432	888.7	5.8	0.8680	700.3	3.1
0.3243	660.5	-1.8						
1-C₃H₇OH								
0.0998	286.8	1.7	0.5029	963.3	4.1	0.7951	956.9	-3.4
0.2069	538.7	-5.9	0.5904	1025.5	6.8	0.8679	785.3	-0.1
0.2976	714.7	3.2	0.7176	1029.2	-4.5	0.9254	537.2	1.0
0.4053	862.7	0.0						
2-C₃H₇OH								
0.0865	375.4	-1.7	0.4411	1176.5	-1.9	0.7251	1188.2	-1.2
0.1607	630.1	2.5	0.5696	1267.9	-0.9	0.7632	1132.0	8.6
0.2383	837.9	4.1	0.5983	1265.7	-6.9	0.8009	1038.2	4.2
0.3326	1023.8	-0.9	0.6360	1263.4	-2.9	0.8947	680.2	-2.8

RESULTS

The H_m^E and V_m^E results are given in Tables 1 and 2, respectively, together with the deviations δY_m^E calculated from the smoothing equation

$$\delta Y_m^E = Y_m^E - x(1-x) \sum_{r=0}^n Z_r (1-2x)^r \quad (1)$$

where x denotes the mole fraction, Y denotes either H or V and Z_r represents A_r for the H_m^E data and B_r for the V_m^E data.

The values of the coefficients A_r and B_r are given in Table 3, together with the standard deviations σ_H and σ_V for the heats and volumes, respectively. The estimated error in H_m^E is 4 J mol^{-1} , while the estimated error in V_m^E is $0.005 \text{ cm}^3 \text{ mol}^{-1}$. The results have also been plotted as graphs in Figs. 1 and 2.

TABLE 2

Molar excess volumes V_m^E at 298.15 K for $x\text{C}_9\text{H}_{12} + (1-x)\text{C}_y\text{H}_{2y+1}\text{OH}$ and the deviations δV_m^E calculated from eqn. (1) and the coefficients of Table 4

x	V_m^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})
CH₃OH								
0.0324	0.0405	11	0.2770	0.1587	28	0.7007	0.1515	-28
0.0662	0.0714	-8	0.3364	0.1601	21	0.7537	0.1433	-30
0.1101	0.1030	-11	0.4243	0.1652	35	0.8624	0.1065	-40
0.1522	0.1225	-32	0.5123	0.1638	26	0.9320	0.0681	20
0.1993	0.1388	-32	0.5985	0.1658	55			
C₂H₅OH								
0.0841	0.0376	15	0.3470	0.1296	25	0.7291	0.1731	-36
0.1471	0.0648	-3	0.5137	0.1540	56	0.8382	0.1672	-27
0.2097	0.0866	-40	0.6023	0.1642	45	0.8854	0.1464	-22
0.2578	0.1024	-40	0.6493	0.1678	12	0.9483	0.0903	14
1-C₃H₇OH								
0.1388	0.0856	25	0.4350	0.2035	49	0.7391	0.2337	-28
0.2150	0.1210	-47	0.5062	0.2136	25	0.8332	0.2147	-26
0.2701	0.1506	-3	0.6038	0.2283	27	0.9188	0.1502	11
0.3393	0.1719	-34						
2-C₃H₇OH								
0.0788	0.0983	21	0.4607	0.3656	57	0.7727	0.3562	-15
0.1417	0.1617	39	0.5190	0.3746	17	0.8396	0.3051	-65
0.2589	0.2658	-12	0.6007	0.3911	79	0.9024	0.2305	-20
0.3622	0.3204	-51	0.6868	0.3812	-3	0.9320	0.1818	-32

TABLE 3

Coefficients A_r and B_r of eqn. (1) for $x\text{C}_9\text{H}_{12} + (1-x)\text{C}_v\text{H}_{2v+1}\text{OH}$ at 298.15 K. The standard deviations σ_H and σ_V are also included

Alcohol	A_0	A_1	A_2	A_3	σ_H	B_0	B_1	B_2	B_3	σ_V
CH_3OH	2922.4	-1236.8	2161.6	-894.6	3.4	0.6453	0.0073	0.6128	0.0827	0.0035
$\text{C}_2\text{H}_5\text{OH}$	3239.7	-1376.5	2555.0	-1123.3	5.6	0.5870	-0.2251	0.6629	-0.6792	0.0038
1- $\text{C}_3\text{H}_7\text{OH}$	3827.0	-1679.6	2236.2	-1447.9	4.6	0.8400	-0.3249	0.6706	-0.6989	0.0040
2- $\text{C}_3\text{H}_7\text{OH}$	4933.5	-1499.9	1700.9	-147.9	4.3	1.4764	-0.4158	0.7916	-0.6067	0.0050

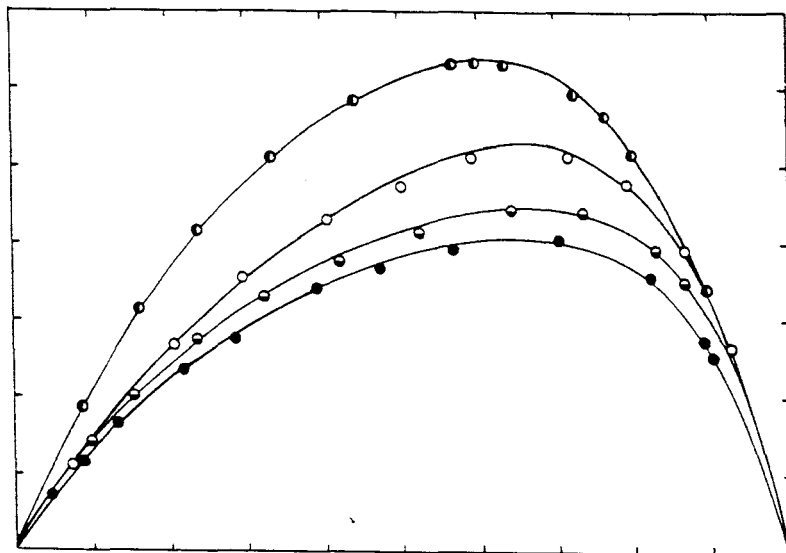


Fig. 1. H_m^E at 298.15 K for $xC_9H_{12} + (1-x)C_yH_{2y-1}OH$: CH_3OH , $\bullet$; C_2H_5OH , $\circ$; $1-C_3H_7OH$, $\circ$; $2-C_3H_7OH$, $\bullet$.

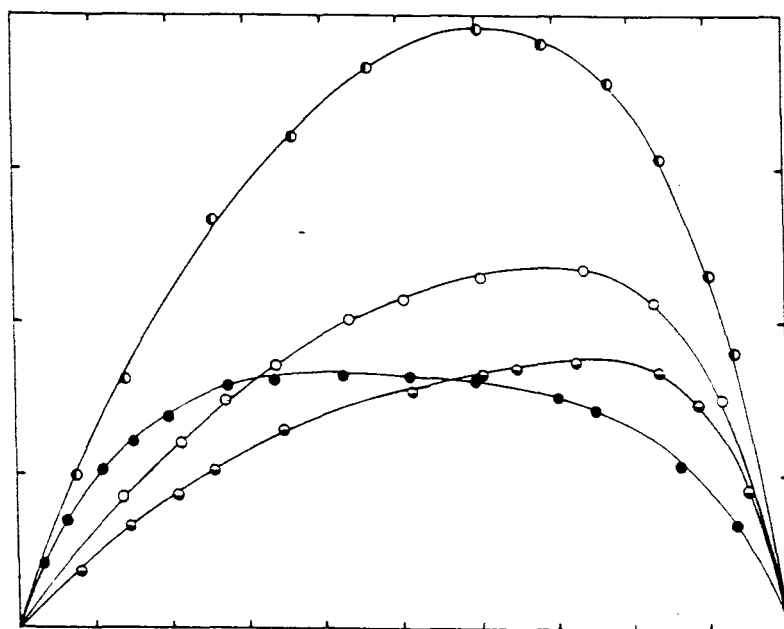


Fig. 2. V_m^E at 298.15 K for $xC_9H_{12} + (1-x)C_yH_{2y+1}OH$: CH_3OH , $\bullet$; C_2H_5OH , $\circ$; $1-C_3H_7OH$, $\circ$; $2-C_3H_7OH$, $\bullet$.

TABLE 4

The H_m^E (maximum) and V_m^E (maximum) for $x\text{C}_9\text{H}_{12} + (1-x)\text{C}_x\text{H}_{2x+1}\text{OH}$ and for $x\text{C}_6\text{H}_6 + (1-x)\text{C}_x\text{H}_{2x+1}\text{OH}$. The values of x (maximum) are given in parentheses. The results for the benzene mixtures have been obtained from the literature quoted in the text

Alcohol	H_m^E (maximum) (J mol^{-1})		V_m^E (maximum) ($\text{cm}^3 \text{mol}^{-1}$)	
	C_9H_{12}	C_6H_6	C_9H_{12}	C_6H_6
CH_3OH	813 (0.71)	722 (0.72)	0.17 (0.60)	0.03 (0.80)
$\text{C}_2\text{H}_5\text{OH}$	890 (0.65)	890 (0.65)	0.17 (0.75)	0.09 (0.80)
1- $\text{C}_3\text{H}_7\text{OH}$	1040 (0.63)	1045 (0.63)	0.24 (0.70)	0.15 (0.70)
2- $\text{C}_3\text{H}_7\text{OH}$	1270 (0.60)	1322 (0.60)	0.39 (0.62)	0.29 (0.65)

DISCUSSION

There is a close similarity between the shape and the magnitude of the H_m^E - x curve for mesitylene + an alcohol and the H_m^E - x curve for benzene + the same alcohol. This can be seen from the H_m^E (maximum) and x (maximum) data summarized in Table 4. These results suggest that, as far as the H_m^E results are concerned, the three substituent methyl groups have little overall effect. The positive enthalpy contribution from the dissociation of the benzene molecules and the negative enthalpy contribution from the benzene-alcohol association are similar in magnitude to the enthalpy contribution resulting from the dissociation of the mesitylene molecules and the enthalpy from the association of mesitylene and alcohol molecules. The H_m^E results are shown graphically in Fig. 1.

The V_m^E values for mesitylene + an alcohol, however, differ in shape, magnitude and sign from the V_m^E for benzene + the same alcohol. The packing of a mixture of mesitylene and alcohol molecules is obviously very different from the packing of a mixture of benzene and alcohol molecules. The V_m^E for mesitylene + an alcohol is always more positive than the V_m^E for benzene + the same alcohol. In both sets of data (mesitylene + an alcohol and benzene + an alcohol), the V_m^E (maximum) increases with increasing carbon number of the alcohol. This information is summarized in Table 4 and the V_m^E results are plotted in Fig. 2.

ACKNOWLEDGEMENTS

The authors thank the FRD (South Africa) and Rhodes University for financial assistance.

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EXCESS ENTHALPIES AND VOLUMES OF BINARY MIXTURES OF 1-ALKENES WITH METHANOL AND WITH ETHANOL

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ABSTRACT

Molar excess enthalpies H_m^E have been determined using an LKB flow calorimeter, and molar excess volumes V_m^E using a Paar DMA 601 densitometer over the whole composition range, for all the binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K. The results were compared with H_m^E and V_m^E values for mixtures of an *n*-alkane with methanol and with ethanol in order to determine the effect of the double bond in the 1-alkene with alcohol mixtures.

INTRODUCTION

Previous studies have determined molar excess enthalpies H_m^E and molar excess volumes V_m^E at 298.15 K for binary mixtures of an *n*-alkane with methanol and with ethanol [1–8]. In the present work we report H_m^E and V_m^E values for binary mixtures of a 1-alkene (1-hexene, 1-heptene or 1-octene) with methanol and with ethanol. The patterns generated are compared to the patterns of H_m^E and V_m^E results for mixtures of an *n*-alkane with methanol and with ethanol. The results are discussed in terms of specific interactions between the double bonds in the 1-alkene and the hydroxyl group in the alcohol.

EXPERIMENTAL

1-Hexene, 1-heptene and 1-octene were supplied by the Aldrich Chemical Co., and distilled before use. Analysis by GLC showed that total impurities were less than 0.2 mol% for the 1-hexene and 1-heptene, and less than 0.5 mol% for the 1-octene. The densities of the 1-hexene, 1-heptene and 1-octene were 0.66840, 0.69260 and 0.71070, respectively, which compared well with literature values [9].

The methanol (Merck, Urasol grade) and ethanol (absolute grade from NCP, South Africa) were dried repeatedly using the method of Lund and

Bjerrum described by Vogel [10]. The method involves refluxing with magnesium metal activated with iodine before distillation. The water impurity in both methanol and ethanol was determined by a Karl Fischer titration to be less than 0.01 mol%. The alcohols were kept in a dry box before use.

The excess volumes were measured using a vibrating tube densitometer (Paar DMA 601) method which has been described elsewhere [11]. The temperature was controlled to within 2 mK, and the densitometer calibrated for each measurement using water, methanol and ethanol. The excess molar

TABLE 1

Excess enthalpy H_m^E data for binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K

x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)
$x1-C_6H_{12} + (1-x)CH_3OH$								
0.0473	123.6	1.0	0.3462	497.4	3.7	0.6632	573.4	-0.1
0.1249	274.6	-0.8	0.4113	529.1	4.9	0.7693	530.9	-1.2
0.1915	363.2	-4.9	0.4845	553.2	3.4	0.8166	480.9	-5.6
0.2732	442.4	-4.0	0.5614	570.1	1.9	0.9221	285.0	1.8
$x1-C_7H_{14} + (1-x)CH_3OH$								
0.0842	234.5	2.2	0.3346	516.3	-3.3	0.6852	590.8	1.4
0.1388	330.7	-4.8	0.4268	560.9	5.5	0.7775	540.1	-5.5
0.1833	399.6	1.1	0.5428	587.7	3.4	0.9065	340.0	1.1
0.2360	453.5	-0.5	0.6548	592.5	-0.7			
$x1-C_8H_{16} + (1-x)CH_3OH$								
0.0630	201.5	1.3	0.4650	596.3	1.8	0.7318	601.0	-3.4
0.1550	385.7	-2.1	0.5394	617.4	4.5	0.8342	501.3	-4.7
0.2161	457.3	-6.6	0.6425	626.1	1.4	0.9050	360.7	2.5
0.3216	546.3	5.3						
$x1-C_6H_{12} + (1-x)C_2H_5OH$								
0.1120	167.1	0.7	0.5421	575.6	2.0	0.7798	585.9	-4.9
0.2417	332.3	-3.0	0.6556	616.1	0.9	0.8273	550.2	6.6
0.3196	414.7	-1.1	0.7132	613.1	-4.1	0.8655	480.1	-1.6
0.4466	521.3	4.3						
$x1-C_7H_{14} + (1-x)C_2H_5OH$								
0.0696	136.8	2.3	0.3751	518.0	4.7	0.7310	648.1	-7.7
0.1289	235.9	-0.6	0.4855	591.9	8.2	0.8105	601.9	-4.3
0.1687	290.2	-6.8	0.6489	655.6	2.1	0.8712	513.0	3.9
0.1879	322.0	-1.8						
$x1-C_8H_{16} + (1-x)C_2H_5OH$								
0.0898	186.5	2.2	0.6120	660.7	7.3	0.8823	548.4	-4.9
0.1638	323.5	-3.2	0.7018	686.0	4.3	0.9102	478.7	4.2
0.2579	458.7	-5.4	0.7891	668.3	-6.9	0.9189	448.8	4.3
0.3385	538.6	-0.3	0.8669	580.4	-6.3	0.9384	365.5	-7.5
0.4576	605.0	5.6						

enthalpies were measured using an LKB 2107 calorimeter. The method has been described elsewhere [12].

RESULTS

Results for H_m^E and V_m^E are given in Tables 1 and 2, respectively, together with the corresponding deviations δH_m^E and δV_m^E . The deviations were

TABLE 2

Excess volume V_m^E data for binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K

x	V_m^E (cm ³ mol ⁻¹)	$10^4 \delta V_m^E$ (cm ³ mol ⁻¹)	x	V_m^E (cm ³ mol ⁻¹)	$10^4 \delta V_m^E$ (cm ³ mol ⁻¹)	x	V_m^E (cm ³ mol ⁻¹)	$10^4 \delta V_m^E$ (cm ³ mol ⁻¹)
$x1-C_6H_{12} + (1-x)CH_3OH$								
0.0979	0.1211	25	0.3934	0.2751	36	0.7934	0.2290	-55
0.1434	0.1601	-18	0.5430	0.2807	75	0.8602	0.1916	-60
0.2499	0.2246	-81	0.7162	0.2616	56	0.9414	0.1121	20
$x1-C_7H_{14} + (1-x)CH_3OH$								
0.0843	0.1886	6	0.4709	0.3641	-8	0.7964	0.2761	-47
0.2066	0.3150	-31	0.5063	0.3680	46	0.8565	0.2315	33
0.3553	0.3644	19	0.6531	0.3437	-7	0.8968	0.1800	-4
0.3586	0.3620	-7						
$x(1-C_8H_{16} + (1-x)CH_3OH$								
0.0501	0.1482	13	0.4170	0.3952	-1	0.7753	0.3138	3
0.0994	0.2484	-6	0.5372	0.3833	48	0.8738	0.2177	-123
0.1588	0.3255	-34	0.5704	0.3791	57	0.9544	0.1070	30
0.2510	0.3845	-34	0.6809	0.3561	48			
$x1-C_6H_{12} + (1-x)C_2H_5OH$								
0.1005	0.0340	20	0.3978	0.1587	12	0.7546	0.2306	22
0.1582	0.0524	-25	0.4622	0.1862	37	0.8030	0.2092	-49
0.2414	0.0895	-10	0.5488	0.2138	27	0.8534	0.1817	-39
0.2807	0.1037	-39	0.6884	0.2366	22	0.9405	0.0994	14
$x1-C_7H_{14} + (1-x)C_2H_5OH$								
0.0854	0.0967	14	0.5024	0.2929	85	0.7871	0.2688	-52
0.2307	0.2013	-47	0.6620	0.3056	59	0.8997	0.1894	44
0.2629	0.2175	-52	0.7693	0.2781	-89	0.9603	0.0888	-4
0.3586	0.2635	42						
$x1-C_8H_{16} + (1-x)C_2H_5OH$								
0.0478	0.0841	24	0.5375	0.3527	87	0.8596	0.2450	-106
0.1042	0.1555	-47	0.5488	0.3540	99	0.8955	0.2067	-73
0.2457	0.2750	-83	0.6943	0.3381	20	0.9421	0.1448	63
0.3947	0.3342	14						

TABLE 3

Values at 298.15 K of coefficients A_r for eqn. (1)

Mixture	A_r (J mol ⁻¹)			
	A_0	A_1	A_2	A_3
$x1-C_6H_{12} + (1-x)CH_3OH$	2216.7	-548.8	1506.5	-314.9
$x1-C_7H_{14} + (1-x)CH_3OH$	2300.8	-467.2	1793.4	-244.3
$x1-C_8H_{16} + (1-x)CH_3OH$	2415.0	-502.4	1955.0	-116.7
$x1-C_6H_{12} + (1-x)C_2H_5OH$	2202.2	-1169.6	1346.3	-926.1
$x1-C_7H_{14} + (1-x)C_2H_5OH$	2366.8	-1079.2	1732.2	-1011.2
$x1-C_8H_{16} + (1-x)C_2H_5OH$	2457.1	-680.1	2336.6	-2204.9

TABLE 4

Values at 298.15 K of coefficients B_r for eqn. (1)

Mixture	B_r (cm ³ mol ⁻¹)			
	B_0	B_1	B_2	B_3
$x1-C_6H_{12} + (1-x)CH_3OH$	1.0991	0.0467	0.7376	-0.5219
$x1-C_7H_{14} + (1-x)CH_3OH$	1.4549	0.1019	1.0999	0.2344
$x1-C_8H_{16} + (1-x)CH_3OH$	1.5362	0.2938	1.4724	0.1275
$x1-C_6H_{12} + (1-x)C_2H_5OH$	0.7833	-0.6741	0.3180	-0.1842
$x1-C_7H_{14} + (1-x)C_2H_5OH$	1.1562	-0.2835	0.7447	-0.3740
$x1-C_8H_{16} + (1-x)C_2H_5OH$	1.3709	-0.0895	1.0080	-0.4342

calculated from the smoothing equation

$$\delta X_m^E = X_m^E - x(1-x) \sum_{r=0}^{r=3} X_r(1-2x)^r$$

where X_m^E may be either H_m^E or V_m^E , and X_r may be either A_r or B_r , respectively. The coefficients A_r and B_r are given in Tables 3 and 4.

DISCUSSION

At 298.15 K, CH_3OH does not mix in all proportions with the n -alkanes C_6H_{14} , C_7H_{16} and C_8H_{18} , but does mix with the 1-alkenes $1-C_6H_{12}$, $1-C_7H_{14}$ and $1-C_8H_{16}$. This could be considered as evidence for specific interactions between the double bond of the 1-alkene and the hydroxyl group of the alcohol.

The H_m^E results for the $1-C_6H_{12}$, $1-C_7H_{14}$ and $1-C_8H_{16} + C_2H_5OH$ mixtures show skew curves with single maxima at about 0.7 mole fraction 1-alkene of 620, 660 and 700 J mol⁻¹, respectively. These H_m^E (maximum) values are between 40 and 50 J mol⁻¹ more positive than those for C_6H_{14} , C_7H_{16} and $C_8H_{18} + C_2H_5OH$ mixtures [2,7,8].

The self association between 1-alkene molecules is relatively weak, as judged by the small positive values of $H_m^E(\text{maximum})$ for 1-C₆H₁₂ + *n*-C₆H₁₄ [13], 1-C₇H₁₄ + *n*-C₇H₁₆ [13] and 1-C₈H₁₆ + *n*-C₈H₁₈ [14] mixtures, of between 40 and 55 J mol⁻¹. The small positive enthalpy effect resulting from the dissociation of 1-alkene molecules is probably the cause of the $H_m^E(\text{maximum})$ values for 1-alkene + C₂H₅OH mixtures being slightly more positive than those for *n*-alkane + C₂H₅OH mixtures. The fact that the $H_m^E(\text{maximum})$ results for the 1-alkene + C₂H₅OH mixtures are only slightly more positive than those for the corresponding *n*-alkane + C₂H₅OH mixtures indicates that the association between 1-alkene and C₂H₅OH molecules is not strong. In both sets of data, the dominant feature is the dissociation of alcohol molecules, resulting in relatively large positive $H_m^E(\text{maximum})$ values.

The $H_m^E(\text{maximum})$ values for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + C₂H₅OH at 298 K are between 50 and 70 J mol⁻¹ more positive than those for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + CH₃OH.

The $V_m^E(\text{maximum})$ values for 1-C₆H₁₂, 1-C₇H₁₄ and 1-C₈H₁₆ + C₂H₅OH are 0.23, 0.30 and 0.35 cm³ mol⁻¹, respectively, and are less positive than those for 1-C₆H₁₄, 1-C₇H₁₆ and 1-C₈H₁₈ + C₂H₅OH (0.41, 0.47 and 0.52 cm³ mol⁻¹, respectively [3-6]).

The fact that the $V_m^E(\text{maximum})$ values obtained for the 1-alkene + C₂H₅OH mixtures studied in the present work are less positive than those for the corresponding *n*-alkane + C₂H₅OH mixtures could be a result of a packing effect induced by specific interaction of the double bond and the hydroxyl group.

The $V_m^E(\text{maximum})$ values for the 1-alkene + C₂H₅OH mixtures are less positive than those for the corresponding 1-alkene + CH₃OH mixtures.

The Flory-Patterson theory of liquid mixtures will be fitted to the V_m^E and H_m^E results presented here once the compressibilities of the 1-alkenes have been determined.

ACKNOWLEDGEMENT

The authors wish to thank the FRD (South Africa) and AECI for financial aid.

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M-2507(N)

J. Chem. Thermodynamics 1990, 22, 815–816

Note

The excess enthalpy and excess volume of (benzene + oct-1-yne) at 298.15 K

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H_m^E and V_m^E for (benzene + hex-1-yne or hept-1-yne) at 298.15 K have been reported.^(1,2) This paper reports H_m^E and V_m^E for (benzene + oct-1-yne) at 298.15 K.

The benzene (Analar grade) obtained from B.D.H. Chemicals Ltd. was purified as previously described.⁽³⁾ The oct-1-yne was obtained from Fluka Chemicals (99 mass per cent) and was not purified but was degassed, as was the benzene, before use. The excess molar enthalpies were measured using an LKB 2107 microflow calorimeter and the excess molar volumes were measured using an Anton Paar DMA 601 vibrating tube densitometer. The methods have been described.⁽¹⁾

The H_m^E results are given in table 1 together with the deviations Δ :

$$\Delta = H_m^E/(\text{J} \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^n A_r(1-2x)^r \quad (1)$$

The V_m^E results are also given in table 1 together with the deviations Δ' :

$$\Delta' = V_m^E/(\text{cm}^3 \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^n B_r(1-2x)^r \quad (2)$$

The coefficients A_r and B_r are given in table 2.

The H_m^E s for $\{xC_6H_6 + (1-x)HC \equiv CC_{k-2}H_{2k-3}\}$ where $k = 6$, to 8,^(1,2) are significantly lower than the H_m^E s for $\{xC_6H_6 + (1-x)C_kH_{2k-2}\}$ ⁽⁴⁻⁶⁾ and also lower than the H_m^E s for $\{xc-C_6H_{12} + (1-x)HC \equiv CC_{k-2}H_{2k-3}\}$.⁽⁷⁾ This can be clearly seen in figure 1 where values of $H_m^E(x=0.5)$ for each of the binary mixtures in the three sets discussed above have been plotted against k for $k = 6$, 7, and 8. The very much smaller $H_m^E(x=0.5)$ for $\{xC_6H_6 + (1-x)HC \equiv CC_{k-2}H_{2k-3}\}$ is probably due to the strong $\pi-\pi$ interaction between the benzene and the alk-1-yne.

TABLE 1. Excess molar enthalpies H_m^E and volumes V_m^E for $\{xC_6H_6 + (1-x)HC \equiv CC_6H_9\}$ at 298.15 K and the deviations Δ and Δ' calculated from equations (1) and (2) respectively and the coefficients of table 2

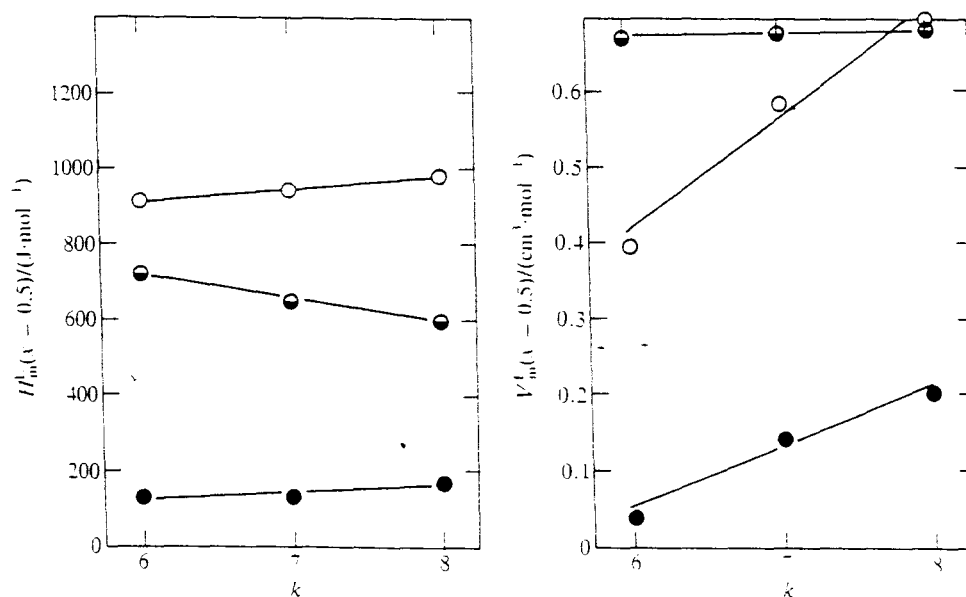
x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ	x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$10^4 \Delta'$	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$10^4 \Delta'$
0.0854	40.0	-2.2	0.5739	181.9	-2.7	0.0893	0.0511	16	0.6793	0.2065	27
0.1436	69.3	1.6	0.6330	185.3	-0.9	0.1625	0.0889	-22	0.7483	0.1900	-19
0.2242	101.9	2.5	0.7320	171.8	-2.6	0.2768	0.1414	-49	0.8170	0.1672	-18
0.3079	129.5	1.4	0.8156	144.3	-2.0	0.3687	0.1780	2	0.8787	0.1281	-60
0.3926	155.5	2.7	0.8892	102.9	-0.9	0.4788	0.2023	22	0.9127	0.1070	0
0.4665	171.2	1.4	0.9389	65.4	1.5	0.5501	0.2107	40	0.9440	0.7790	24
0.5290	180.3	0.2				0.6255	0.2113	38			

0021-9614/90/080815-02 \$02.00/0

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TABLE 2. A_i and B_i for equations (1) and (2) for $(H_m^E$ and $V_m^E)$ $\{xC_6H_6 + (1-x)HC\}CC_kH_{2k-3}$ at 298.15 K

A_0	A_1	A_2	B_0	B_1	B_2	B_3
703.4	-327.3	157.8	0.8105	-0.2185	0.2404	-0.3339

FIGURE 1. Excess molar enthalpies H_m^E and excess molar volumes V_m^E for $(0.5C_6H_6$ or $0.5C_6H_{12} - 0.5C_kH_{2k-2}$ or $0.5HC : CC_{k-2}H_{2k-3})$ at 298.15 K as a function of k . $\circ$, $(0.5C_6H_6 - 0.5C_kH_{2k-3})$; $\bullet$, $(0.5C_6H_{12} + 0.5HC : CC_{k-2}H_{2k-3})$; $\bullet$, $(0.5C_6H_6 - 0.5HC : CC_{k-2}H_{2k-3})$.

The V_m^E s for $\{xC_6H_6 + (1-x)HC : CC_{k-2}H_{2k-3}\}$ show a similar pattern when compared with the V_m^E s for $\{xC_6H_6 + (1-x)C_kH_{2k-2}\}$,⁽⁸⁾ and $\{xC_6H_{12} + (1-x)HC : CC_{k-2}H_{2k-3}\}$.⁽⁹⁾ This can also be seen in figure 1 where values of $V_m^E(x=0.5)$ have been plotted against k .

The authors wish to thank the FRD (South Africa) for financial help.

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M-2505

J. Chem. Thermodynamics **1990**, 22, 765-770

Excess enthalpies of (a xylene + an alkanol) at 298.2 K

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Excess molar enthalpies H_m^E were measured as a function of mole fraction at 298.2 K and atmospheric pressure for the 12 mixtures $[x\{\text{isomer of } C_6H_4(CH_3)_2\} + (1-x)C_kH_{2k-1}OH]$ where $k = 1, 2$, or 3 . An LKB 2107 flow microcalorimeter was used in the measurements. The H_m^E s for these mixtures are discussed in terms of the position of the methyl groups and also in terms of the carbon chain length of the alkanol.

1. Introduction

Recently Rodriguez-Nuñez *et al.*^(1,2) reported H_m^E for $[x\{\text{isomer of } C_6H_4(CH_3)_2\} + (1-x)C_kH_{2k-1}OH]$ for $k = 3, 4, 5, 6, 7$, and 8 , and Christensen *et al.*⁽³⁾ and Nagata and Orgasawara⁽⁴⁾ reported H_m^E for $\{xp-C_6H_4(CH_3)_2 + (1-x)C_kH_{2k-1}OH\}$ for $k = 1, 2$, and 3 . Our work complements their work and completes all the H_m^E measurements for mixtures of each of the three xylene isomers with each of the C_1 , C_2 , or C_3 alkanols.

2. Experimental

The *o*-, *m*-, and *p*-xylene (Merck) were each distilled at a reflux ratio of 0.1, using a 1 m long column filled with glass helices. Analysis by g.l.c. showed that in each case the purity was better than 99.5 moles per cent.

The alkanols: methanol (Merck, Uvasol grade), ethanol (absolute grade from N.C.P., South africa), and propan-1-ol (Merck, synthesis grade) were each dried with magnesium metal activated with iodine, using the method of Lund and Bjerrum.⁽⁵⁾ The propan-2-ol (Aldrich, Gold label, 99.5 moles per cent) was dried using potassium carbonate. All the alkanols were stored in a dry box and were distilled before use. Analysis by g.l.c. showed in each case the purity of the alkanol was better than 99.8 moles per cent. Analysis, using the Karl-Fisher technique, showed that the water impurity in each of the alkanols was less than 0.02 mole per cent.

An LKB 2107 microcalorimeter, in the flow mode, was used in these measurements; the method has been described.⁽⁶⁾

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TABLE 1. Excess molar enthalpies $H_m^E(xC_6H_4(CH_3)_2 - (1-x)C_6H_4(OH)_2)$ at 298.2 K and the deviations calculated from equation (1) and the coefficients of table 2

x	$\frac{H_m^E}{J \cdot mol^{-1}}$	Δ	x	$\frac{H_m^E}{J \cdot mol^{-1}}$	Δ	x	$\frac{H_m^E}{J \cdot mol^{-1}}$	Δ	x	$\frac{H_m^E}{J \cdot mol^{-1}}$	Δ
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)CH ₃ OH											
0.0575	138.8	1.7	0.3120	530.6	1.3	0.6070	746.6	1.3	0.8260	704.7	-3.5
0.1058	223.4	-6.0	0.4259	643.3	-1.0	0.6755	762.6	1.4	0.9004	563.3	7.3
0.1617	325.8	3.6	0.4995	696.7	0.2	0.7547	752.1	-4.9	0.9473	360.4	-2.2
0.2373	433.6	0.4									
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)C ₂ H ₅ OH											
0.0835	178.4	-0.2	0.3234	587.9	-2.9	0.5993	840.7	4.5	0.7788	840.2	-5.1
0.1512	311.3	-0.7	0.4070	683.5	-5.8	0.6435	852.8	-2.5	0.8512	753.6	6.2
0.2252	448.1	4.2	0.5430	810.2	6.8	0.6954	865.3	-2.0	0.8852	656.0	-2.5
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)C ₃ H ₇ -OH											
0.1064	256.2	-1.1	0.3859	791.9	0.7	0.6513	990.7	6.7	0.8138	912.1	-2.5
0.1893	428.4	4.5	0.4854	906.8	-4.8	0.6963	980.3	-1.7	0.8699	810.9	2.3
0.2828	606.0	-4.1	0.6081	982.3	4.4	0.7480	963.2	-4.2	0.9284	580.4	-0.2
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)CH ₃ CH(OH)CH ₃											
0.0898	331.8	0.3	0.3961	1076.3	1.7	0.5517	1204.7	-1.0	0.7000	1203.4	-1.8
0.1978	676.0	-1.6	0.4888	1168.9	1.1	0.6207	1226.4	2.5	0.8213	1029.4	0.5
0.2881	896.8	1.4	0.5132	1183.7	-1.0	0.6563	1220.7	-1.0			
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)CH ₃ OH											
0.0567	133.4	-1.3	0.3187	529.4	-6.1	0.6727	742.2	-0.3	0.9077	530.5	4.7
0.1046	230.4	2.4	0.4301	633.3	-4.6	0.7025	742.2	-3.6	0.9344	419.2	-2.1
0.1589	323.2	3.3	0.5189	699.7	7.8	0.7670	733.9	-4.1			
0.2382	434.2	-2.2	0.5872	727.5	7.2	0.8423	675.1	-1.0			
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)C ₂ H ₅ OH											
0.0777	157.8	-1.3	0.3951	658.4	-8.8	0.5803	818.7	8.8	0.8364	780.4	0.1
0.1402	287.5	4.7	0.4249	696.2	-0.4	0.6822	849.9	-2.4	0.8896	661.4	7.2
0.2079	405.1	-1.8	0.4897	757.9	6.9	0.7186	850.3	-7.0	0.9206	531.7	-3.5
0.2968	545.8	-1.5	0.5221	775.9	1.8	0.7569	849.4	-2.5			
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)C ₃ H ₇ -OH											
0.1002	239.9	-0.8	0.4631	868.5	-2.5	0.6791	975.0	-3.7	0.8612	814.1	4.6
0.1796	408.9	3.1	0.5152	921.0	3.6	0.7297	964.9	-5.2	0.9078	650.8	-1.3
0.2637	570.1	-1.0	0.5797	958.8	2.6	0.7724	947.6	0.9			
0.3721	752.2	-4.1	0.6325	980.4	6.6	0.8017	914.9	-2.8			
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)CH ₃ CH(OH)CH ₃											
0.1008	349.1	0.8	0.4211	1100.7	1.8	0.6042	1205.4	6.4	0.8676	891.6	-7.1
0.1795	613.1	1.6	0.4716	1141.9	-0.7	0.6692	1200.5	2.8	0.9123	700.5	5.3
0.2604	827.3	-6.0	0.5326	1180.6	2.8	0.7314	1165.1	-3.6			
0.3680	1029.1	-5.7	0.5714	1199.0	7.1	0.8002	1075.8	-5.6			
<i>p</i> -C ₆ H ₄ (CH ₃) ₂ + (1- <i>x</i>)CH ₃ OH											
0.0680	139.5	-2.0	0.3419	526.8	-3.1	0.6519	709.4	1.7	0.8174	689.6	-5.1
0.1174	227.2	4.3	0.4368	615.7	-2.7	0.6739	715.0	3.2	0.8754	617.4	-2.5
0.2186	376.1	4.2	0.5616	680.5	-3.2	0.7142	720.8	3.6	0.9136	520.5	2.4
0.2934	465.9	-6.2	0.6058	705.3	8.3	0.7430	715.0	-3.0			

$$H_m^E[x_1C_6H_4(CH_3)_2 \text{ OR } m\text{- OR } p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_{7-9}\text{OH}]$$

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TABLE 1—continued

x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ	x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ	x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ	x	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	Δ
$x p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_5\text{OH}$											
0.0701	123.5	-1.2	0.3860	615.6	-8.6	0.6589	805.3	3.8	0.8188	774.2	-0.51
0.1289	222.3	1.8	0.5106	740.2	-0.6	0.7039	810.0	1.5	0.8748	685.8	-2.5
0.1958	336.7	5.2	0.5693	778.0	5.5	0.7381	806.2	-2.7	0.9226	535.7	1.5
0.2819	470.6	-3.8	0.6095	790.5	2.6	0.7700	801.3	-1.9			
$x p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$											
0.0986	212.1	-1.0	0.4605	820.2	-4.5	0.6543	940.3	3.1	0.8900	732.5	-1.8
0.1780	358.5	2.1	0.5113	867.0	-5.4	0.6981	942.7	2.1	0.9364	530.1	1.2
0.2604	513.5	3.6	0.5756	915.3	2.5	0.7281	942.7	4.8			
0.3549	674.6	-4.9	0.6242	935.0	4.3	0.7963	899.8	-7.1			
$x p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$											
0.0539	190.0	1.6	0.3614	978.4	0.9	0.6115	1181.4	3.2	0.8585	905.1	3.9
0.0936	324.5	1.7	0.4549	1090.6	2.6	0.6619	1175.9	-4.5	0.8895	780.9	2.6
0.1672	550.4	-6.0	0.5032	1140.6	13.0	0.7144	1156.0	-5.6			
0.2476	760.0	-5.8	0.5649	1170.4	7.3	0.7884	1065.2	-13.1			

3. Results

The measured excess molar enthalpies H_m^E are given in table 1. To each set of experimental values, a polynomial of the type:

$$\Delta = H_m^E/(\text{J} \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^n A_r(1-2x)^r. \quad (1)$$

was fitted by the method of unweighted least squares. The coefficients A_r are given in table 2.

4. Discussion

All the mixtures reported here give $H_m^E > 0$ with a maximum occurring at $0.6 < x < 0.7$ where x denotes the mole fraction of the xylene. The $H_m^E(\text{maximum})$ for these mixtures increases with increasing carbon number of the alkanol and for any one of the three xylenes, $H_m^E(\text{maximum})\{xC_6H_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}\} > H_m^E(\text{maximum})\{xC_6H_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}$. These results can be seen in table 3 where our values of $H_m^E(\text{maximum})$ are calculated, together with the mole fraction at $H_m^E(\text{maximum})$. The results from references 2, 3, and 4 are also included in this table.

With the exception of two results, our results are in good agreement with the values reported in the literature.⁽²⁻⁴⁾ For the mixtures $\{xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 \text{ or } xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}\}$ our results for $H_m^E(\text{maximum})$ are about $30 \text{ J} \cdot \text{mol}^{-1}$ lower than that reported by Rodriguez-Nuñez *et al.*⁽²⁾ Our results for $H_m^E\{xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}\}$ agree within experimental error with the results of Nagata and Orgasawara⁽⁴⁾ and also of Christensen *et al.*⁽³⁾ although Christensen *et al.*'s values were measured at 170 kPa.

TABLE 2. Coefficients A_i for equation (1) for $H_m^E\{xC_6H_4(CH_3)_2 + (1-x)C_kH_{2k-1}OH\}$

Mixture	A_0	A_1	A_2	A_3	A_4
$xo-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2787.0	-1189.1	1337.5	-1810.8	1633.9
$xo-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	3091.0	-1533.7	1784.0	-1901.6	791.6
$xo-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3696.2	-1605.1	594.4	-2558.5	3001.9
$xo-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4703.6	-1404.5	2235.3	-1813.1	—
$xm-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2728.6	-1070.8	1455.0	-1917.2	1508.4
$xm-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	3034.4	-1452.4	1843.2	-2230.6	868.3
$xm-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3621.0	-1665.1	1080.2	-2216.9	2012.9
$xm-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4644.5	-1168.6	2332.9	-2665.6	—
$xp-C_6H_4(CH_3)_2 + (1-x)CH_3OH$	2631.2	-1021.0	988.4	-2368.2	2285.1
$xp-C_6H_4(CH_3)_2 + (1-x)C_2H_5OH$	2934.6	-1389.0	796.7	-2665.0	2339.5
$xp-C_6H_4(CH_3)_2 + (1-x)C_3H_7OH$	3452.6	-1716.7	607.9	-2565.8	3031.9
$xp-C_6H_4(CH_3)_2 + (1-x)CH_3CH(OH)CH_3$	4500.9	-1449.8	2296.9	-1890.7	—

The results reported here show that the sequence in H_m^E (maximum) for mixtures with CH_3OH is H_m^E (maximum, $o-C_6H_4(CH_3)_2$) $\approx H_m^E$ (maximum, $m-C_6H_4(CH_3)_2$) $> H_m^E$ (maximum, $p-C_6H_4(CH_3)_2$). Our results show that this is also true for each of the other alkanols: C_2H_5OH , C_3H_7OH , and $CH_3CH(OH)CH_3$. With the exception of the two results discussed in the previous paragraph this result is similar to the conclusion of Rodriguez-Nuñez *et al.*⁽¹¹⁾ who based their conclusion on their own results for $H_m^E\{x\{o\text{- or }m\text{- or }p\text{-}C_6H_4(CH_3)_2\} + (1-x)C_kH_{2k-1}OH\}$ where $k = 3, 4, 5, 6, 7$, and 8, and all the alkanols are primary.

An estimate of the partial molar enthalpy at infinite dilution for the mixtures discussed here is given in table 4. These values were determined from the coefficients in table 2 and equation (1) using the method described by Letcher and Jerman.⁽⁷⁾ For

TABLE 3. Values of H_m^E (maximum) for $\{xC_6H_4(CH_3)_2 + (1-x)C_kH_{2k-1}OH\}$ at 298.2 K and at 101.325 kPa together with the mole fraction x at H_m^E (maximum) given in parenthesis. Literature values for six of the mixtures are also given. The results from reference 3 were measured at 170 kPa; t.w., this work

$\frac{H_m^E(\max)}{J \cdot mol^{-1}}$	Ref.	$\frac{H_m^E(\max)}{J \cdot mol^{-1}}$	Ref.	$\frac{H_m^E(\max)}{J \cdot mol^{-1}}$	Ref.	$\frac{H_m^E(\max)}{J \cdot mol^{-1}}$	Ref.
CH_3OH		C_2H_5OH		C_3H_7OH		$CH_3CHOHCH_3$	
		$o-C_6H_4(CH_3)_2$					
763 (0.68)	t.w.	865 (0.69)	t.w.	992 (0.65)	t.w.	1227 (0.63)	t.w.
				994 (0.65)			
		$m-C_6H_4(CH_3)_2$					
743 (0.69)	t.w.	851 (0.69)	t.w.	981 (0.64)	t.w.	1208 (0.62)	t.w.
				1019 (0.65)	2		
		$p-C_6H_4(CH_3)_2$					
722 (0.70)	t.w.	812 (0.70)	t.w.	944 (0.70)	t.w.		
747 (0.69)	3	833 (0.70)	3	991 (0.68)	2	1182 (0.62)	t.w.
725 (0.70)	4	816 (0.70)	4	972 (0.68)	3	1188 (0.61)	4
				948 (0.70)	4		

$$H_m^E[x\{o\text{- OR } m\text{- OR } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$$

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TABLE 4. Partial molar enthalpies at infinite dilution: $H_1^{E,\infty}$ and $H_2^{E,\infty}$ for $[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$ for $k = 1, 2$, and 3

<i>i</i>	CH ₂ OH		C ₂ H ₅ OH		C ₃ H ₇ -OH		CH ₃ CH(OH)CH ₃	
	1	2	1	$H_1^{E,\infty}/(\text{J}\cdot\text{mol}^{-1})$ 2	1	2	1	2
<i>o</i> -C ₆ H ₄ (CH ₃) ₂	2760	8760	2230	9100	3130	11460	3720	10160
<i>m</i> -C ₆ H ₄ (CH ₃) ₂	2520	9293	2020	10130	2810	11380	3460	10140
<i>p</i> -C ₆ H ₄ (CH ₃) ₂	2700	8680	2060	9430	2830	10600	3140	10810

all mixtures $H_2(x_2 = 0) > H_1(x_1 = 0)$, where 2 refers to *o*- or *m*- or *p*-xylene and 1 to an alkanol. These results support the explanation given by Rodriguez-Nuñez *et al.*⁽¹⁾ that the addition of a small amount of xylene to a large amount of alkanol does not result in the rupture of a significant fraction of the hydrogen bonds. On the other hand, the addition a small amount of alkanol to a large amount of xylene does result in the rupture of a significant fraction of the hydrogen bonds.

Comparing our results of $H_m^E[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$ for $k = 1, 2$, and 3 with those of Rodriguez-Nuñez *et al.*^(1,2) and Nagata and Orgasawara⁽⁴⁾ for $H_m^E[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$, where $k = 3, 4, 5, 6, 7$, and 8 , it appears that $H_m^E(\text{maximum})$ increases from $k = 1$ to $k = 4$ and decreases for $k > 4$. An explanation of these results is possible if we assume that the overall H_m^E for these mixtures is due to (i) a positive contribution due to the breakdown of π — π association between the aromatic species, (ii) a positive contribution due to the breakdown of hydrogen bonding between alkanol molecules, and (iii) a negative contribution as a result of π —OH association between the aromatic and alkanol species. Furthermore, it is reasonable to assume that (a) the positive hydrogen-bond contribution (ii above) decreases as k increases, and (b) the magnitude of the negative contribution of the π —OH association, decreases by smaller amounts as k increases from 1 to 8. Assumption (a) is supported by the evidence of $H_m^E[x\text{C-C}_6\text{H}_{12} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$ which show that $H_m^E(\text{maximum})$ decreases steadily as k increases for 2 to 4.⁽⁸⁻¹⁰⁾ Methanol does not dissolve in cyclohexane in all proportions.

Assumption (b) is reasonable when we consider that the association between the aromatic group and the OH of our alkanol will decrease with increasing alkanol chain length because the longer the alkanol chain length the smaller is the contribution of the OH group to the overall property of the alkanol.

The results for $H_m^E[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{CH}_3\text{CH(OH)CH}_3]$ and $H_m^E[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_3\text{H}_7\text{-OH}]$ show that for each xylene isomer the two propanol isomers behave significantly differently. In all cases $H_m^E[\text{CH}_3\text{CH(OH)CH}_3] > H_m^E[\text{C}_3\text{H}_7\text{-OH}]$. This could be due to a weaker interaction of the aromatic component with the secondary alkanol than with the primary alkanol as a result of the steric effect of the methyl groups in the secondary alkanol which would tend to hide the OH group from the π -electron system of the aromatic component. This would have the effect of a smaller negative contribution to the overall H_m^E resulting in a larger positive H_m^E .

The authors wish to thank the FRD (South Africa) for financial support.

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M-2538

J. Chem. Thermodynamics 1990, 22, 1175–1179

Excess molar volumes of (a xylene + an alkanol) at 298.15 K

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(Received 16 July 1990)

The excess molar volumes V_m^E were measured as a function of mole fraction x at 298.15 K and atmospheric pressure for $[x\{\text{isomer of } C_6H_4(CH_3)_2\} + (1-x)C_kH_{2k+1}OH]$ where $k = 1, 2$, or 3 . A vibrating-tube densimeter (Paar DMA 601) was used to determine the excess molar volumes. The results are discussed in terms of the relative position of the methyl groups on the benzene ring, the carbon chain length of the alkanol, and the excess partial molar volumes at infinite dilution.

1. Introduction

We have previously reported the H_m^E s for $[x\{\text{isomer of } C_6H_4(CH_3)_2\} + (1-x)C_kH_{2k+1}OH]$ where $k = 1, 2$, or 3 .⁽¹⁾ In this work we report the V_m^E s for the same twelve pairs of liquids. V_m^E for six of the pairs have previously been reported by other workers,^(2–4) and are compared with our results.

In this paper we also report the excess partial molar volumes at infinite dilution. The excess partial molar volume of a xylene at infinite dilution in an alkanol is either negative or small and positive. By contrast the excess partial molar volume of an alkanol at infinite dilution in a xylene is large and positive.

2. Experimental

The xylenes and alkanols were the same as used in previous work.⁽¹⁾ All the liquids were degassed before use. The alkanols were dried⁽¹⁾ and kept in a glove box. They were analysed before use for water contamination. In all cases the mole fraction of H_2O was found to be less than 0.0001.

V_m^E s were calculated from molar masses and densities of pure liquids and mixtures measured using an Anton-Paar DNA 601 vibrating-tube density meter, thermostatted at (298.15 ± 0.005) K. As a check on the technique V_m^E s were obtained for $\{xC_6H_6 + (1-x)c\text{-}C_6H_{12}\}$. Our results agree well with the literature values.⁽⁵⁾

0021-9614/90/121175+05 \$02.00/0

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3. Results

The excess molar volumes V_m^E at 298.15 K are listed in table 1 for each of the twelve mixtures over the complete range of the mole fraction x . The composition dependence of V_m^E has been determined by the equation:

$$\Delta = V_m^E/(\text{cm}^3 \cdot \text{mol}^{-1}) - x(1-x) \sum_{r=0}^n A_r (1-2x)^r, \quad (1)$$

estimating the coefficients A_r by a method of unweighted least squares. The coefficients A_r are given in table 2 and the values of Δ are given in table 1.

4. Discussion

$V_m^E(298.15 \text{ K})$ has previously been measured for $\{xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$, ($k=2$ or 3),^(2,3) $\{xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$, ($k=2$ or 3),^(2,3) and $\{xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$, ($k=2$ or 3).⁽²⁻⁴⁾ The V_m^E s reported in this work compare well with the literature values; in no case is the difference greater than $0.010 \text{ cm}^3 \cdot \text{mol}^{-1}$.

The $V_m^E(x)$ curves for most of the mixtures reported here, are sine-shaped, being negative at low x values and positive at high x values. The $V_m^E(x)$ curves for the $[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}]$, ($k=1$) are similar in magnitude and in shape. The same is true for $k=2$ and also for $k=3$. In all cases the V_m^E s for the m -xylene mixtures are slightly more positive than the V_m^E s for either the o -xylene mixtures or the p -xylene mixtures. This is similar to the result reported by Rodríguez Nuñez, Paz Andrade, and Ortega⁽³⁾ for $[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}]$, ($k=3, 4$, or 5).

For the set of results $V_m^E[x\{o\text{- or } m\text{- or } p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}]$, ($k=1, 2$, or 3), the $V_{m,\text{max}}^E(\text{CH}_3\text{OH}) < V_{m,\text{max}}^E(\text{C}_2\text{H}_5\text{OH}) < V_{m,\text{max}}^E(\text{C}_3\text{H}_7\text{OH}) < V_{m,\text{max}}^E\{\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}$ and in most cases $V_{m,\text{min}}^E(\text{C}_2\text{H}_5\text{OH}) < V_{m,\text{min}}^E(\text{CH}_3\text{OH}) < V_{m,\text{min}}^E\{\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}$.

The excess partial molar volumes at infinite dilution offer a way of interpreting the interactions which give rise to these positive and negative V_m^E s. In this work $V_1^E(x \rightarrow 0)$ and $V_2^E(x \rightarrow 1)$ (where 1 refers to a xylene and 2 to an alkanol) have been calculated from the coefficients A_r given in table 2. The excess partial molar volume V_1^E at a mole fraction x is given by

$$V_1^E = (1-x)(dV_m^E/dx) + V_m^E,$$

and hence

$$V_1^E(x \rightarrow 0) = dV_m^E/dx, \quad V_1^E(x \rightarrow 0) = \sum_{r=0}^n A_r,$$

and similarly

$$V_2^E(x \rightarrow 1) = \sum_{r=0}^{n(\text{even})} A_r - \sum_{r=1}^{n(\text{odd})} A_r.$$

The $V_1^E(x \rightarrow 0)$ and $V_2^E(x \rightarrow 1)$ results are given in table 3. The negative or small and positive values for $V_1^E(x \rightarrow 0)$ are likely to be due to the formation of π electron-hydrogen-bond (π -HO) interactions and also to interstitial accommodation of the aromatic compound between the hydrogen-bonded alkanol network. The positive values of $V_2^E(x \rightarrow 1)$ are most likely due to the rupture of the alkanol-alkanol hydrogen bonds and alkanol dipole-dipole interactions.

$$V_m^E[x\{o\text{- or }m\text{- or }p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$$

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TABLE 1. Experimental excess molar volumes V_m^E at 298.15 K

x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$								
0.0147	-0.0042	13	0.1942	-0.0334	-7	0.7831	0.0125	-7
0.0236	-0.0074	12	0.3205	-0.0333	-20	0.8600	0.0183	-16
0.0304	-0.0105	2	0.3544	-0.0315	-15	0.9256	0.0191	9
0.0388	-0.0123	9	0.4388	-0.0243	12	0.9694	0.0143	41
0.0736	-0.0210	3	0.5659	-0.0123	27	0.9807	0.0108	39
0.1249	-0.0295	-8	0.6415	-0.0038	22	0.9893	0.0065	24
0.1746	-0.0302	17	0.7422	0.0036	-42	0.9934	0.0039	13
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$								
0.0117	-0.0093	31	0.2370	-0.0960	-29	0.7888	0.0536	13
0.0195	-0.0172	29	0.2936	-0.0918	-35	0.8471	0.0642	0
0.0247	-0.0227	22	0.3786	-0.0749	13	0.8752	0.0704	-20
0.0303	-0.0307	-8	0.4730	-0.0467	28	0.9345	0.0593	36
0.0462	-0.0414	11	0.5192	-0.0300	51	0.9706	0.0344	35
0.0604	-0.0514	8	0.6052	-0.0022	21	0.9798	0.0259	35
0.0917	-0.0688	3	0.6774	0.0216	-24	0.9889	0.0143	13
0.1543	-0.0868	13	0.7304	0.0380	-63	0.9911	0.0119	14
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$								
0.0106	-0.0081	2	0.2683	-0.0472	5	0.7666	0.0944	-3
0.0197	-0.0153	-4	0.3231	-0.0388	-1	0.7998	0.1009	-11
0.0316	-0.0237	-13	0.3851	-0.0270	-7	0.9010	0.0947	8
0.0427	-0.0290	-4	0.4678	-0.0050	9	0.9574	0.0556	5
0.0716	-0.0385	24	0.5324	0.0138	7	0.9777	0.0328	7
0.1248	-0.0521	10	0.6174	0.0424	-1	0.9804	0.0286	0
0.1984	-0.0572	-22	0.7097	0.0766	-1	0.9942	0.0091	0
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$								
0.0298	-0.0094	-6	0.2988	0.0421	-12	0.7223	0.1942	58
0.0356	-0.0118	-16	0.3313	0.0577	-12	0.7457	0.1935	-16
0.0580	-0.0140	0	0.3819	0.0830	-7	0.7968	0.1908	-21
0.0788	-0.0170	-10	0.4595	0.1179	-17	0.8742	0.1653	-20
0.1353	-0.0136	-3	0.5156	0.1427	3	0.8961	0.1515	-9
0.1433	-0.0118	2	0.5390	0.1520	11	0.9442	0.1063	43
0.1915	0.0023	26	0.6245	0.1764	0	0.9707	0.0613	8
0.2523	0.0241	18	0.6885	0.1930	35	0.9848	0.0345	10
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$								
0.1193	0.0038	2	0.5154	0.0260	10	0.8346	0.0465	-10
0.1735	0.0023	16	0.6006	0.0325	21	0.8639	0.0450	-13
0.2058	0.0041	2	0.6755	0.0380	12	0.9398	0.0352	37
0.2845	0.0095	-19	0.7622	0.0422	-24	0.9642	0.0241	27
0.3509	0.0155	-10	0.8117	0.0465	-8	0.9821	0.0131	13
0.4371	0.0208	-3	0.8250	0.0470	-6	0.9907	0.0072	8
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$								
0.0172	-0.0097	3	0.2647	-0.0344	5	0.7655	0.0868	-11
0.0377	-0.0199	1	0.3541	-0.0202	-4	0.8265	0.0936	-2
0.0484	-0.0215	27	0.4165	-0.0063	2	0.8802	0.0857	-16
0.0667	-0.0284	19	0.4643	0.0060	10	0.9374	0.0650	35
0.1064	-0.0389	-1	0.5155	0.0192	7	0.9674	0.0379	8
0.1725	-0.0438	-11	0.5604	0.0327	15	0.9789	0.0261	7
0.2206	-0.0427	-27	0.6833	0.0663	-16	0.9907	0.0140	21

TABLE 1—*continued*

x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$	x	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\Delta \cdot 10^4$
<i>xm-C₆H₄(CH₃)₂ + (1-x)C₃H₇-OH</i>								
0.0122	-0.0053	1	0.3011	0.0160	10	0.8548	0.1330	10
0.0260	-0.0081	21	0.3795	0.0329	-5	0.9212	0.1022	26
0.0409	-0.0112	29	0.4646	0.0604	62	0.9627	0.0587	12
0.0701	-0.0157	30	0.5301	0.0719	6	0.9756	0.0409	9
0.1198	-0.0176	13	0.6050	0.0923	-3	0.9859	0.0250	8
0.1977	-0.0113	-34	0.7077	0.1181	-37	0.9948	0.0095	2
0.2565	-0.0004	-50	0.7904	0.1344	-20			
<i>xm-C₆H₄(CH₃)₂ + (1-x)CH₃CH(OH)CH₃</i>								
0.0151	0.0033	-20	0.3148	0.1480	-11	0.7831	0.2935	-10
0.0273	0.0051	-42	0.3865	0.1930	-4	0.8668	0.2569	-27
0.0411	0.0118	-18	0.4768	0.2390	-9	0.9311	0.1832	15
0.0519	0.0160	-10	0.5286	0.2603	0	0.9722	0.0900	5
0.1218	0.0450	37	0.6010	0.2833	22	0.9811	0.0652	18
0.1967	0.0800	31	0.6655	0.2943	14	0.9905	0.0390	58
0.2664	0.1159	-24	0.7285	0.2972	-7			
<i>xp-C₆H₄(CH₃)₂ + (1-x)CH₃OH</i>								
0.0206	-0.0097	5	0.1915	-0.0462	-4	0.7857	0.0128	3
0.0268	-0.0128	11	0.2503	-0.0487	-23	0.8392	0.0160	-14
0.0361	-0.0168	-1	0.3105	-0.0453	-13	0.9015	0.0177	-6
0.0498	-0.0210	8	0.3694	-0.0390	8	0.9591	0.0157	42
0.0606	-0.0248	5	0.4535	-0.0306	14	0.9707	0.0096	7
0.1097	-0.0367	5	0.5819	-0.0144	18	0.9851	0.0053	3
0.1600	-0.0428	10	0.6879	-0.0031	-21	0.9943	0.0022	2
<i>xp-C₆H₄(CH₃)₂ + (1-x)C₂H₅OH</i>								
0.0207	-0.0216	-2	0.4014	-0.0614	-10	0.8480	0.0746	-24
0.0302	-0.0298	1	0.4770	-0.0369	33	0.9100	0.0680	-8
0.0513	-0.0423	37	0.5293	-0.0247	-6	0.9344	0.0628	45
0.0944	-0.0696	-2	0.5612	-0.0096	37	0.9594	0.0438	20
0.1594	-0.0864	-2	0.6133	0.0042	-13	0.9754	0.0297	20
0.2174	-0.0898	-10	0.6818	0.0312	-5	0.9850	0.0179	1
0.2583	-0.0850	10	0.7506	0.0558	-8	0.9885	0.0140	1
0.3234	-0.0799	-31	0.7915	0.0671	-13			
<i>xp-C₆H₄(CH₃)₂ + (1-x)C₃H₇-OH</i>								
0.0213	-0.0114	19	0.3066	-0.0382	14	0.8498	0.1080	-4
0.0445	-0.0260	-13	0.3802	-0.0260	-9	0.9075	0.0921	6
0.0576	-0.0279	25	0.4421	-0.0078	14	0.9558	0.0567	8
0.0726	-0.0339	17	0.4897	0.0077	26	0.9740	0.0375	16
0.1283	-0.0474	2	0.5312	0.0174	-14	0.9827	0.0265	16
0.1886	-0.0527	-17	0.6137	0.0503	9	0.9923	0.0120	4
0.2522	-0.0500	-29	0.7342	0.0903	-25			
<i>xp-C₆H₄(CH₃)₂ + (1-x)CH₃CH(OH)CH₃</i>								
0.0234	-0.0040	0	0.3139	0.1013	-10	0.7458	0.2292	-6
0.0439	-0.0048	-3	0.3891	0.1360	-13	0.8158	0.2164	6
0.0582	0.0000	34	0.4668	0.1722	29	0.8654	0.1877	-17
0.0754	0.0023	31	0.5308	0.1945	27	0.9049	0.1575	25
0.1281	0.0126	-18	0.5809	0.2083	15	0.9612	0.0792	14
0.1862	0.0374	-17	0.6236	0.2164	-10	0.9793	0.0452	8
0.2616	0.0756	-7	0.6835	0.2237	-39	0.9853	0.0329	7

$$V_m^E[x\{o\text{- or }m\text{- or }p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$$

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TABLE 2. Coefficients A_r of equation (1) for $V_m^E[x\{o\text{- or }m\text{- or }p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$ at 298.15 K

	A_0	A_1	A_2	A_3	A_4
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.0846	-0.1627	-0.0830	-0.2420	—
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.1653	-0.6280	-0.2215	-0.5512	—
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.0126	-0.5895	0.3745	-0.6326	—
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.5454	-0.7850	0.161	-0.5709	0.4474
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	0.0966	-0.0998	0.1679	-0.3538	—
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	0.0569	-0.5360	0.2856	-0.4520	—
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.2529	-0.5250	0.4220	-0.6306	—
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.9985	-0.7949	0.1011	-0.8667	0.9347
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.1071	-0.2359	0.0198	-0.2153	—
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.1336	-0.6146	0.2107	-0.5969	—
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.0335	-0.6524	0.4005	-0.4766	—
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.7254	-0.7028	0.2999	-0.5819	—

TABLE 3. The excess partial molar volumes at infinite dilution: $V_1^E(x \rightarrow 0)$ and $V_2^E(x \rightarrow 1)$ for $[x\{o\text{- or }m\text{- or }p\text{-C}_6\text{H}_4(\text{CH}_3)_2\} + (1-x)\text{C}_k\text{H}_{2k-1}\text{OH}]$, ($k = 1, 2$, or 3) at 298.15 K

	$V_1^E(x \rightarrow 0)$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_2^E(x \rightarrow 1)$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.57	0.24
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-1.12	1.24
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.84	1.61
$xo\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	-0.20	2.51
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.19	0.72
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.65	1.33
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.48	1.83
$xm\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.37	3.70
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{OH}$	-0.54	0.36
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$	-0.87	1.29
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{C}_3\text{H}_7\text{OH}$	-0.70	1.56
$xp\text{-C}_6\text{H}_4(\text{CH}_3)_2 + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	-0.26	2.31

At low mole fractions of xylene relatively few alkanol-alkanol bonds break and one imagines that the alkanol network is largely intact. This is supported by the fact that methanol does not mix with *m*-xylene at low mole fractions of *m*-xylene.

The work was supported by a grant from the CSIR (FRD) (South Africa).

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¹Copies of the results may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

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CAN. J. CHEM. VOL. 69, 1991

pp. 287 - 292

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Excess molar volumes of (a cycloalkane + an alkanol) at 298.15 K

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Received December 7, 1990

T. M. LETCHER and J. MERCER-CHALMERS. Can. J. Chem. 69, 000 (1991).

In this work we report the excess molar volumes, V_m^E , for the miscible mixtures $\{xc-C_5H_{10} + (1-x)CH_3OH\}$ and $\{xc-C_kH_{2k} + (1-x)C_lH_{2l+1}OH\}$ where $k = 5, 6, 7, 8$, or 10 and $l = 2$ or 3 . The V_m^E results are discussed in terms of the size of the cycloalkane ring and the type of alcohol.

Key words: Excess volumes, cycloalkane + alkanol.

T. M. LETCHER et J. MERCER-CHALMERS. Can. J. Chem. 69, 000 (1991).

On a déterminé les volumes molaires en excès, V_m^E , pour des mélanges miscibles de $\{xc-C_5H_{10} + (1-x)CH_3OH\}$ et de $\{xc-C_kH_{2k} + (1-x)C_lH_{2l+1}OH\}$ dans lesquels $k = 5, 6, 7, 8$ ou 10 et $l = 2$ ou 3 . On discute des valeurs de V_m^E obtenues en fonction de la grandeur du cycloalkane et du type d'alcool.

Mots clés : volumes en excès; cycloalkane + alcool.

Introduction

The excess molar volume, V_m^E , was measured as a function of mole fraction x at 298.15 K and one atmospheric pressure for the mixtures $\{xc-C_5H_{10} + (1-x)CH_3OH\}$ and $\{xc-C_kH_{2k} + (1-x)C_lH_{2l+1}OH\}$ where $k = 5, 6, 7, 8$, or 10 and $l = 2$ or 3 . The mixtures defined by $k = 6, 7, 8$, or 10 with $l = 1$ are not included as they are not miscible over the whole composition range. Of the sixteen data sets presented in this work four have been reported (1-4).

Experimental

The cycloalkanes were purified as previously described (5). The alkanols were dried as before (6, 7) and in all cases the water impurity (by Karl Fischer titration) was found to be less than 2×10^{-3} mole fraction. The cycloalkanes and the alkanols were analysed by g.l.c. and in all cases the purity was found to be better than 99.8 mol%.

The V_m^E values were calculated from molar masses and densities of pure liquids and mixtures using an Anton-Paar DMA 601 vibrating-tube density meter, thermostated at 298.15 ± 0.002 K. The method has been described (8).

Results

The V_m^E results have been deposited with the National Research Council of Canada and the Redlich Kister equation:

$$[1] \quad V_m^E = x(1-x)\sum_{r=0}^n A_r(1-2x)^r$$

has been fitted to the results. The coefficients A_r are given in Table 1, together with the standard deviation σ calculated from

$$\sigma = \sqrt{\sum (V_{m,exp} - V_{m,calc})^2 / (n - n_p)}$$

where n is the number of observations and n_p the number of parameters.

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Discussion

Our V_m^E results for (cyclopentane + ethanol) and (cyclohexane + ethanol) are within $0.005 \text{ cm}^3 \text{ mol}^{-1}$ of the results reported by Marsh and Burfitt (1). The V_m^E values reported here for (cyclohexane + ethanol) and those of ref. 1 compare well to those reported by Pardo and van Ness (2) but differ by as much as $0.03 \text{ cm}^3 \text{ mol}^{-1}$, in the worst case, when compared to the published results of Scatchard and Satkiewicz (3). Our results for (cyclohexane + 1-propanol) compare reasonably well with those published by Janssens and Ruel (4) and differ by only $0.012 \text{ cm}^3 \text{ mol}^{-1}$ from their smoothing curve.

The V_m^E values for all the mixtures, except for (cyclodecane + 2-propanol) at low cyclodecane concentrations, are positive over the whole composition range. This is most likely a result of the breakdown of the hydrogen bonding between the alcohol molecules on addition of the cycloalkane. The $V_{m,\text{maximum}}^E$ for all the systems presented here lie between $+0.16$ and $+0.57 \text{ cm}^3 \text{ mol}^{-1}$.

The $V_m^E(x = 0.5)$ results for all sixteen systems has been plotted as a function of cycloalkane carbon number, k , in Fig. 1. The values for the cyclopentane systems are very much lower than the values predicted by the pattern generated by the other cycloalkanes. This is reminiscent of the $V_m^E(x = 0.5)$ values obtained for cycloalkane + n -alkane mixtures (9). For these mixtures the $V_m^E(x = 0.5)$ values for the cyclopentane systems are all less positive than the $V_m^E(x = 0.5)$ predicted by the pattern generated by the cyclohexane, cycloheptane, cyclooctane, and cyclodecane systems. It is possible that the small size of the cyclopentane molecule results in a compact packing structure within the hydrogen bonded network of alcohol molecules, resulting in a small overall volume of mixing.

The magnitude of $V_m^E(x = 0.5)$, for mixtures of a cycloalkane + a 1-alkanol is also dependant on the 1-alkanol chain length. From Fig. 1, for any given cycloalkane, $V_m^E(x = 0.5)$ decreases with increasing alkanol chain length. This could be a direct result of the fact that hydrogen bonding decreases in alcohols with increasing chain length. The breakdown of this hydrogen bonding on mixing results in methanol producing a more positive V_m^E than ethanol, and ethanol in turn producing a more positive effect than 1-propanol. The effect of the branched alkane chain in 2-propanol produces an effect which lies between that of ethanol and 1-propanol.

Acknowledgement

The authors thank the F.R.D. (South Africa) for financial assistance.

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List of Publications

DIRECTORY: CHEMISTRY (August)

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TABLE 1. Coefficients A_r for eq. [1] for $x\text{C}_k\text{H}_{2k} + (1-x)\text{C}_m\text{H}_{2m+1}$ at 298.15 K together with the standard deviation σ

Mixture	A_0	A_1	A_2	A_3	$10^3 \sigma$ $\text{cm}^3 \text{mol}^{-1}$
$x\text{C}_5\text{H}_{10} + (1-x)\text{CH}_3\text{OH}$	1.9514	0.4342	0.9656	-0.1687	4.1
$x\text{C}_5\text{H}_{10} + (1-x)\text{C}_2\text{H}_5\text{OH}$	1.6064	-0.0402	0.5416	-0.5086	2.2
$x\text{C}_5\text{H}_{10} + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.8450	-0.5754	0.0151	-0.2571	4.1
$x\text{C}_5\text{H}_{10} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.5852	-0.8136	0.3208	-0.1953	4.1
$x\text{C}_6\text{H}_{12} + (1-x)\text{C}_2\text{H}_5\text{OH}$	2.2415	0.0929	0.5840		2.3
$x\text{C}_6\text{H}_{12} + (1-x)\text{C}_3\text{H}_7\text{OH}$	1.6630	0.4139	0.5662	0.2748	2.3
$x\text{C}_6\text{H}_{12} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	2.2612	-0.5714	0.7348	-0.4252	3.1
$x\text{C}_7\text{H}_{14} + (1-x)\text{C}_2\text{H}_5\text{OH}$	2.1221	-0.1844	1.0334		2.2
$x\text{C}_7\text{H}_{14} + (1-x)\text{C}_3\text{H}_7\text{OH}$	1.4371	-0.3566	0.5649	-0.1863	2.0
$x\text{C}_7\text{H}_{14} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.8969	-0.6406	0.6743		1.8
$x\text{C}_8\text{H}_{16} + (1-x)\text{C}_2\text{H}_5\text{OH}$	1.6103	-0.0137	0.8618	-0.2123	3.1
$x\text{C}_8\text{H}_{16} + (1-x)\text{C}_3\text{H}_7\text{OH}$	1.1572	-0.4122	0.5879	-0.1477	3.0
$x\text{C}_8\text{H}_{16} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.4506	-0.6456	0.4786		2.7
$x\text{C}_{10}\text{H}_{20} + (1-x)\text{C}_2\text{H}_5\text{OH}$	0.9207	-0.2672	0.4438		2.6
$x\text{C}_{10}\text{H}_{20} + (1-x)\text{C}_3\text{H}_7\text{OH}$	0.6797	-0.6150	0.2116	-0.2023	2.9
$x\text{C}_{10}\text{H}_{20} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.5563	-0.6250	-0.1743		2.0

—END OF FILE 2—

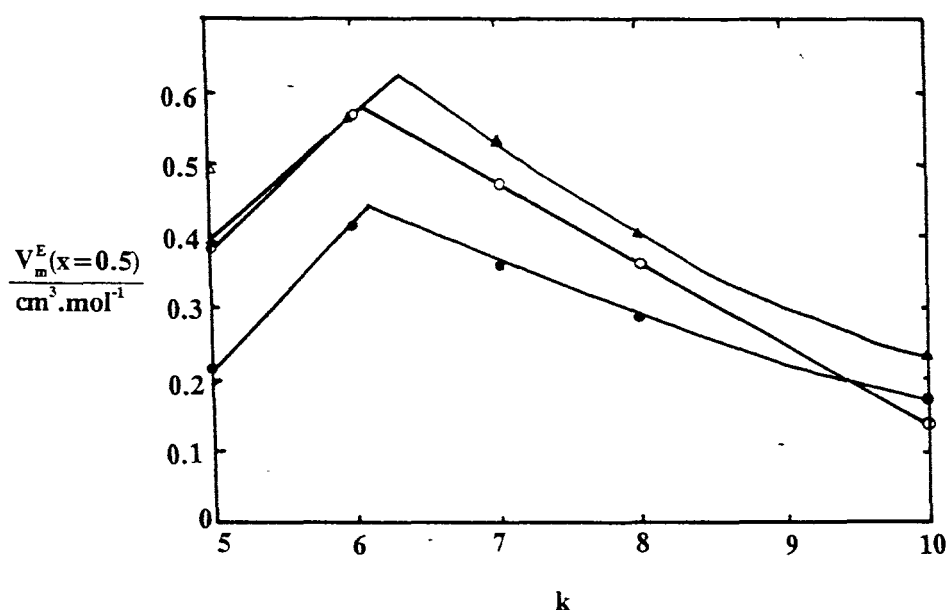


FIG. 1. $V_m^E(x=0.5)$ for $\{x\text{C}-\text{C}_k\text{H}_{2k} + (1-x)\text{C}_l\text{H}_{2l+1}\text{OH}\}$ against k . Δ , CH_3OH ; $\blacktriangle$, $\text{C}_2\text{H}_5\text{CH}_3$; $\bullet$, $\text{C}_3\text{H}_7\text{OH}$; $\circ$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.

Excess molar enthalpies of mixtures of a cycloalkane and an alkanol

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Abstract

The excess molar enthalpies, H_m^E , for the sixteen mixtures, (cyclo- $C_kH_{2k} + CH_3OH$) and (cyclo- $C_kH_{2k} + C_lH_{2l+1}OH$) with $k = 5, 6, 7, 8$ and 10 and $l = 2$ and 3 , were measured at 298.15 K. The H_m^E results are discussed in terms of the size of the cycloalkane ring and the length of the alkanol chain.

INTRODUCTION

In the present work, we investigated the excess molar enthalpy (H_m^E) values obtained on mixing a cycloalkane with an alkanol. Our results show the effect on H_m^E of increasing the ring size of the cycloalkane and also the effect of increasing the chain length of the alkanol. We studied the systems (x c- $C_5H_{10} + (1-x)CH_3OH$) and (x c- $C_kH_{2k} + (1-x)C_lH_{2l+1}OH$) for $k = 5, 6, 7, 8$ and 10 , and $l = 2$ and 3 . These mixtures are miscible over the whole concentration range.

The H_m^E values for five of these sixteen systems have been published [1–9] and are compared with our results.

EXPERIMENTAL

The purification procedures used [10–12] and the flow calorimeter (LKB 2107) method for determining H_m^E have been previously described [13].

RESULTS

The H_m^E results for each of the sixteen systems are given in Table 1 together with the deviations, Δ , calculated from the smoothing equation

$$\Delta(\text{J mol}^{-1}) = H_m^E(\text{J mol}^{-1}) - x(1-x) \sum_{r=0}^r A_r(1-2x)^r \quad (1)$$

where x denotes the mole fraction. The coefficients, A_r , are given in Table 2.

TABLE 1

Molar excess enthalpies, H_m^E for $(xC_kH_{2k} + (1-x)C_lH_{2l-1}OH)$ at 298.15 K and the deviations, Δ , from eqn. (1) and the coefficients of Table 2

x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)
$xc-C_5H_{10} + (1-x)CH_3OH$								
0.0747	249.8	-4.9	0.3754	556.1	-0.2	0.6735	513.6	-0.7
0.1332	375.9	4.0	0.4072	562.0	-0.7	0.7964	438.1	0.7
0.1953	452.5	1.3	0.4817	566.3	-0.6	0.8523	375.4	-3.7
0.2410	491.4	0.2	0.5762	553.7	2.7	0.9188	269.5	3.3
0.3009	526.0	-2.1						
$xc-C_5H_{10} + (1-x)C_2H_5OH$								
0.0639	119.1	-4.7	0.4114	482.8	-4.3	0.6659	537.2	3.2
0.1251	210.3	-1.2	0.4836	519.4	-0.1	0.7752	497.7	-9.4
0.1911	297.0	5.9	0.5732	538.7	2.2	0.8863	404.5	3.6
0.2398	346.8	2.7	0.6205	541.0	3.7	0.9493	240.7	1.8
0.3365	430.9	-3.9						
$xc-C_5H_{10} + (1-x)C_3H_7OH$								
0.1005	127.2	-2.2	0.4839	455.0	-5.0	0.7215	528.4	2.0
0.1833	200.4	1.0	0.5220	478.2	-1.9	0.7965	512.3	-5.2
0.3001	311.7	3.8	0.5610	500.7	4.6	0.8512	480.7	-3.3
0.4070	405.1	-0.7	0.6198	520.3	7.4	0.9183	376.4	6.6
0.4536	437.5	3.3	0.6833	521.0	-2.5	0.9581	232.8	-0.3
$xc-C_5H_{10} + (1-x)CH_3CH(OH)CH_3$								
0.1025	192.7	-3.5	0.4137	604.8	-4.2	0.7757	662.8	-6.7
0.1745	304.3	-0.1	0.5225	685.9	-0.9	0.8427	595.6	0.2
0.1806	317.0	3.7	0.6040	715.3	3.7	0.9183	419.4	2.4
0.2971	477.8	2.5	0.6302	715.8	2.0	0.9503	291.2	0.8
0.3497	539.6	-1.2	0.7251	699.6	1.8			
$xc-C_6H_{12} + (1-x)C_2H_5OH$								
0.0983	241.1	0.7	0.4884	632.0	-2.4	0.7150	602.5	2.8
0.1736	361.5	-1.9	0.5317	637.7	-2.1	0.8009	540.5	-8.7
0.2558	473.5	4.2	0.5844	639.4	2.3	0.8619	475.0	-5.6
0.3586	570.1	0.2	0.6533	627.5	5.6	0.8967	426.2	9.9
0.4530	621.5	-2.7						
$xc-C_6H_{12} + (1-x)C_3H_7OH$								
0.1436	230.7	-1.7	0.5543	604.5	-3.8	0.7483	592.3	-5.0
0.2511	356.7	3.2	0.6018	619.5	2.8	0.8198	554.2	-1.5
0.3642	479.4	-0.9	0.6415	621.3	3.6	0.8936	451.6	1.1
0.4157	528.0	-1.4	0.6935	614.8	2.7	0.9344	338.2	1.4
$xc-C_6H_{12} + (1-x)CH_3CH(OH)CH_3$								
0.1347	313.6	-4.2	0.5536	826.1	-0.9	0.7455	766.2	-6.1
0.2619	542.1	10.2	0.5942	836.7	4.6	0.8362	651.4	-7.6
0.3557	663.0	-5.5	0.6251	835.3	5.4	0.8991	517.6	8.4
0.4471	762.3	-6.1	0.6895	812.0	2.8			

TABLE 1 (continued)

x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)
$xc-C_7H_{14} + (1-x)C_2H_5OH$								
0.0889	243.6	-2.2	0.5299	660.9	-3.6	0.7526	592.1	-6.0
0.1641	383.4	0.1	0.6003	657.6	3.2	0.8369	530.3	-1.7
0.2447	499.7	4.0	0.6646	639.8	4.3	0.8891	449.3	-0.7
0.3431	594.8	-1.2	0.6856	630.6	2.7	0.9521	265.0	5.2
0.4076	635.9	2.1						
$xc-C_7H_{14} + (1-x)C_3H_7OH$								
0.0913	171.6	-5.2	0.4174	557.7	-2.6	0.6589	636.0	1.8
0.1685	296.5	4.6	0.5438	619.2	-2.1	0.7026	626.7	-2.4
0.2519	402.8	3.1	0.5850	633.6	3.4	0.8655	495.7	-9.8
0.3516	503.0	-3.6	0.6073	636.2	3.2	0.9132	407.2	10.1
$xc-C_7H_{14} + (1-x)CH_3CH(OH)CH_3$								
0.0969	259.8	0.9	0.5051	837.1	2.7	0.6320	865.2	-7.0
0.1776	440.6	0.4	0.5462	860.1	3.3	0.7298	815.2	6.3
0.3191	656.4	-5.5	0.5732	865.0	-1.9	0.7998	690.6	1.9
0.4205	774.6	5.9	0.6003	867.9	-4.6	0.9008	388.0	-3.0
$xc-C_8H_{16} + (1-x)C_2H_5OH$								
0.0793	237.1	-1.6	0.4362	615.0	-3.6	0.7244	575.8	2.2
0.1473	369.4	-1.7	0.4718	623.2	-1.4	0.8065	517.3	-6.1
0.2182	472.6	3.1	0.5023	624.6	-1.6	0.8695	442.8	-5.9
0.3047	557.2	3.9	0.5632	623.4	1.9	0.9219	345.1	9.7
0.3791	596.3	-2.7	0.6237	614.0	5.5			
$xc-C_8H_{16} + (1-x)C_3H_7OH$								
0.0430	95.5	-2.0	0.5220	617.6	3.6	0.8202	563.4	-1.8
0.1531	284.5	-0.5	0.5663	632.2	1.1	0.8772	476.6	-6.3
0.2314	394.2	2.8	0.6095	638.7	3.3	0.9151	395.2	3.9
0.3902	552.7	-6.0	0.6433	637.9	2.4	0.9542	255.3	5.0
0.4402	584.6	-1.8	0.7015	628.2	-0.2			
$xc-C_8H_{16} + (1-x)CH_3CH(OH)CH_3$								
0.0631	192.9	-5.2	0.5287	788.6	0.2	0.7033	767.4	-4.6
0.1371	377.2	2.4	0.5852	796.1	2.1	0.7828	712.9	-7.2
0.2371	558.2	5.4	0.6093	796.8	3.5	0.8512	630.3	5.5
0.3402	675.3	-5.6	0.6459	793.1	4.4	0.9217	430.1	0.3
0.4458	757.1	-2.6						
$xc-C_{10}H_{20} + (1-x)C_2H_5OH$								
0.1168	450.2	0.7	0.4037	489.6	1.1	0.6513	450.4	1.5
0.2081	367.4	-1.3	0.4818	496.5	-1.3	0.7512	370.9	-1.4
0.3034	445.6	-0.5	0.5362	490.1	2.4	0.8921	211.0	0.7
0.3523	473.0	1.7	0.6034	474.3	1.7	0.9317	117.4	-0.5

TABLE 1 (continued)

x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	Δ (J mol ⁻¹)
$x\text{-C}_{10}\text{H}_{20} + (1-x)\text{C}_3\text{H}_7\text{OH}$								
0.1394	246.2	-2.4	0.5350	489.4	-1.6	0.7236	460.2	1.5
0.2453	353.7	4.1	0.5736	494.2	0.9	0.7850	419.9	-0.7
0.3465	420.8	0.1	0.6019	494.0	1.8	0.8693	320.1	-10.0
0.4502	466.6	-4.2	0.6575	485.6	2.8	0.9321	223.1	10.3
$x\text{-C}_{10}\text{H}_{20} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$								
0.0729	233.1	6.1	0.5037	662.2	-4.1	0.6512	658.2	1.7
0.1467	353.2	-6.7	0.5448	668.2	-4.7	0.7126	636.2	9.9
0.2172	448.0	-1.1	0.5819	670.0	-2.5	0.8382	493.3	-11.9
0.3560	593.3	8.7	0.6156	668.9	1.7	0.9301	312.6	7.3
0.4362	638.2	-1.1						

TABLE 2

Smoothing coefficients, A_r , for $x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_l\text{H}_{2l+1}\text{OH}$

k	Alkanol	A_0	A_1	A_2	A_3	A_4
5	CH ₃ OH	2262.1	194.0	958.3	-226.7	1345.0
5	C ₂ H ₅ OH	2097.1	-542.5	507.3	-1288.6	1582.6
5	C ₃ H ₇ OH	1876.2	-1068.9	300.3	-1407.0	2295.6
5	CH ₃ CH(OH)CH ₃	2699.9	-1149.8	493.0	-1254.6	1666.8
6	C ₂ H ₅ OH	2546.4	-324.6	495.3	-1270.7	1876.9
6	C ₃ H ₇ OH	2350.1	-1005.1	104.3	-1197.5	2467.1
6	CH ₃ CH(OH)CH ₃	3223.4	-1104.3	280.7	-1034.4	1978.1
7	C ₂ H ₅ OH	2655.7	-153.3	643.9	-1463.8	1935.0
7	C ₃ H ₇ OH	2425.1	-828.2	762.7	-1331.1	1346.1
7	CH ₃ CH(OH)CH ₃	3324.0	-1307.3	1437.0	661.1	-1402.0
8	C ₂ H ₅ OH	2505.1	-24.3	961.5	-1114.6	1533.1
8	C ₃ H ₇ OH	2456.4	-719.4	793.3	-1372.3	1369.4
8	CH ₃ CH(OH)CH ₃	3125.7	-590.4	1262.9	-1378.6	1197.5
10	C ₂ H ₅ OH	1988.6	133.5	360.3	198.4	76.0
10	C ₃ H ₇ OH	1940.8	-434.6	507.8	-205.4	956.1
10	CH ₃ CH(OH)CH ₃	2661.3	-538.8	452.4	-301.8	1905.9

DISCUSSION

The H_m^E values for five of the sixteen systems investigated here have been published previously. The results of Stokes and Burfitt [1] for cyclopentane plus ethanol and cycloheptane plus ethanol are within 5 J mol⁻¹ of the smoothing curves fitted to our results, except at very low alcohol concentrations. For cyclohexane plus ethanol, our results are within 10 J mol⁻¹, in the worst case, of the results given by Nagata and Kazuma [2] and also by

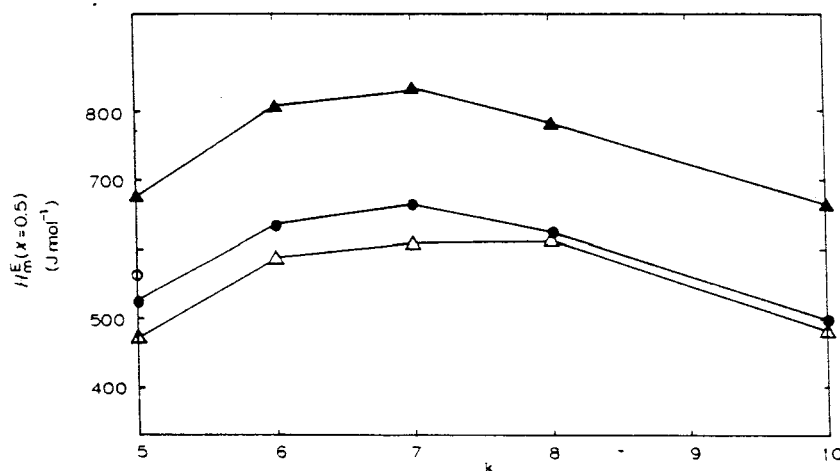


Fig. 1. Interpolated excess molar enthalpy data, $H_m^E(x=0.5)$, for $(x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_l\text{C}_{2l+1}\text{OH})$ as a function of k : ○, CH_3OH ; ●, $\text{C}_2\text{H}_5\text{OH}$; △, $\text{C}_3\text{H}_7\text{OH}$; and ▲, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.

Stokes and Adamson [3]. Our results for cyclohexane plus 2-propanol are within 10 J mol^{-1} of the smoothing curves based on the data of Veselý et al. [4] and Nagata et al. [5].

There are four sets of data in the literature for the H_m^E value for $(x\text{C}_6\text{H}_{12} + (1-x)\text{C}_3\text{H}_7\text{OH})$ [6–9]. Our results are within 5 J mol^{-1} , in the worst case, of the smoothing curve for the data given by Nagata and Kazuma [6] but almost 30 J mol^{-1} higher than the published data of Veselý and Pick [7,8] and 80 J mol^{-1} lower than the published data of Belousov et al. [9].

The H_m^E values for all the sixteen systems discussed here are positive, with $H_m^E(\text{maximum})$ ranging from 490 to 866 J mol^{-1} . This reflects the breakdown of the hydrogen bonding between the alkanol molecules on mixing with a cyclo compound.

For each particular alkanol, the value of $H_m^E(\text{maximum})$ or $H_m^E(x=0.5)$ increases with increasing cycloalkane carbon number from $k=5$ to $k=7$ and decreases from $k=7$ to $k=10$. This can be seen in Fig. 1 where $H_m^E(x=0.5)$ has been plotted against k . The concentration of the cycloalkane at which $H_m^E(\text{maximum})$ occurs for a particular alkanol, decreases with increasing cycloalkane carbon number. For example for ethanol systems, $H_m^E(\text{maximum})$ occurs at $x=0.61$ for $k=5$, $x=0.56$ for $k=6$, $x=0.54$ for $k=7$, $x=0.51$ for $k=8$ and $x=0.45$ for $k=10$.

For cyclopentane systems, $H_m^E(x=0.5)$ decreases with increasing chain length of the 1-alkanols from $l=1$ to $l=3$. The same is true for each of the other cycloalkanes for $l=2$ and 3. This can be attributed to the decreasing hydrogen bonding between alcohol molecules as l increases from 1 to 3.

The $H_m^E(x=0.5)$ value for $(x\text{-C}_k\text{H}_{2k} + (1-x)\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)$ is larger than $H_m^E(x=0.5)$ for $(x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_2\text{H}_5\text{OH})$ or $(x\text{-C}_k\text{H}_{2k} + (1-x)\text{C}_3\text{H}_7\text{OH})$ for k between 5 and 10. This implies a stronger hydrogen bonding between 2-propanol molecules than between ethanol molecules or between 1-propanol molecules. This could be due to the inductive effect of the methyl groups of 2-propanol.

ACKNOWLEDGEMENTS

The authors wish to thank the FRD (South Africa) and Rhodes University for financial help.

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Excess molar enthalpies and excess molar volumes on mixing an aromatic compound with an alcohol at 298,15 K

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Received 3 August 1990

Excess molar volumes for (toluene + methanol, + ethanol, + propan-1-ol, and + propan-2-ol) have been determined. These results together with the excess molar enthalpies and excess molar volumes for related binary systems of (benzene, toluene, *o*-, *m*-, *p*-xylene, and mesitylene + methanol, + ethanol, + propan-1-ol, and + propan-2-ol) are compared and discussed in terms of the influence of the methyl groups on the benzene ring. The excess molar volume results for mesitylene mixtures do not fit the patterns generated by the other aromatic systems.

Oortollige molêre volumes vir (tolueen + metanol, + etanol, + propan-1-ol, en + propan-2-ol) is vasgestel. Hierdie resultate saam met die oortollige molêre entalpieë en oortollige molêre volumes vir die verwante binêre sisteme van (benseen, tolueen, *o*-, *m*-, *p*-xileen, en mesitileen + metanol, + etanol, + propan-1-ol, en + propan-2-ol), word vergelyk en bespreek in terme van die invloed van die metielgroepe op die benseenring. Die oortollige molêre volume-resultate vir mesitileenmengsels volg nie die patrone wat ander aromatiese sisteme genereer nie.

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The aim of this work is to investigate the effect on H_m^E and V_m^E of the methyl groups in toluene, *o*-, *m*-, *p*-xylene, and mesitylene on mixing with an alcohol. In this work, the alcohols included methanol, ethanol, propan-1-ol, and propan-2-ol. Most of the H_m^E and V_m^E data for these systems have been reported in the literature.¹⁻⁹ The outstanding data, V_m^E (toluene + methanol, + ethanol, + propan-1-ol, and + propan-2-ol) are reported here.

Experimental

The V_m^E results were determined from accurate density data using a Paar (DMA 601) vibrating tube density meter. The method has been described.^{10,11}

The toluene was obtained from BDH (Analar grade) and was distilled before use. The alcohols, methanol (Merck, Uvasol grade), ethanol (NCP South Africa, absolute grade), propan-1-ol and propan-2-ol (BDH) were repeatedly dried

with magnesium metal activated with iodine, using the method of Lund and Bjerrum,¹² before distillation.

Gas chromatography was used to determine the purity of the liquids. The results (mol %) were toluene (99,8), methanol (99,9), ethanol (99,9), propan-1-ol (99,8), and propan-2-ol (99,7). The concentration of water in the alcohols was determined by the Karl Fisher method and was always found to be less than 0,01 mol %.

Results and Discussion

The V_m^E results are given in Table 1 together with the residual value Δ obtained by fitting the following Redlich-Kister equation to the data:

$$\Delta = V_m^E / (\text{cm}^3 \text{mol}^{-1}) - x(1-x) \sum_{i=0}^n A_i (1-2x)^i \quad (1)$$

where x refers to the mole fraction of the aromatic component. The coefficients A_i are given in Table 2.

Table 1 Excess molar volumes and the deviations Δ from eqn. (1) for $\{x \text{C}_6\text{H}_5(\text{CH}_3) + (1-x)\text{C}_k\text{H}_{2k+1}\text{OH}\}$ at 298,15 K

V^E			V^E			V^E		
$10^4 \Delta$			$10^4 \Delta$			$10^4 \Delta$		
x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$
Methanol								
0.0039	-0.0013	12	0.3793	-0.0767	-27	0.8588	0.0125	-10
0.0318	-0.0169	17	0.4173	-0.0700	12	0.9399	0.0174	26
0.0854	-0.0415	5	0.4981	-0.0593	25	0.9405	0.0165	26
0.1315	-0.0536	24	0.6433	-0.0323	12	0.9877	0.0053	8
0.1734	-0.0668	-20	0.7794	-0.0044	-37	0.9964	0.0019	5
0.2039	-0.0705	-11	0.8303	0.0091	-2			
Ethanol								
0.0031	-0.0035	0	0.4537	-0.0748	11	0.9058	0.0506	-4
0.0428	-0.0406	11	0.5132	-0.0570	8	0.9542	0.0368	28
0.1222	-0.0863	16	0.6085	-0.0222	13	0.9775	0.0207	15
0.2269	-0.1096	-14	0.7234	0.0182	-27	0.9963	0.0055	19
0.2792	-0.1092	-16	0.8629	0.0538	-4			

Table 1 Continued

V^E			$10^4\Delta$			V^E			$10^4\Delta$		
x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	x	$\text{cm}^3 \text{mol}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$
Propan-1-ol											
0.0042	-0.0033	-1	0.5062	-0.0111	18	0.9215	0.0613	10			
0.0528	-0.0298	32	0.5603	0.0078	26	0.9615	0.0379	17			
0.1443	-0.0624	-2	0.6451	0.0345	-3	0.9826	0.0203	22			
0.2787	-0.0671	-25	0.7496	0.0626	-41	0.9917	0.0100	9			
0.3504	-0.0543	-4	0.8792	0.0744	4						
Propan-2-ol											
0.0065	-0.0013	8	0.5157	0.1700	26	0.9289	0.1209	31			
0.1154	-0.0017	6	0.5684	0.1877	18	0.9716	0.0529	18			
0.1230	0.0007	11	0.6488	0.2056	-17	0.9879	0.0243	-3			
0.2349	0.0404	-12	0.7422	0.2140	-23	0.9929	0.0143	-4			
0.3467	0.0926	-18	0.8957	0.1538	4						

Table 2 The coefficients A_i for the Redlich-Kister equation $H_m^E = x(1-x) \sum_{i=0}^n A_i (1-2x)^i$ for H_m^E ($x \text{C}_6\text{H}_6 - m - (\text{CH}_3)_m + (1-x)\text{C}_n\text{H}_{2n+1}\text{OH}$), together with the references and $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ (where 1 refers to the aromatic component and 2 refers to the alcohol)

System	A_0	A_1	A_2	A_3	A_4	A_5	Ref.	$H^E(x_1 = 0)$	$H^E(x_2 = 0)$
								J mol ⁻¹	J mol ⁻¹
$\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}$	2435.0	-1669.0	883.0	-703.0	2406.0	-1925.0	1	1427	10021
+ $\text{C}_2\text{H}_5\text{OH}$	3134.5	-2235.7	1112.2	-1710.8	1817.1		2	2117	10011
+ $\text{C}_3\text{H}_7\text{OH}$	3829.1	-1905.0	108.0	-2742.0	3798.5		3	3089	12383
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	5055.3	-1309.0	2149.0	-3142.2			3	2753	11655
$\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_3\text{OH}$	2392.4	-1000.8	2553.6	-3291.1			3	654	92379
+ $\text{C}_2\text{H}_5\text{OH}$	2914.2	-1549.9	140.8	-2823.5	3763.9		3	2445	11192
+ $\text{C}_3\text{H}_7\text{OH}$	3433.9	-1699.7	2316.2	-3245.0			3	805	10694
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4959.0	-2080.7	1374.0				4	4252	8413
$o\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	2787.0	-1189.1	1337.5	-1810.8			5(a)	1125	7125
+ $\text{C}_2\text{H}_5\text{OH}$	3091.0	-1533.7	1784.0	-1901.6			5(a)	1439	5310
+ $\text{C}_3\text{H}_7\text{OH}$	3696.2	-1605.1	594.4	-2558.5			5(a)	126	8454
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4703.6	-1404.5	2235.3	-1813.1			5(a)	3721	10157
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	2728.6	-1070.8	1455.0	-1917.2			5(a)	1196	7172
+ $\text{C}_2\text{H}_5\text{OH}$	3034.4	-1452.4	1843.2	-2230.6			5(a)	1194	8560
+ $\text{C}_3\text{H}_7\text{OH}$	3621.0	-1665.1	1080.2	-2216.9			5(a)	819	8583
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4644.5	-1168.6	2332.9	-2665.6			5(a)	3143	10812
$p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	2631.2	-1021.0	988.4	-2368.2			5(a)	230	7009
+ $\text{C}_2\text{H}_5\text{OH}$	2934.6	-1389.0	796.7	-2665.0			5(a)	-323	7786
+ $\text{C}_3\text{H}_7\text{OH}$	3452.6	-1716.7	607.9	-2565.8			5(a)	-223	8344
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4500.9	-1449.8	2296.9	-1890.7			5(a)	3457	10139
1,3,5- $\text{C}_6\text{H}_3(\text{CH}_3)_3 + \text{CH}_3\text{OH}$	2922.4	-1236.8	2161.6	-894.6			6	-2952	7215
+ $\text{C}_2\text{H}_5\text{OH}$	3239.7	-1376.5	2555.0	-1123.3			6	-3294	8294
+ $\text{C}_3\text{H}_7\text{OH}$	3827.0	-1679.6	2236.2	-1447.9			6	-2935	9190
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4933.5	-1499.9	1700.9	-147.9			6	-4986	8281

The only reported values of V_m^E (toluene + an alcohol) are for the (toluene + ethanol) system and have been reported by Pardo and Van Ness⁸ and also by Myers and Clever.⁹ The more precise work of Pardo and Van Ness is very similar to ours over most of the composition range, but values are lower than ours by 0.010 $\text{cm}^3 \text{mol}^{-1}$ at the V_m^E minimum region at $x = 0.25$. Our results are within the experimental errors calculated for the Myers and Clever data.⁹

The H_m^E and V_m^E data for the binary mixtures of benzene, toluene, *o*-, *m*-, *p*-xylene, and mesitylene + methanol, + ethanol, + propan-1-ol and + propan-2-ol are summarized in Figures 1 and 2. The coefficients of the Redlich-Kister equation fitted to the H_m^E and V_m^E data, together with the literature references, are given in Tables 2 and 3 respectively.

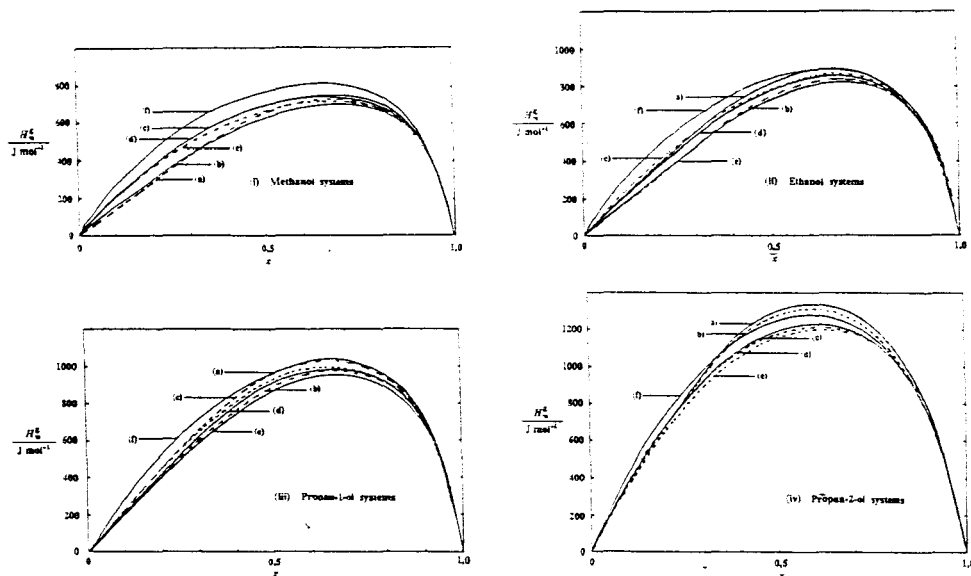


Figure 1 The H_m^E for $\{x C_6H_{6-m}(CH_3)_m + (1-x)C_6H_{2k+1}OH\}$ at 298.25 K: (a) C_6H_6 ; (b) $C_6H_5CH_3$; (c) $o-C_6H_4(CH_3)_2$; (d) $m-C_6H_4(CH_3)_2$; (e) $p-C_6H_4(CH_3)_2$; (f) $1,3,5-C_6H_3(CH_3)_3$.

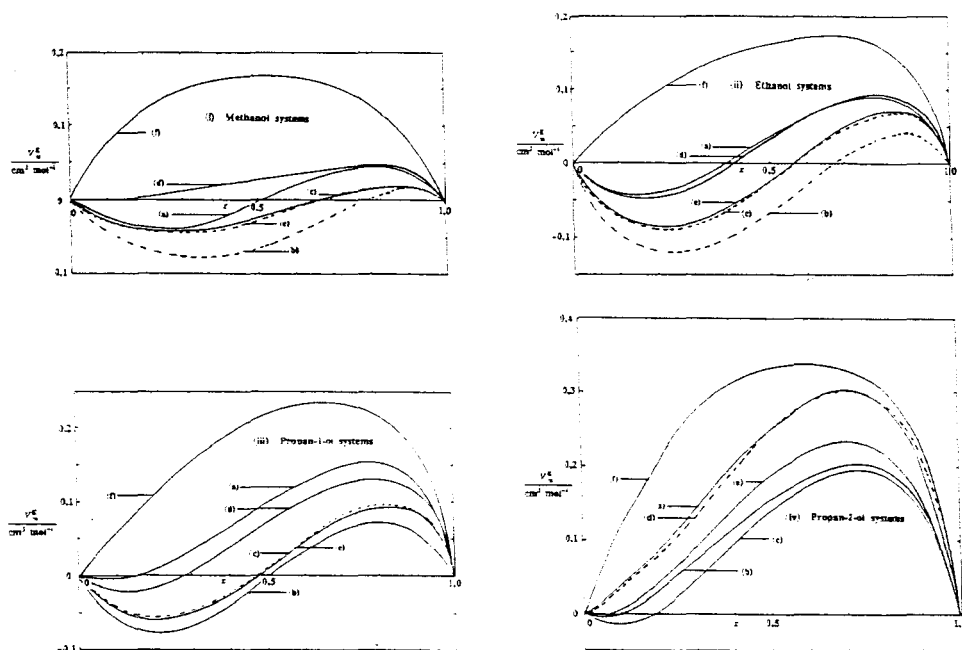


Figure 2 The V_m^E for $\{x C_6H_{6-m}(CH_3)_m + (1-x)C_6H_{2k+1}OH\}$ at 298.25 K: (a) C_6H_6 ; (b) $C_6H_5CH_3$; (c) $o-C_6H_4(CH_3)_2$; (d) $m-C_6H_4(CH_3)_2$; (e) $p-C_6H_4(CH_3)_2$; (f) $1,3,5-C_6H_3(CH_3)_3$.

Table 3 The coefficients B_i for the Redlich–Kister equation $V_m^E = x(1-x) \sum_{i=0}^n B_i(1-2x)^i$ for V_m^E of $\{x\text{C}_6\text{H}_5\text{--}m(\text{CH}_3)_m + (1-x)\text{C}_4\text{H}_{2k+1}\text{OH}\}$, together with the references and $V_m^E(x_1 = 0)$ and $V_m^E(x_2 = 0)$ (where 1 refers to the aromatic component and 2 refers to the alcohol; tw refers to this work)

System	B_0	B_1	B_2	B_3	B_4	Ref.	$V_m^E(x_1 = 0)$	$V_m^E(x_2 = 0)$
							cm ³ mol ⁻¹	cm ³ mol ⁻¹
$\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}$	-0.0054	-0.1765	0.0766	-0.2015		7	-0.31	0.45
+ $\text{C}_2\text{H}_5\text{OH}$	0.1162	-0.5603	0.1126	-0.3897		7	-0.72	1.18
+ $\text{C}_3\text{H}_7\text{OH}$	0.3828	-0.6692	0.2645	-0.1558		7	-0.18	1.47
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.0638	-0.7789	0.3294	-0.0762		7	0.54	2.25
$\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_3\text{OH}$	-0.2463	-0.2965	0.1194	-0.2258		tw	-0.65	0.40
+ $\text{C}_2\text{H}_5\text{OH}$	-0.2486	-0.6345	0.1594	-0.4243		tw	-1.15	0.97
+ $\text{C}_3\text{H}_7\text{OH}$	-0.0596	-0.6348	0.2381	-0.3143		tw	-0.77	1.13
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.6456	-0.7757	0.2396	-0.4685		tw	-0.36	2.13
$o\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	-0.0846	-0.1627	-0.0830	-0.2420		5(b)	-0.57	0.24
+ $\text{C}_2\text{H}_5\text{OH}$	-0.1653	-0.6280	-0.2215	-0.5512		5(b)	-1.57	0.79
+ $\text{C}_3\text{H}_7\text{OH}$	0.0126	-0.5895	0.3745	-0.6326		5(b)	-0.84	1.61
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.5454	-0.7850	0.1610	-0.5709	0.4474	5(b)	-0.20	2.51
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	0.0966	-0.0998	0.1679	-0.3538		5(b)	-0.19	0.72
+ $\text{C}_2\text{H}_5\text{OH}$	0.0569	-0.5360	0.2856	-0.4520		5(b)	-0.65	1.33
+ $\text{C}_3\text{H}_7\text{OH}$	0.2529	-0.5250	0.4220	-0.6306		5(b)	-0.48	1.83
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.9985	-0.7949	0.1011	-0.8667	0.9347	5(b)	-0.37	3.70
$p\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{OH}$	0.1071	-0.2359	0.0198	-0.2153		5(b)	-0.54	0.36
+ $\text{C}_2\text{H}_5\text{OH}$	-0.1336	-0.6146	0.2107	-0.5969		5(b)	-0.87	1.29
+ $\text{C}_3\text{H}_7\text{OH}$	0.0335	-0.6524	0.4005	-0.4766		5(b)	-0.70	1.56
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	0.7254	-0.7028	0.2999	-0.5819		5(b)	-0.26	2.31
$1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3 + \text{CH}_3\text{OH}$	0.6453	0.0073	0.6128	0.0827		6	1.35	1.17
+ $\text{C}_2\text{H}_5\text{OH}$	0.5870	-0.2251	0.6629	-0.6792		6	0.35	2.15
+ $\text{C}_3\text{H}_7\text{OH}$	0.8400	-0.3249	0.6706	-0.6989		6	0.49	2.54
+ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	1.4764	-0.4158	0.7916	-0.6067		6	1.25	3.29

The heats of mixing for each of the four sets of data for H_m^E (aromatic component + an alcohol) show similar patterns. These can be seen in Figures 1(i), (ii), (iii), and (iv). The H_m^E for benzene, toluene, *o*-, *m*-, *p*-xylene, and mesitylene + methanol all have the same shape with a maximum value of H_m^E at a mole fraction of $0.6 < x < 0.7$. This is also true for the ethanol, propan-1-ol, and propan-2-ol systems. The $H_m^E(x = 0.5)$ for the six methanol systems range between 610 and 730 J mol⁻¹ while, for the six ethanol, six propan-1-ol, and six propan-2-ol systems, $H_m^E(x = 0.5)$ ranges between 730 and 810 J mol⁻¹, 860 and 950 J mol⁻¹, and 1120 and 1230 J mol⁻¹ respectively. The H_m^E for these binary systems of (an aromatic compound + an alcohol) are thus less dependent on the number and position of the methyl groups of the aromatic compound than on the carbon number of the alcohol.

The nature of the interactions is best discussed in terms of the partial molar excess enthalpies at infinite dilution. In this work, $H^E(x_1 = 0)$ and $H^E(x_2 = 0)$ (where 1 refers to an aromatic compound and 2 to an alcohol) have been calculated from the coefficients A_i (given in Table 2) of the Redlich–Kister equation:

$$H^E / (\text{J mol}^{-1}) = x_1(1-x_1) \sum_{i=0}^n A_i(1-2x_1)^i$$

The excess partial molar volume H_2^E at a mole fraction x_1 , where $x_1 = n_1 / (n_1 + n_2)$, is given by:

$$H_1^E = (1-x_1) [dH_m^E / dx_1] + H_m^E$$

and hence

$$H_1^E = H_m^E + (1-x_1)(A_0 + A_1 + A_2 + \dots + \text{terms in } x_1)$$

so

$$H_1^E(x_1 = 0) = \sum_{i=0}^n A_i$$

similarly,

$$H_2^E(x_2 = 0) = \sum_{i=0}^n (\text{even}) A_i - \sum_{i=0}^n (\text{odd}) A_i$$

The precision of $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ is dependent on the precision of the H_m^E data at low and high concentrations. We estimate the precision for $H_1^E(x_1 = 0)$ for the systems discussed in this work to be better than 500 J mol⁻¹. The calculated values of $H_1^E(x_1 = 0)$ and $H_2^E(x_2 = 0)$ are given in Table 2. In all cases $H_2^E(x_2 = 0) \gg H_1^E(x_1 = 0)$. The large positive $H_2^E(x_2 = 0)$ is primarily due to the endothermic dissociation of the hydrogen bonds linking the alcohol molecules as a result of adding a small amount of alcohol to a large amount of the aromatic component.

The very much smaller $H_1^E(x_1 = 0)$ is a result of (i) the smaller endothermic effect due to the breakdown of the

association between the aromatic molecules, and (iii) the exothermic effect due to the association of the aromatic compound and the alcohol.

The volume of mixing for each of the four sets of data, V_m^E (aromatic compound + an alcohol) is summarized in Figures 2(i), (ii), (iii), and (iv). The shapes of the curves are very much more complicated than the shapes of the heats of mixing curves for the same sets. The shape of the V_m^E (benzene, toluene, *o*-, *m*-, *p*-xylene, + methanol) curves are all sine shaped being negative at low aromatic concentration and positive at high aromatic concentration [Figure 1(i)]. The shape of the V_m^E (mesitylene + methanol) curve is, however, positive over the whole concentration range and does not follow the pattern of the other curves.

The features of the V_m^E curves, seen above, are also characteristic of the ethanol and the propan-1-ol set of curves. The V_m^E for the (aromatic compound + propan-2-ol) systems are, however, more positive than the other three sets. In general the V_m^E for (an aromatic compound + an alcohol) increases in the order methanol < ethanol < propan-1-ol < propan-2-ol.

The nature of the interactions can be interpreted using excess partial molar volumes at infinite dilution, i.e. $V_1^E(x_1 = 0)$ and $V_2^E(x_2 = 0)$. The properties have been calculated from the Redlich-Kister coefficients of Table 3 in a similar manner to the excess partial molar enthalpies at infinite dilution.

In all systems, except for the (mesitylene + methanol) system, $V_1^E(x_1 = 0) \ll V_2^E(x_2 = 0)$. Again, as in the case of $H_2^E(x_2 = 0)$, the relatively large $V_2^E(x_2 = 0)$ is caused by the breakdown of the hydrogen bonding between the alcohol molecules when one mol of alcohol is added to an infinite amount of the aromatic component. Furthermore, the largest values of $V_2^E(x_2 = 0)$ are associated with the six systems involving propan-2-ol.

The relatively low values (usually negative values) for $V_1^E(x_1 = 0)$ could be a reflection of the association of the aromatic component and the alcohol.

The fact that the shapes of the mesitylene systems do not fit the pattern generated by the five other aromatic systems could be a result of the molecular packing of mesitylene, and highlights the difficulties in interpreting excess molar volume data. No other sets of excess volume data for mesitylene mixtures are available for comparison.

Acknowledgement

The authors thank the Foundation for Research Development for financial support.

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Journal of Solution Chemistry, Vol. 21, No. 5, 1992

Partial Molar Volumes of 18-Crown-6 Ether in Organic Solvents at 25°C

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Received March 26, 1991; Revised December 6, 1991

The partial molar volumes at infinite dilution of 18-crown-6 ether (CE) in a variety of polar and polarizable solvents with molar volumes ranging from 18 to 170 cm³·mol⁻¹, were measured at concentrations ranging from 0.02 to 0.1 mol·L⁻¹ at 25°C. The partial molar volumes of the solute at infinite dilution showed remarkable dependancy on the molar volume of the solvent. The partial molar volumes at infinite dilution for the CE increases as the solvent molar volume increases.

KEY WORDS: Partial molar volume at infinite dilution; apparent molar volume, 18-crown-6 ether.

1. Introduction

The excess molar volume of mixing is a complex property in that it depends not only on the solute-solute, solvent-solvent and solute-solvent interactions, but also on the packing nature of the solute and solvent molecules. The partial molar volumes at infinite dilution are slightly easier to interpret because the solute-solute interaction is absent.

In this work, the partial molar volumes of 18-crown-6 ether (CE) in dilute solutions of organic solvents (methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, dimethylsulfoxide, *tert*-butylmethylether, butyl-methylketone, chloroform, carbontetrachloride, 1,4-dioxane, benzene, tetrahydrofuran, cyclohexylbenzene, tetrahydronaphthalene, acetonitrile) and water, have been obtained by extrapolation of the apparent molar volumes measured at concentrations ranging from 0.02 to 0.1 mol·L⁻¹ at 25°C. The solvents studied include a variety of polar and polarizable solvents, with molar volumes ranging from 18 to 170 cm³·mol⁻¹. This work was prompted by earlier measurements of the volume change resulting from the complexing of cations by CE.⁽¹⁾

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Table I. Chemicals, Suppliers, Purity and Purification Methods

Chemical	Supplier	Purity (G.C.%)	Purification Method
CE	Fluka AG	> 98	
2-Butanol	Riedel-de Haen	99	^a
Dimethylsulfoxide	Merck	> 99	^b
Butylmethylketone	Fluka	98	
Chloroform	Hopkin and Williams	96	
1-Propanol	Riedel-de Haen	99.9	^a
1-Butanol	BDH	99.9	^a
Ethanol	Merck	99.9	^a
Carbontetrachloride	Sarchem	98	
1,4-Dioxane	Sarchem	98	
Benzene	BDH	> 99	^b
Tetrahydrofuran	Carlo Erba	> 99	^b
Methanol	Merck	99.9	^a
Cyclohexylbenzene	Fluka	99	^b
Tetrahydronaphthalene	BDH	99	^b
Acetonitrile	Merck	99	^b

^a Dried with magnesium metal activated with iodine and distilled before use (Ref. 3).

^b Purified by repeated distillation.

2. Experimental

The compounds used, their suppliers, purity and purification methods are listed in Table I. The alcohols were tested for dryness by means of Karl Fischer titrations. Density measurements were made using a Paar DMA 601 density measuring cell linked to a Paar DMA 60 frequency counter. The temperature of the measuring cell was kept constant by pumping water from a thermostated bath. The temperature of the bath was controlled to within $\pm 0.002^\circ\text{C}$ using a Tronac temperature controller. The period of vibration of the tube for each density measurement was obtained from the average of consecutive readings taken over two minutes.⁽²⁾ Furthermore, each measurement was standardized against water, air and pure solvent in order to overcome minor fluctuations in temperature.

The apparent molar volume of the CE V_ϕ was calculated from⁽³⁾

$$V_\phi = M_2/d_0 - 1000(d - d_0)/d_0c \quad (1)$$

where M_2 is the molar mass of the CE, c the concentration in $\text{mol}\cdot\text{L}^{-1}$ of

Table II. The Apparent Molar Volumes of CE in Various Solvents^a

c^a	V_o^b	c^a	V_o^b	c^a	V_o^b
1,4-Dioxane					
0.01829	240.845	0.05117	240.068	0.06711	239.589
0.02868	240.339	0.05603	240.015	0.09911	240.187
0.03691	239.733				
Chloroform					
0.01034	230.159	0.03186	229.363	0.06067	226.969
0.01166	229.691	0.03681	228.488	0.08018	227.319
0.01657	230.389	0.03832	227.319	0.09027	227.180
0.02749	229.959	0.05614	227.805		
Carbontetrachloride					
0.01383	235.993	0.04610	236.328	0.08210	235.888
0.01880	235.521	0.04988	235.987	0.09547	235.517
0.02948	236.548	0.06412	235.635		
Cyclohexylbenzene					
0.01993	242.601	0.05200	242.559	0.07664	242.036
0.03415	242.621	0.06979	242.388	0.09796	242.508
Tetrahydronaphthalene					
0.04059	241.986	0.05535	242.490	0.08859	244.120
0.04883	242.184	0.07288	243.188	0.10318	244.041
0.05100	242.027	0.08135	243.188		
Ethanol					
0.02659	229.722	0.05447	232.204	0.08610	233.560
0.03487	230.031	0.07420	233.232	0.09529	233.832
0.04328	231.178				
Acetonitrile					
0.02990	225.539	0.07638	225.178	0.09256	225.790
0.06770	225.399	0.08620	225.511	0.09773	225.855
0.07182	225.223				
Tetrahydrofuran					
0.02395	236.178	0.04805	237.277	0.07765	237.668
0.03290	236.478	0.05062	236.786	0.09359	238.109
0.03425	236.372	0.05809	237.285	0.09591	238.275
Benzene					
0.01453	236.575	0.05386	236.237	0.09123	236.137
0.03614	236.705	0.06494	236.629	0.09469	236.721
0.04908	236.295	0.07141	236.743		

Table II. Continued

c^a	V_o^b	c^a	V_o^b	c^a	V_o^b
Methanol					
0.04152	227.745	0.06019	227.961	0.08410	228.786
0.04805	227.511	0.07183	228.709	0.09042	228.880
0.05696	227.330	0.07309	228.295		
1-Butanol					
0.02887	239.978	0.05675	240.343	0.08071	240.847
0.03037	239.856	0.07621	239.976	0.08521	240.042
0.05318	239.164				
2-Butanol					
0.02489	238.146	0.04292	238.108	0.07420	240.497
0.02985	237.729	0.05087	238.522	0.07974	239.702
0.03237	238.192	0.06394	239.947	0.09363	240.847
0.04084	238.626				
Burylmethylketone					
0.03732	238.133	0.06421	238.004	0.08229	238.089
0.05187	237.652	0.07563	237.653	0.09229	238.187
Dimethylsulphoxide					
0.03099	232.554	0.05370	232.744	0.08758	232.766
0.04325	232.938	0.07143	232.410		
1-Propanol					
0.03594	235.342	0.05868	236.324	0.08942	236.977
0.04655	234.981	0.06831	236.177	0.09139	237.600
0.05357	236.314	0.06988	235.644	0.09430	237.572
0.05581	235.398	0.08544	237.120		
Water					
0.03536	222.981	0.04673	223.289	0.08004	223.962
0.04475	223.855	0.06447	223.815	0.09561	224.587

^a Concentration CE; units, mol-L⁻¹. ^b Units: cm³-mol⁻¹.

the CE in solution, d the density of the solution and d_o the density of the pure solvent. V_2^o of CE in each solvent was obtained by extrapolation of a plot of V_o vs. c . At infinite dilution the apparent molar volume, $V_o(x = 0)$ is identical to the partial molar volume V_2^o . The CE solutions were prepared by weight by adding approximately 10 cm³ of solvent to a weighed mass of CE. The solutions and pure solvents were degassed before use by connecting the sample flasks to a vacuum system and pumping for a few minutes. The solutions were then weighed to deter-

Table III. Parameters of Eq. (2) and Molar Volumes of the Solvents

Solvent	$V_2^{\circ a}$	m	σ	V_1^a
2-Butanol	236.7	44.6	0.5	91.84
Dimethylsulfoxide	232.7	-0.9	0.3	70.96
Butylmethylketone	237.8	2.2	0.3	123.89
Chloroform	230.4	-42.6	0.8	80.01
1-Propanol	233.5	40.9	0.5	74.75
1-Butanol	239.5	8.7	0.6	91.51
Ethanol	228.3	62.4	0.5	58.69
Carbontetrachloride	236.2	-4.7	0.4	96.5
1,4-Dioxane	240.5	-6.6	0.5	85.21
Benzene	236.6	-0.9	0.3	89.37
Tetrahydrofuran	235.6	28.1	0.2	81.38
Methanol	226.2	29.5	0.4	40.55
Cyclononylbenzene	242.7	-5.2	0.2	170.13
Tetrahydronaphthalene	240.4	37.7	0.3	136.72
Water	222.4	21.4	0.3	18.02
Acetonitrile	225.2	4.2	0.3	52.63

^a Units: cm³·mol⁻¹.

mine the solvent mass, and a sample was injected into the cell.

3. Results

The experimental results for the apparent molar volumes V_ϕ as a function of the concentration c are given in Table II. The equation

$$V_\phi = V_2^\circ + mc \quad (2)$$

was fitted to the data, and the results are given in Table III. The standard deviation σ of the fit was calculated from

$$\sigma^2 = \frac{\sum (V_{\phi, \text{exp}} - V_{\phi, \text{cal}})^2}{n - 2} \quad (3)$$

where n is the number of observations.

4. Discussion

The slope of the plot of the apparent molar volumes V_ϕ vs. c , has been generally regarded to reflect solute-solute interaction forces⁽⁴⁾. In this work, most of the slopes were either slightly positive or virtually horizontal. The only exceptions were those of CE + ethanol and CE +

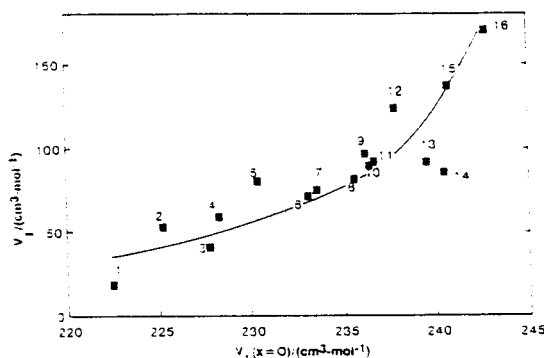


Fig. 1(a). Partial molar volumes at infinite dilution V_2^∞ of 18-crown-6 ether in various solvents as a function of the molar volume of the pure solvent V_1 : 1, water; 2, acetonitrile; 3, methanol; 4, ethanol; 5, chloroform; 6, dimethylsulfoxide; 7, 1-propanol; 8, tetrahydrofuran; 9, carbon tetrachloride; 10, benzene; 11, 2-butanol; 12, butyl-methylketone; 13, 1-butanol; 14, 1,4-dioxane; 15, tetrahydronaphthalene; 16, cyclohexylbenzene.

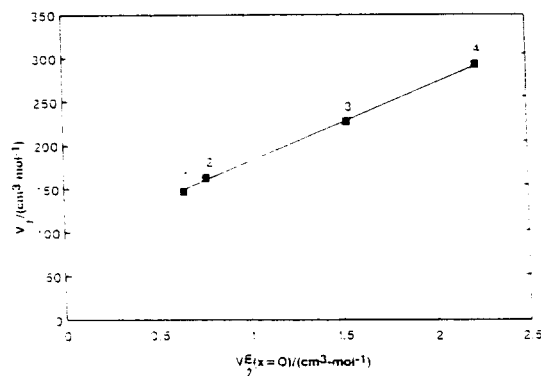


Fig. 1(b). Excess partial molar volumes at infinite dilution of cyclohexane in n -alkanes $V_2^E(x_2 = 0)$ as a function of the molar volume of the pure solvent V_1 : 1, pentane; 2, hexane; 3, dodecane; 4, hexadecane.

2-butanol. This can be seen from the values of m in Table III. This suggests weak solute-solute interactions, as strong interactions would have resulted in a relatively large positive slope.⁽⁵⁾ Figure 1(a) shows V_2^∞ plotted vs. the pure solvent molar volumes V_1 . The value of V_2^∞ varies as much as 10 percent, from 222 to 244 $\text{cm}^3\cdot\text{mol}^{-1}$, as V_1 varies from 18 to 170 $\text{cm}^3\cdot\text{mol}^{-1}$. This variation is significantly larger than the usual partial molar excess volume for mixtures involving strong solute-solvent

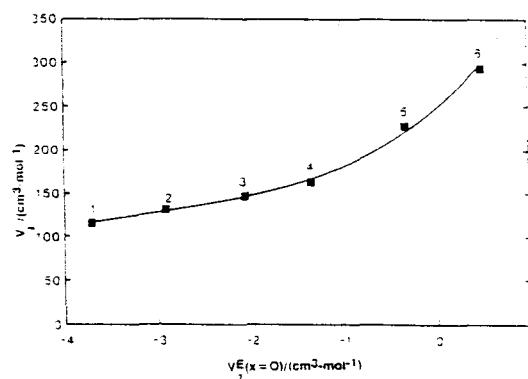


Fig. 1(c). Excess partial molar volumes at infinite dilution of decalin in *n*-alkanes $V_2^E(x_2 = 0)$ as a function of the molar volume of the pure solvent V_2^0 : 1, pentane; 2, hexane; 3, heptane; 4, octane; 5, dodecane; 6, hexadecane.

interactions. For example, the partial molar excess volume at infinite dilution for benzene in 1-octyne is only $-0.8 \text{ cm}^3\text{-mol}^{-1(6)}$ which amounts to about 1 percent of the molar volume of benzene. The variation of V_2^0 seems independent of the chemical nature of the solvent, (ranging from hydrogen bonded solvents such as water, alcohols and chloroform, to polarizable aromatic solvents such as benzene and cyclohexylbenzene and ethers such as tetrahydrofuran and 1,4-dioxane), but does depend significantly on the molar volume of the solvent. This suggests that the dominant factor is attributable to the packing of the solvent molecules, and that the addition of solute molecules to the solvent disturbs the order in the solvent packing. The larger the solvent molecule, (as judged by the solvent molar volume), the larger the partial molar volume of the solute CE, and the larger the apparent disorder in the packing arrangement of the solvent molecules. The same trend is also found in mixtures of cyclohexane⁽⁷⁾ or decahydronaphthalene⁽⁸⁾ in *n*-alkane solvents. The excess partial molar volumes at infinite dilution for solutes cyclohexane or decahydronaphthalene in *n*-alkane solvents have been calculated from

$$V_2^E(x_2 = 0) = V_2^0 - V_2$$

using the method described by Letcher *et al.*⁽⁹⁾ and have been graphed in Figs. 1(b) and 1(c). Here, V_2 is the molar volume of the solute. All the results presented here for the solute CE involve solute-solvent systems which can be described as "like-like" mixtures. Attempts to obtain results for CE in non-polar solvents have not been successful, as the CE

is not soluble in solvents such as alkanes or cycloalkanes.

Acknowledgment

The authors wish to thank the FRD (South Africa) for financial help.

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INTERSET 101498 15.06.92 [01] 1.01

M-2758

J. Chem. Thermodynamics 1992, 24, 000-000

Excess molar volumes and excess molar enthalpies of $[x\{0.5\text{CH}_3(\text{CH}_2)_{k-2}\text{CH}_3 + 0.5\text{CH}_3(\text{CH}_2)_{l-2}\text{CH}_3\} + (1-x)\text{CH}_3(\text{CH}_2)_{m-2}\text{CH}_3]$ at the temperature 298.15 K

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(Received 12 December 1991; in final form May 1992)

Excess molar volumes and enthalpies have been measured at atmospheric pressure and $T = 298.15$ K for three-component mixtures. A pseudo-*n*-alkane of carbon number m was mixed with the *n*-alkane of carbon number m over the whole composition range. The value of m ranged from 7 to 14. The results show excellent agreement with the principle of congruence.

1. Introduction

The principle of congruence⁽¹⁾ has been applied to the excess molar volumes and excess molar enthalpies for many binary mixtures⁽²⁾ and also to multicomponent mixtures.^(3,4) In this work a novel set of mixtures involving accurately made pseudo-*n*-alkanes⁽³⁾ has been used to test the principle. The principle implies that a pseudo-*n*-alkane ($0.5\text{C}_k\text{H}_{2k+2} + 0.5\text{C}_l\text{H}_{2l+2}$) will behave like $\text{C}_m\text{H}_{2m+2}$, where $m = (k+l)/2$. In this work such mixtures were used to test the principle, the method having been applied to both excess molar volumes and excess molar enthalpies. V_m^E and H_m^E for $\{x(0.5\text{C}_k\text{H}_{2k+2} + 0.5\text{C}_l\text{H}_{2l+2}) + (1-x)\text{C}_m\text{H}_{2m+2}\}$, where $m = (k+l)/2$, were determined over the whole composition range. The aim of this work was to test the principle of congruence using this novel null method. Ten pseudo-*n*-alkanes were made for V_m^E and five for H_m^E .

2. Experimental

Excess molar volumes were measured using an Anton-Paar DMA 601 vibrating-tube densimeter. The technique was checked as previously described.⁽⁵⁾ The temperature was controlled to within 2 mK of 298.150 K and the measurement for

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each density was standardized against water, air, and octane (B.D.H. Chemicals Ltd). Excess molar enthalpies were measured using an LKB 2107 microcalorimeter; the method has been described.⁽⁶⁾

The alkanes were used without further purification. The compounds were each analysed by g.l.c. and the mole-fraction purity of each compound was found to be >0.995 .

TABLE 1. V_m^E results for $\{x(0.5C_4H_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}\}$ at $T = 298.15$ K and $p = 97.4$ kPa

$1-x$	$\frac{10^3 \cdot V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$1-x$	$\frac{10^3 \cdot V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$1-x$	$\frac{10^3 \cdot V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$1-x$	$\frac{10^3 \cdot V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$
$k=6 \quad l=8 \quad m=7$							
0.1422	-2.8	0.4553	-4.2	0.6135	-2.1	0.6953	-4.1
0.3869	-4.6	0.5615	-4.4				
$k=7 \quad l=9 \quad m=8$							
0.0399	0.3	0.2996	-0.6	0.5434	-2.0	0.7194	-0.8
0.1438	1.9	0.4551	0.4	0.6931	-0.4	0.8681	0.1
0.1876	0.4	0.5429	-0.9	0.7073	0.7	0.9457	-0.4
0.2983	0.3						
$k=6 \quad l=10 \quad m=8$							
0.1837	-0.9	0.5473	-4.5	0.7180	-4.3	0.8915	-2.0
0.4331	-4.7	0.6204	-4.2				
$k=6 \quad l=12 \quad m=9$							
0.1636	-0.9	0.3280	-1.9	0.4969	-3.0	0.7211	-1.1
0.2517	-1.6	0.4138	-2.8	0.5684	-1.8	0.8369	-0.5
$k=8 \quad l=10 \quad m=9$							
0.1614	-0.6	0.3955	-3.1	0.5541	-2.5	0.7057	-1.4
0.1714	-1.2	0.4483	-1.6	0.6234	-1.7	0.8123	-1.4
0.3020	-3.5	0.4599	-2.1	0.6245	-2.2	0.9016	-2.3
0.3817	-0.9	0.5509	-1.2	0.6903	-3.2	0.9352	-1.7
$k=6 \quad l=14 \quad m=10$							
0.2375	-1.4	0.4019	-2.8	0.5969	-2.0	0.8611	-1.2
0.3715	-1.9	0.5223	-2.9	0.8352	-1.5		
$k=8 \quad l=16 \quad m=12$							
0.1819	0.3	0.3997	-4.2	0.5176	-3.2	0.6851	-2.1
0.3165	1.9	0.4379	-5.3	0.5937	-3.0	0.9037	-1.4
$k=10, \quad l=14 \quad m=12$							
0.1236	-0.8	0.4995	-1.8	0.6180	-4.2	0.8010	-1.9
0.3715	-0.9	0.4998	-4.3	0.6513	-3.9		
$k=10 \quad l=16 \quad m=13$							
0.1827	-0.7	0.4877	-4.1	0.5604	-2.5	0.8596	-0.3
0.3457	-2.9	0.4948	-4.1	0.6933	-0.7		
$k=12 \quad l=16 \quad m=14$							
0.1228	-1.0	0.4545	-4.6	0.5580	-3.7	0.8659	-0.5
0.2697	-1.7	0.4877	-1.2	0.6561	-1.4		

$$(V_m^E \text{ AND } H_m^E) \left\{ x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2} \right\} \quad 03$$

The pseudo-*n*-alkane mixture was made to within $1 \cdot 10^{-4}$ of $x = 0.5$. The liquids were degassed, by connecting the flask to a vacuum system, before weighing and mixing. The (pseudo-*n*-alkane + *n*-alkane) for the excess volumes were made in 5 cm³ bottles, and the vapour space was kept as small as possible. In all cases the least volatile component was added to the bottle first.

The V_m^E s are believed to be accurate to $\pm 0.004 \text{ cm}^3 \cdot \text{mol}^{-1}$ and the H_m^E s to $\pm 1 \text{ J} \cdot \text{mol}^{-1}$.

3. Results

The V_m^E and the H_m^E for $\{x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}\}$, where $m = (k+l)/2$ are given in tables 1 and 2, respectively. The values of k , l , and m for each of the 10 sets used for V_m^E were 6, 8, 7; 7, 9, 8; 6, 10, 8; 6, 12, 9; 8, 10, 9; 6, 14, 10; 8, 16, 12; 10, 14, 12; 10, 16, 13; and 12, 16, 14. The values for each of the four sets used for H_m^E were 7, 9, 8; 8, 10, 9; 12, 16, 14; and 10, 16, 13.

Attempts were made to prepare pseudo-*n*-alkanes using pentane, but the results showed a scatter of V_m^E in excess of $\pm 0.004 \text{ cm}^3 \cdot \text{mol}^{-1}$. This was thought to be a result of evaporation. These results are not recorded here.

4. Discussion

Our results given in tables 1 and 2 confirm the application of the principle of congruence to the volumetric and enthalpic behaviour of mixtures containing a wide range of components of widely different chain lengths. The results show that V_m^E and H_m^E for (an *n*-alkane of carbon number m + a pseudo-*n*-alkane of the same carbon number) over the whole composition range were within zero $\pm 0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $\pm 1.1 \text{ J} \cdot \text{mol}^{-1}$, respectively, for all the mixtures studied here.

TABLE 2. H_m^E results for $\{x(0.5C_kH_{2k+2} + 0.5C_lH_{2l+2}) + (1-x)C_mH_{2m+2}\}$ at $T = 298.15 \text{ K}$ and $p = 97.4 \text{ kPa}$

$1-x$	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	$1-x$	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	$1-x$	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$	$1-x$	$\frac{H_m^E}{\text{J} \cdot \text{mol}^{-1}}$
$k=7 \quad l=9 \quad m=8$							
0.2006	0.0	0.3639	0.5	0.4596	1.1	0.7067	0.03
0.2946	0.0	0.4026	0.0	0.5082	0.0	0.7974	0.02
$k=8 \quad l=10 \quad m=9$							
0.1907	0.0	0.3512	0.1	0.5191	0.1	0.7743	0.0
0.2401	0.0	0.4007	0.2	0.6309	0.2	0.8411	0.0
$k=12 \quad l=16 \quad m=14$							
0.1156	0.5	0.2895	0.5	0.4434	0.8	0.6869	0.7
0.2354	0.6	0.3692	0.4	0.5142	0.9	0.8410	0.5
$k=10 \quad l=16 \quad m=13$							
0.1211	0.0	0.3464	0.6	0.4796	1.1	0.6812	0.7
0.2592	0.2	0.3915	0.8	0.5432	0.7	0.8528	0.5

The authors wish to thank the FRD (South Africa) for financial assistance.

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Partial Molar Volumes of Cryptand-222 in Organic Solvents
at 298.15 K

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ABSTRACT

The partial molar volumes at infinite dilution of cryptand-222 (c-222) in water, methanol, acetonitrile, ethanol, dimethylsulphoxide, 1-propanol, 2-propanol, chloroform, benzene, 1-butanol, cyclohexane, butylmethylketone, hexane, tetrahydronaphthalene, heptane, octane, cyclohexylbenzene and decane were measured at concentrations ranging from 0.01 to 0.1 mol-l⁻¹ at 298.15 K. The partial molar volumes at infinite dilution showed remarkable dependency on the molar volume of the solvent. The partial molar volumes at infinite dilution for c-222 increases as the solvent molar volume increases.

KEY WORDS: Partial molar volume at infinite dilution; apparent molar volume; cryptand-222.

1. INTRODUCTION

In an earlier investigation⁽¹⁾ the partial molar volumes at infinite dilution of 18-crown-6 ether in various solvents were reported. In this work, the partial molar volumes of c-222 in dilute solutions of water, methanol (MeOH), acetonitrile (AC), ethanol (EtOH), dimethylsulphoxide (DMSO), 1-propanol (1-PROH), 2-propanol (2-PROH), chloroform (CHCl₃), benzene, 1-butanol (1-BuOH), cyclohexane (cyclo-6), butylmethylketone (BMK), hexane, tetrahydronaphthalene (THN), heptane, octane, cyclohexylbenzene (CHB) and decane have been obtained by extrapolation from the apparent molar volumes measured at concentrations ranging from 0.01 to 0.1 mol-L⁻¹ at 298.15 K.

2. EXPERIMENTAL

The cryptand-222 was obtained from Merck (> 99%) and was used without further purification. The methanol and 1-butanol were supplied by Merck (99.9%), the ethanol, heptane and octane by SARchem (>99%), the 1-propanol and 2-propanol by BDH (99.5%). All the alcohols were dried with magnesium metal activated with iodine and distilled before use.⁽²⁾ The acetonitrile (99%) and the dimethylsulphoxide (> 99%) were supplied by Merck and were purified by repeated distillation. The BMK, THN and benzene were supplied by Merck (>99%) and used without further purification. The hexane was supplied by Aldrich (97%), the cyclohexane by SARchem (99%), the chloroform by Kleber Chemicals (99%), and the cyclohexylbenzene by Aldrich (97%). The decane was obtained from Fluka (>99%). The solvents were tested for dryness by means of Karl Fischer titrations. Density measurements were made using a Paar DMA 601 density measuring cell linked to a Paar DMA 60 frequency counter. The temperature of the measuring cell was kept constant by pumping water from a thermostated bath. The temperature of the bath was controlled to within 0.001 K using a Tronac temperature controller. The period of vibration of the tube for each density measurement was obtained from the average of consecutive readings taken over two minutes.⁽³⁾ Furthermore, each measurement was standardised against water, air and pure solvent in order to overcome minor fluctuations in temperature and solvent purity.

The apparent molar volume V_ϕ was calculated from⁽⁴⁾

$$V_\phi = M_1/d_0 - 1000(d - d_0)/d_0c_1 \quad (1)$$

where M_1 is the molar mass of c-222, c_1 the concentration in $\text{mol}\cdot\text{l}^{-1}$ of the c-222 in solution, d the density of the solution and d_0 the density of the pure solvent. The partial molar volume at infinite dilution, $V_1(c_1=0)$, for each solvent was obtained by extrapolation of the plot of V_ϕ against solute concentrations, c_1 . At infinite dilution the apparent molar volume, $V_\phi(c_1=0)$ is

identical to the partial molar volume $V_1(c_1=0)$. The c-222 solutions were made up by adding approximately 5 cm³ of solvent to a weighed mass of c-222. The solutions and pure solvents were degassed before use. This was done by connecting the sample flasks to a vacuum system, and pumping for five minutes, and by placing the sample flasks in an ultrasonic bath for an average of 10 minutes or longer. The solutions were then reweighed to determine the solvent mass, and injected into the cell.

3. RESULTS

The experimental results for the apparent molar volumes, V_ϕ , at a concentration of c_1 are given in Table I. Equation (2) has been fitted to the data

$$V_\phi = mc_1 + V_\phi(c_1=0) \quad (2)$$

and the results are given in Table II. The values of $V_1(c_1=0)$ have been plotted in Figure 1. The standard deviation (σ) was calculated from :

$$\sigma^2 = \Sigma(V_{\phi, \text{exp}} - V_{\phi, \text{cal}})^2 / (n-1) \quad (3)$$

where n is the number of observations.

4. DISCUSSION

The slope of the plot of the apparent molar volumes V_ϕ against concentration, c_1 , have been generally regarded to reflect solute-solute interactions.⁽⁵⁾ In this work, most of the slopes were either very slightly positive or virtually horizontal. This can be seen from the values of m in Table II. This suggests weak solute-solute interactions. The exceptions

are c-222 in MeOH, EtOH, 1-PrOH, 1-butanol and DMSO. Fig. 1 shows the partial molar volumes at infinite dilution $V_1(c_1=0)$ of c-222 plotted against the pure solvent molar volume V_2^0 .

The trends in the solvent-c-222 slopes are similar to those observed with 18-crown-6 ether in similar solvents. Once again it seems that the variation of the partial molar volume at infinite dilution (V_1) is largely dependent on the molar volume of the solvent, (ranging from hydrogen bonded solvents such as water and alcohols to polarizable aromatic solvents such as benzene and benzene derivatives, as well as an alkane and a cycloalkane).

ACKNOWLEDGEMENT

The authors wish to thank the FRD (South Africa) for financial assistance.

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TABLE I: The apparent molar volumes, V_ϕ^a , at concentrations c_1^b resulting from the data being fitted to Equation (1), for c-222 + a solvent

c_1	V_ϕ	c_1	V_ϕ	c_1	V_ϕ
Water					
0.03606	316.008	0.05605	316.560	0.09497	316.166
0.04547	316.751	0.06961	316.320		
Methanol					
0.01599	323.413	0.03787	322.875	0.05220	324.431
0.02373	323.023	0.04697	323.901		
Acetonitrile					
0.02087	330.724	0.03279	330.893	0.06398	332.845
0.02802	330.723	0.03634	330.558	0.06739	330.610
0.02963	329.604	0.05304	329.135		
EtOH					
0.02127	325.379	0.04293	327.396	0.05666	328.887
0.02955	326.338	0.05070	328.503	0.06141	329.905
0.03751	326.988				
DMSO					
0.01919	342.110	0.03369	342.998	0.05831	344.962
0.02192	342.300	0.04557	343.881	0.05947	345.300
0.032319	342.991				

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1-PrOH

0.01742	323.775	0.03830	324.599	0.05627	327.159
0.02348	324.214	0.04329	325.973	0.05903	327.369
0.03135	324.932	0.04741	326.382		

2-PrOH

0.01835	325.673	0.04965	326.080	0.06365	326.546
0.02270	325.970	0.05077	326.132	0.06710	326.750
0.03928	326.026	0.05565	326.192		

CHCl₃

0.02344	332.306	0.04174	331.358	0.05148	330.713
0.03822	331.428	0.04449	331.351	0.05458	330.321

Benzene

0.01575	343.844	0.03938	344.501	0.05187	344.187
0.02545	344.427	0.04079	344.529	0.07821	344.830

1-Butanol

0.02358	330.525	0.04216	333.616	0.06341	334.491
0.03793	332.804	0.05837	334.917	0.06546	334.174

Cyclohexane

0.01302	346.128	0.03681	346.363	0.05337	346.228
0.02156	346.473	0.05076	346.287	0.05616	346.199
0.03079	346.200				

Butyl-methyl-ketone

0.02725	345.783	0.03875	345.383	0.06839	346.568
0.03674	345.623	0.04365	345.365	0.07934	345.996

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Tetrahydronaphthalene

0.03463	341.581	0.04941	341.965	0.05523	342.860
0.04060	341.833	0.05176	342.714	0.08490	342.343

Heptane

0.01563	337.176	0.03814	337.745	0.04171	337.234
0.03283	336.077	0.03978	336.811	0.05943	337.735

Octane

0.02047	341.761	0.04742	342.993	0.07349	343.570
0.04691	342.715	0.05720	343.210		

Cyclohexylbenzene

0.02494	348.685	0.04510	347.020	0.05836	346.176
0.03850	347.569	0.05586	346.246	0.06966	345.094
0.03982	347.455				

Decane

0.02151	353.423	0.03765	354.065	0.05846	354.544
0.02924	353.699	0.04779	354.242	0.06446	354.618

^aUnits: cm³-mol⁻¹. ^bUnits: mol-L⁻¹

TABLE II: The partial molar volumes at infinite dilution, $V_1(c_1=0)$ for c-222 in various solvents, the solvent molar volumes V_2^0 , and the slope m , resulting from Equation (2) being fitted to the data; and the standard deviations resulting from fitting Equation (3) to the data.

Solvent	$V_1(c_1=0)^a$	m	σ	V_2^{0a}
Water	316.51	-2.5	0.34	18.02
MeOH	322.54	27.8	0.56	40.55
AN	329.89	18.0	0.12	52.63
EtOH	323.04	107.0	0.21	58.69
DMSO	340.81	68.1	0.26	70.96
1-PROH	322.05	88.6	0.37	74.75
2-PROH	325.39	16.9	0.16	76.85
CHCl ₃	333.79	-60.1	0.16	80.01
Benzene	343.90	11.4	0.25	89.37
1-BuOH	329.10	87.6	0.73	91.51
Cylo-6	346.29	-0.66	0.13	108.04
BMK	345.07	14.6	0.38	123.89
Hexane	326.91	-42.5	0.32	130.77
THN	341.45	14.5	0.49	136.72
Heptane	336.48	17.2	0.65	146.51
Octane	341.14	34.7	0.15	162.49
cHB	350.69	-78.1	0.08	170.13
Decane	352.89	27.8	0.08	194.92

^aUnits: cm³-mol⁻¹

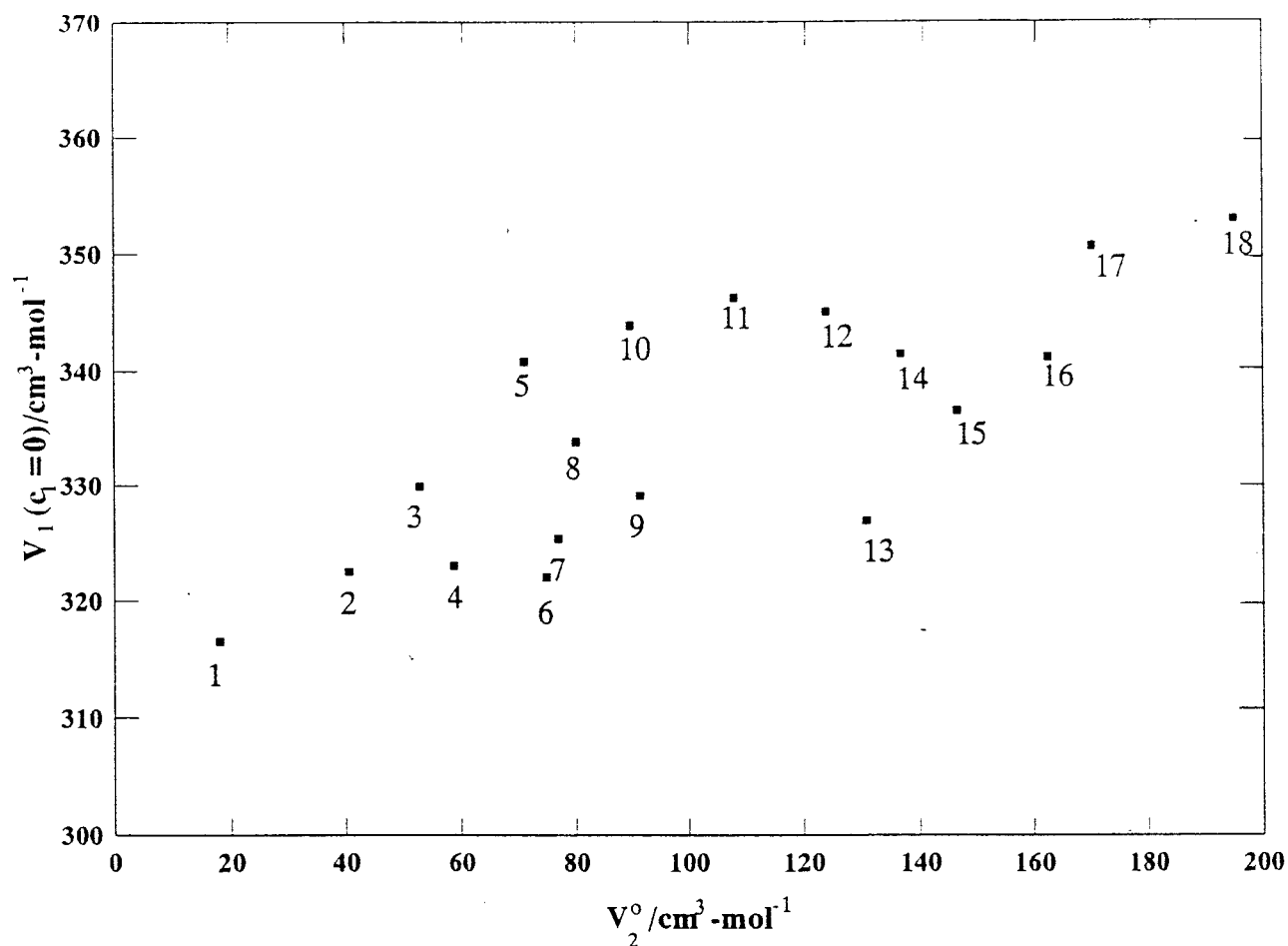


Fig.1. Partial molar volumes at infinite dilution $V_1(c_1=0)$ of c-222 in various solvents as a function of the molar volume of the pure solvent V_2^0 : 1, water; 2, methanol; 3, acetonitrile; 4, ethanol; 5, dimethylsulfoxide; 6, 1-propanol; 7, 2-propanol; 8, chloroform; 9, 1-butanol; 10, benzene; 11, cyclohexane; 12, butyl-methylketone; 13, hexane; 14, tetrahydronaphthalene; 15, heptane; 16, octane; 17, cyclohexylbenzene; 18, decane.

Volume Changes in Complex Formation Between Cryptand-222 and

Alkali Metal Chlorides and Iodides in Methanol,

Dimethylsulphoxide and Acetonitrile at 298.15 K.

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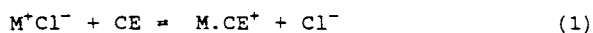
ABSTRACT

The apparent molar volumes of equimolar concentrations of cryptand-222 (c-222) and MCl or MI (M = Na, K, or Cs) in dilute solution of anhydrous methanol (MeOH), dimethylsulfoxide (DMSO), or acetonitrile (AN) have been calculated from density measurements at 298.15 K. After extrapolation to infinite dilution, these results together with the apparent molar volumes of the cryptand and the alkali metal chlorides or iodides in MeOH, DMSO, or AN were used to calculate the partial molar volume change, ΔV , for the formation of the MCl.c-222 and MI.c-222 complexes. The sign and magnitude of ΔV are discussed in terms of the solvent electrostriction and the size effect of the metal ion.

KEY WORDS: cryptand-222; apparent molar volume; partial molar volume change on complex formation.

1. INTRODUCTION

Høiland^(1,2) has shown that the partial molar volume change, ΔV , for the reaction



(where $M = Na, K, Rb$ or Cs and $CE = 18$ -crown-6-ether) in aqueous solution can be related to the electrostriction effect of the metal ion. Related work has been done on the apparent molar volumes of crown ether complexes in several organic solvents by Letcher et al.⁽³⁾ In this work the partial molar volume changes at infinite dilution for the reactions involving c-222 with MX (where $M = Na, K$, or Cs and $X = Cl$ or I) have been determined in anhydrous methanol (MeOH), dimethylsulfoxide (DMSO) or acetonitrile (AN) at 298.15 K.

2. EXPERIMENTAL

The c-222, supplied by Merck, was found to be of greater than 99 mole percent fraction purity by g.c. analysis, and was used without further purification. The $CsCl$ was supplied by Fisher Scientific, the KCl by Apache Chemicals, and the $NaCl$, KI , CsI and NaI by Aldrich Chemical Co. The metal salts were rated by their suppliers at 99.999 mole percent. They were oven dried for 48 hours at 393.15 K and stored in a desiccator. The MeOH (HPLC grade) was supplied by BDH Chemicals Ltd. and was dried with magnesium metal activated with iodine and distilled before use.⁽⁴⁾

The AN (HPLC grade) and DMSO (HPLC grade) were supplied by Merck and were used without further purification. Karl Fischer analysis on each of the solvents showed that the water concentration was always less than 0.02 mole percent.

The density was measured using a Paar DMA 601 density measuring cell linked to a Paar DMA 60 density meter. The

temperature of the vibrating tube chamber was kept constant by pumping water from a water bath, the temperature of which was controlled to within 0.001 K using a Tronac temperature controller. The density d of a solution was obtained from the density of pure solvent d_0 and the periods of vibration of the tube when it contained the solution (τ) and the pure solvent (τ_0) using the relationship:

$$d = d_0 + B(\tau^2 - \tau_0^2) \quad (2)$$

where B is the densimeter constant. This constant was calculated using pure water and pure solvent. The precision of the frequency, judged by repeated measurements for the same solution at different times was estimated to be better than $2 \text{ in } 1 \times 10^6$. The τ values for water and the pure solvent were determined, and B calculated, both before and after the τ values for each of the solutions. This was done in order to eliminate the effect of small temperature drifts within the densimeter cell. The apparent molar volume V_ϕ was calculated from⁽⁵⁾

$$V_\phi = M/d_0 - 1000(d - d_0)/d_0 C \quad (3)$$

where M is the molar mass of the solute and C the concentration in moles per litre. V_ϕ was determined for the solutes MX, c-222 and MX.c-222.

The pure solvents and solutions were degassed by connecting the sample flask to a vacuum system, as well as immersing them in a sonic bath for between 10 and 20 minutes. The solutions were weighed immediately before being injected into the densimeter cell.

The metal halide cryptand complexes were made up by weighing equimolar amounts of reactants (within $5 \times 10^{-5} \text{ mol-L}^{-1}$) in flasks which had been oven dried and stored in a dry box. In some cases the solutions had to be gently warmed in order to dissolve the solutes.

3. RESULTS

V_ϕ for each of the solutes can be related to the partial molar volume at infinite dilution V_ϕ^0 through the equation

$$V_\phi = V_\phi^0 + aC \quad (4)$$

The V_ϕ for c-222 in MeOH, DMSO and AN are given in Table I. Over the concentration range given, the values of V_ϕ were found to be independent of composition within experimental error. Details of these results have been reported separately.⁽¹⁷⁾

The V_ϕ for the MX.c-222 in MeOH, DMSO and AN are given in Table III. V_ϕ^0 was calculated for the metal salts and the complexes using the relationship⁽⁶⁾

$$V_\phi - 2/3\delta_v C^{1/2} = V_\phi^0 + bC \quad (5)$$

where $\delta_v = 14.19 \text{ cm}^3\text{-L}^{1/2}\text{-mol}^{-3/2}$ for MeOH⁽⁶⁾, $13.05 \text{ cm}^3\text{-L}^{1/2}\text{-mol}^{-3/2}$ for AN⁽⁷⁾ and $7.55 \text{ cm}^3\text{-L}^{1/2}\text{-mol}^{-3/2}$ for DMSO⁽⁸⁾. The values for V_ϕ^0 and b are given in Table IV and were obtained by weighting the V_ϕ data in proportion to C^2 . The V_ϕ for the metal salts are given in Table II, and the V_ϕ^0 results are given in Table V.

The volume change, ΔV at infinite dilution, for the formation of the complex MX.c-222 in MeOH, DMSO and AC (see eq. (1)) was calculated from

$$\Delta V = V_\phi^0(\text{MX.c-222}) - V_\phi^0(\text{MX}) - V_\phi^0(\text{c-222}) \quad (6)$$

The results for ΔV are given in Table V.

4. DISCUSSION

Previous work on ΔV for the complexation of cryptand-222 with metal salts in water and methanol has been done by Morel et al.⁽¹⁰⁾ The results support the concept that c-222, like 18-crown-6 ether and dibenzo-18-crown-6 ether,⁽³⁾ has the capacity

to envelop metal ions. C-222 was found to be considerably more soluble than the crown ethers in these solvents, and went quickly into solution without the solutions having to be warmed. In this work, we have extended the systems studied to include c-222 complexed with metal salts in AN and DMSO. Our results for c-222 in MeOH, DMSO and AN are reported in Table V. It is interesting to note that Morel⁽¹⁰⁾ working with cryptand 222 and MCl in water obtained 14.2 ± 0.2 and 17.4 ± 0.2 for NaCl and KCl respectively. They also determined ΔV for cryptand 222 with MCl in MeOH and obtained 10.6 ± 0.6 , 15.9 ± 0.6 and 7.4 ± 1.2 for NaCl, KCl and CsCl, respectively. Their ΔV results included a correction factor, of $13 \text{ cm}^3\text{-mol}^{-1}$, for the chloride ion of the metal salt, obtained from work done by Kawaizumi and Zana.⁽¹⁸⁾ We have not included this correction in our results, and have carried out our calculations in the same manner as Letcher et al.⁽³⁾

The stability constants⁽¹⁰⁾ for the formation of most of the complexes are of the order of 10^4 (DMSO), 10^{10} (AN) and 10^5 (MeOH). This implies that at equilibrium, with equimolar concentrations of c-222 and metal salt, most of the material is in the complexed state, and thus no correction for the uncomplexed material has been made. This is not the case with the c-222-Cs⁺ in DMSO, the stability constant (K) of which is of the order of 10^3 . This might explain why we obtained anomalous results for this system. The results are given in Table V. This trend was also observed in work done by Letcher et al.⁽³⁾ in DMSO, where the K values were 10^3 or below.

If it can be assumed that the charge on the cation in the complex is shielded from the complex, that the salt involved is not ion paired, that the effect of the c-222 on the solvent packing is the identical to the effect of the c-222.MX complex on the solvent, and that the formation constants are large enough to ensure no uncomplexed cryptand, then it is possible that these results can be explained in terms of a loss of the electrostrictive effect of the M⁺ ion in forming a complex with the crown ether or the cryptand. The cavity radius of c-222 has

been estimated as 1.40 Å⁽¹¹⁾ and the ionic radii of Na⁺, K⁺ and Cs⁺ ions are 1.02, 1.38 and 1.67 Å respectively.⁽¹²⁾ It would seem, from both the results and the ionic radii, that the Na⁺ and K⁺ slip into the c-222 cavity. The Cs⁺ is significantly larger in volume and yet it seems to fit into the cavities. This is possibly due to the flexibility of the c-222 ring.

Morel et al^(14,15) have reported on the complexation of alkali chlorides by c-222 in both water and MeOH. They have pointed out the anomalous behaviour of Cs⁺ - whose radius is larger than that of the c-222 cavity. Complexation does occur - but it is likely that there is distortion of the molecule. The ΔV for the Cs⁺ complex was observed to be smaller than that for the complex of the (smaller) Rb⁺ ion.⁽¹⁴⁾ Morel et al speculate that this may be due to the formation of a partially exclusive complex with Cs⁺, evidence of which has been given by NMR studies.⁽¹⁶⁾

Support for the concept that ΔV represents the electrostriction effect of the metal ion in the solvent, is given by a reasonable correlation with the Hepler⁽¹³⁾ prediction of the effect. Similar results were obtained by Letcher et al⁽³⁾ with work on 18-crown-6 ether and dibenzo-18-crown-6 ether in various solvents.

The authors wish to thank FRD, South Africa and Rhodes University for financial assistance.

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Table I: The Apparent Molar volumes of the Cryptand in Several Solvents.

Solvent	$V_{\phi}^0(\text{c-222})^a$
MeOH	322.5
AN	329.9
DMSO	348.4

^a Units: $\text{cm}^3\text{-mol}^{-1}$

Table II. The Apparent Molar Volumes of the Alkali Metal Salts in MeOH, AN and DMSO at 298.15 K.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^b
NaCl-MeOH		KCl-MeOH		CsI-MeOH	
4.025	-7.87	1.464	-7.17	2.943	14.34
5.736	-9.07	2.172	-7.53	3.968	13.92
6.721	-9.63	3.180	-7.79	4.167	13.58
8.821	-9.26	3.782	-8.55	4.302	14.06
11.354	-9.76	4.587	-8.62	5.715	13.25
29.844	-12.72	5.185	-9.11	7.075	12.34
				8.981	11.71
				10.090	12.17
NaI-MeOH		KI-MeOH		CsI-MeOH	
2.247	9.15	2.189	19.63	2.489	30.48
4.143	8.74	3.177	19.08	3.927	29.47
5.146	7.81	5.169	18.73	5.097	29.62
6.189	7.51	6.067	17.64	7.259	29.01
8.446	7.63	8.949	17.49	8.430	28.86
9.770	6.76	9.845	16.99	10.632	28.19
NaI-AN		KI-AN		CsI-AN	
2.361	5.14	2.116	15.69	0.929	28.38
3.721	5.29	3.112	16.55	1.682	27.22
5.300	6.41	4.642	17.13	2.208	28.23
6.146	6.00	5.900	16.93	2.319	29.98
7.705	6.31	7.654	16.98	2.356	29.16
9.055	6.68	9.373	16.80	2.403	28.08

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NaI-DMSO		KI-DMSO		CsI-DMSO	
2.796	33.89	2.615	40.81	2.420	52.49
3.501	33.84	3.432	41.22	3.488	52.41
5.112	32.99	4.694	40.35	4.394	52.92
6.239	33.06	5.415	41.08	6.134	51.91
7.943	32.97	6.467	39.92	7.860	51.21
9.226	33.09	9.254	41.08	9.839	51.39
^a Units: mol-L ⁻¹ ; ^b Units: cm ³ -mol ⁻¹					

Table III: The Apparent Molar volumes of c-222 complexes with Alkali Metal Ions in MeOH, AC and DMSO at 298.15 K.

$10^2 c^a$	v_ϕ^b	$10^2 c^a$	v_ϕ^b	$10^2 c^a$	v_ϕ^b
NaCl-MeOH		KCl-MeOH		CsCl-MeOH	
3.326	335.85	1.149	329.35	2.042	346.36
5.750	335.57	2.671	328.16	3.926	345.99
6.897	334.58	5.123	327.47	6.467	345.13
7.997	335.77	7.833	327.40	9.825	342.81
12.237	333.46	8.667	325.92	10.463	342.63
KI-MeOH		NaI-MeOH		CsI-MeOH	
3.184	355.00	2.312	347.17	3.296	362.47
3.793	354.60	3.969	346.29	3.746	362.92
6.082	353.30	6.768	345.63	5.467	361.77
7.744	353.30	8.212	345.79	6.126	361.74
9.020	353.60	9.152	345.49	7.721	361.13
10.191	353.30	10.139	345.30	9.736	360.84
KI-AN		NaI-AN		CsI-AN	
1.529	362.52	2.054	353.05	1.091	368.59
2.058	362.21	4.036	352.59	1.949	367.81
3.597	361.42	5.046	351.91	1.966	368.58
6.520	360.85	6.106	351.59	2.249	368.42
9.294	360.95	6.712	352.05	2.346	367.83
10.856	360.50	10.061	351.25	2.392	367.70
NaI-DMSO		KI-DMSO		CsI-DMSO	
2.079	384.56	2.553	390.98	1.855	402.17
4.175	384.60	3.924	390.54	4.270	401.34
5.036	384.56	4.758	392.55	5.735	400.79
6.179	383.87	6.967	390.18	6.765	400.75
9.190	383.57	7.489	389.69	8.418	401.38
9.974	383.86	9.244	390.43	8.994	400.93

^aUnits: mol-L⁻¹; ^bUnits: cm³-mol⁻¹

Table IV. The Limiting Apparent Molar Volumes of c-222 in MeOH, AN and DMSO.

	MeOH			AN			DMSO	
	v_{ϕ}^{oa}	b		v_{ϕ}^{oa}	b		v_{ϕ}^{oa}	b
NaCl	336.90±0.66	-25.8	-	-	-	-	-	-
NaI	347.40±0.26	-21.1	353.30±0.30	-22.2	384.90±0.26	-12.9		
KCl	329.50±0.57	-35.5	-	-	-	-		
KI	355.40±0.46	-22.7	362.50±0.35	-19.2	391.80±0.92	-18.5		
CsCl	347.68±0.39	-47.3	-	-	-	-		
CsI	363.70±0.27	-30.7	369.29±0.37	-53.2	402.10±0.43	-13.7		

^aUnits: cm³-mol⁻¹

Table V. The Partial Molar Volume Changes for Complex Formation of the Alkali Metal Ions in Three Solvents with c-222 and Comparison with the Hepler Term.⁽¹³⁾

Solvent	Salt	$V_{\phi}^{\circ}(\text{salt})$	ΔV	$B/r^{+ (13)}$
MeOH	NaCl	-7.9	25.9	18
	KCl	-6.4	13.5	13
	CsCl	15.3	9.9	10
	KI	20.2	12.7	13
	NaI	9.2	15.7	18
	CsI	30.8	10.4	10
AN	NaI	4.7	18.7	25
	CsI	27.7	11.7	14
	KI	16.4	16.2	18
DMSO	NaI	34.1	2.4	13
	CsI	53.2	0.5	7
	KI	40.8	2.6	9

Apparent Molar Volumes of Crown Ethers and Crown Ether Complexes

in Several Solvents at 25°C.

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ABSTRACT

The partial molar volumes at infinite dilution of each of the following solutes 15-crown-5 ether (CE5), dicyclohexano-18-crown-6 ether (CY₂CE6) and dibenzo-18-crown-6 ether (B₂CE6) in each of the following solvents methanol (MeOH), acetonitrile (AN) and dimethylsulfoxide (DMSO), were measured at concentrations ranging from 0.02 to 0.1 mol-L⁻¹ at 25°C. The apparent molar volumes of equimolar concentrations of CE or CY₂CE or B₂CE and MCl (M=Na, K and Cs) or MI in dilute solutions of each of the above solvents were calculated from density data measured at 25°C. These results were then extrapolated to infinite dilution and the volume change ΔV^{∞} , for complex formation at infinite dilution was calculated. Some of these ΔV^{∞} results could be explained in terms of the electrostriction effect of the metal ion on the solvent, and were thus compared to predictions made by Hepler in 1957.

KEY WORDS: 15-crown-5 ether; dicyclohexano-18-crown-6 ether; dibenzo-18-crown-6 ether; apparent molar volume; partial molar volume at infinite dilution; partial molar volume change; methanol; acetonitrile; dimethylsulfoxide.

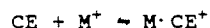
1. Introduction

Results for volume changes for the complexing of metal ions with 18-crown-6 ether (CE6), 15-crown-5 ether (CE5), 12-crown-4 ether (CE4) and cryptand[2.2.2] in water, and in some cases methanol (MeOH) have been published.⁽¹⁻⁴⁾ More recently, Letcher and Kay⁽⁵⁾ have reported the volume changes of complexation of CE6 or dibenzo-18-crown-6 ether (B₂CE6) with MCl (M=Na, K, Cs) or MI in solvents MeOH, acetonitrile (AN) or dimethylsulfoxide (DMSO).

In this work we have repeated the measurement of the volume changes of complexing B₂CE6 with MCl or MI in solvents MeOH or AN or DMSO and have extended the investigation to include measurements on CE5 and dicyclohexano-18-crown-6 ether (Cy₂CE6) with MCl or MI in solvents MeOH or AN or DMSO.

The description of the general equilibrium reaction, and equations for the standard volume change for the formation of the complex have been previously reported.⁽⁵⁾

The volume change at infinite dilution for the reaction involving a crown ether (CE),



obtained for the formation of the complex can be expressed as⁽⁵⁾

$$\Delta V^\infty = V_\phi^\infty(\text{MCl} \cdot \text{CE}) - V_\phi^\infty(\text{MCl}) - V_\phi^\infty(\text{CE}) \quad (1)$$

As in previous work the ΔV^∞ for some systems can be considered to be a measure of the volume change due to electrostriction of the solvent by the cation. These systems include those for which the formation constant of the complex is large ($>10^3$) and the metal ion is small enough to be completely enveloped by the acceptor ligand.⁽⁵⁾

2. Experimental

The compounds used, their suppliers, purity and purification methods are listed in Table I. The solvents were tested for dryness by means of Karl Fischer titrations. Density measurements were made using an Anton Paar DMA 602 density measuring cell linked to a Paar DMA 60 frequency counter. The temperature of the measuring cell was controlled to within ± 0.001 K using a Tronac temperature controller. The experimental method has been previously described.^(6,7) The solvents and solutions were degassed before each measurement by placing them in a sonic bath for 10 minutes. The method of preparation of the metal crown ether complexes has been previously described.⁽⁵⁾

The apparent molar volumes of all the solvents (CE5, B₂CE6, Cy₂CE6, NaCl, NaI, KI, and CsI), V_ϕ , were calculated from⁽⁸⁾

$$V_\phi = M/d_o - 1000(d - d_o)/d_o C \quad (2)$$

where M is the molar mass of crown ether, C the concentration in mol-L⁻¹, d the density of the pure solvent and d_o the density of the solution.

The stability constants of the Cy₂CE6 complexes in MeOH, AN and DMSO are of the order of 10⁴, 10⁵ and 10³ respectively; for the B₂CE6 complexes they are of the order of 10³; and for the CE5 complexes in MeOH and AN, they are of the order of 10³ and 10⁴ respectively, and of the order of 10 for DMSO.^(9,10)

3. Results

The experimental results for the apparent molar volumes, V_ϕ , of the crown ethers in MeOH, AN or DMSO as a function of the concentration are given in Table II. The equation

$$V_\phi = V_\phi^\infty + mC \quad (3)$$

has been fitted to the data in Table II. V_ϕ^∞ (the partial molar

volume at infinite dilution of the crown ethers in the solvents), and m for each system are given in Table III. The standard deviation, σ , of each fit was calculated from

$$\sigma^2 = \Sigma(V_{\phi, \text{exp}} - V_{\phi, \text{cal}})^2 / (n-2) \quad (4)$$

where n is the number of observations. This data also appears in Table III.

The apparent molar volumes, V_{ϕ} , for the crown ether complexes are given in Table IV. These data were extrapolated to infinite dilution using the limiting Debye-Hückel equation

$$V_{\phi} - \delta_v C^{1/2} = V_{\phi}^{\infty} + bC \quad (5)$$

where δ_v is the Debye-Hückel limiting slope and is equal to 14.19, 13.05 and 7.55 $\text{cm}^3\text{-L}^{1/2}\text{-mol}^{-3/2}$ for the solvents MeOH,⁽¹¹⁾ AN,⁽¹²⁾ and DMSO⁽¹³⁾ respectively. The V_{ϕ}^{∞} results obtained from plotting these are given in Table V.

The limiting apparent molar volumes of the metal halide salts, ΔV_{ϕ}^{∞} , required to calculate ΔV^{∞} (equation 1) are listed in Table VI. These values were calculated from data given in Ref. (18). The literature data is given in parentheses.

4. Discussion

The plots of V_{ϕ}^{∞} of the crown ether solutes in the solvents MeOH, AN and DMSO versus the molar volumes of the solvents, V_1^0 follow a similar trend to that we observed in previous investigations of 18-crown-6 ether⁽¹⁷⁾ or cryptand-222⁽¹⁸⁾ in these solvents. The general trend observed is that the V_{ϕ}^{∞} of the solutes in the solvents is largely dependent on the solvent molar volume and independent of the chemical nature of the solvent.

The standard volume changes upon complex formation, ΔV^{∞} , are given in Table VII. These results are compared to values attributed to the electrostriction term of the Hepler equation.⁽¹⁴⁾

$$V_{\phi}^{\infty}(\text{cation}) = Ar^3 - B/r \quad (6)$$

where r is the Pauling radius of the cation, A and B are the coefficients relating to the intrinsic volume term and the electrostatic term respectively. B/r values have been compiled by Zana et al.⁽¹²⁾, for the solvents used in this work, and are given in Table VII.

The comparison of ΔV^{∞} and B/r^+ for the crown ether complexes in solvents MeOH or AN, does suggest that ΔV^{∞} is largely due to the electrostriction of the solvent by the metal ion Na^+ or K^+ . This does support the idea that the Na^+ and K^+ ions fit into the cavity, or are completely enveloped by the crown ether -an observation supported by a similar finding in work done by Letcher, Kay and Paul.⁽⁵⁾ The Cs^+ ion quite clearly is too large to be enveloped by the cavity, and is thus not adequately shielded from the solvent.

The ΔV^{∞} DMSO results do not correlate with the Hepler predictions. It has been suggested^(5,19) that, since B is zero for anions in DMSO, the two methyl groups on DMSO sterically hinder anion-solvent interaction, and thus prevent electrostriction of the solvent by anions.

Acknowledgement

The authors wish to thank FRD (South Africa) for financial support.

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Table I. Chemicals Suppliers, Purity and Purification Methods.

Chemical	Supplier	Purity mole percent	Purification Method
CE5	Merck	>98	-
B ₂ CE6	Aldrich	98	-
CY ₂ CE6	Janssen	99	-
MeOH	BDH	99.8	-
AN	"	99.7	-
DMSO	"	99.3	-
NaCl	Aldrich	99.999	a
NaI	"	99.99	a
KI	"	99.999	a
CsI	"	99.999	a

^aDried in an oven at 120°C for 48 hours and stored in a desiccator.

Table II. The Apparent Molar Volumes, V_ϕ of the Crown Ethers in MeOH, AN and DMSO.

C^a	V_ϕ^b	C^a	V_ϕ^b	C^a	V_ϕ^b
CE5 + MeOH					
0.02994	186.197	0.06514	189.877	0.07602	190.416
0.04058	187.583	0.06970	190.205	0.08111	190.042
0.05024	188.819				
CE5 + AN					
0.02215	186.591	0.06233	189.452	0.08516	192.168
0.03338	187.835	0.06292	189.548	0.08772	190.769
0.04701	189.169	0.06437	189.616		-
CE5 + DMSO					
0.01718	194.108	0.03953	197.691	0.06216	197.982
0.01966	194.134	0.04984	197.465	0.07969	199.750
0.03241	195.532	0.05448	197.501		
Cy ₂ CE6 + MeOH					
0.01568	320.597	0.03827	323.440	0.06161	324.741
0.03132	322.475	0.04509	323.863	0.07381	325.709
0.03289	322.856	0.04783	324.023		
Cy ₂ CE6 + AN					
0.01766	325.936	0.03934	326.944	0.05588	327.353
0.03144	326.488	0.04160	327.066	0.06976	328.313
0.03274	326.744	0.04954	327.191		
Cy ₂ CE6 + DMSO					
0.02007	352.558	0.04517	352.415	0.06219	352.320
0.02856	352.525	0.04838	352.903	0.06408	352.220
0.03574	352.199	0.05482	352.279		

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B₂CE6 + AN

0.01479	271.168	0.03394	271.356	0.04280	271.191
0.02215	271.182	0.04278	271.842	0.04979	271.936

B₂CE6 + DMSO

0.01743	288.614	0.03235	288.592	0.04189	288.866
0.02219	288.865	0.03929	288.026	0.04729	288.819

^aUnits: mol-L⁻¹ ^bUnits: cm³-mol⁻¹

Table III. The Limiting Apparent Molar Volumes of the Crown Ethers, V_{ϕ}^{∞} , in Various Solvents, calculated from the data in Table II using Equation (3). The Molar Volumes of the Pure Solvents, V_1^0 are included.

Solvent	V_{ϕ}^{∞}	m	σ	V_1^{0a}
CE5				
MeOH	184.3	79.7	0.5	40.55
AN	185.3	69.9	0.5	52.63
DMSO	192.8	89.0	0.6	70.96
B ₂ CE6				
AN	270.8	19.1	0.3	52.63
DMSO	288.7	-1.8	0.4	70.96
Cy ₂ CE6				
MeOH	319.9	82.7	0.4	40.55
AN	325.2	42.2	0.1	52.63
DMSO	352.6	-4.8	0.2	70.96

^aUnits : cm³-mol⁻¹

Table IV. The Apparent Molar Volumes, V_ϕ , of the Crown Ether Complexes in MeOH, AN and DMSO at 25°C.

$10^2 C^a$	V_ϕ^b	$10^2 C^a$	V_ϕ^a	$10^2 C^a$	V_ϕ^a
CE5 + NaCl + MeOH		CE5 + NaI + MeOH		CE5 + KI + MeOH	
2.427	191.3	2.572	211.4	2.514	218.3
3.036	193.2	3.546	214.5	4.445	221.1
4.805	193.9	4.624	217.5	4.608	221.5
6.279	194.7	6.659	219.9	5.047	222.1
7.128	194.7	7.177	220.3	7.214	224.4
7.938	195.7	7.551	222.1	7.407	224.5
		10.201	224.6	8.146	224.7
				10.046	227.4
CE5 + CsI + MeOH		CE5 + NaI + AN		CE5 + KI + AN	
1.162	221.5	2.257	214.7	2.296	217.9
1.971	226.7	4.909	216.6	3.842	219.1
2.018	226.7	5.357	215.9	4.325	218.4
2.525	229.1	5.747	216.7	5.435	220.7
2.603	229.1	6.733	218.6	5.827	220.8
2.711	229.1	9.412	220.9	6.810	222.4
3.123	231.7	10.982	222.8	7.788	223.4
3.199	232.2	12.106	225.5	8.166	223.8
CE5 + CsI + AN		B ₂ CE6 + KI + AN		B ₂ CE6 + CsI + DMSO	
1.676	200.4	1.964	308.5	1.078	338.6
1.780	199.6	2.216	308.2	2.351	339.2
1.862	200.7	2.630	308.4	2.871	339.1
2.223	200.5	3.809	307.8	3.652	339.3
2.275	200.5	4.133	307.8	3.844	339.3
2.484	200.9	4.779	307.5	4.373	339.2
2.761	200.6	5.990	307.6	5.345	338.3

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Cy ₂ CE6 + NaI + AN		B ₂ CE6 + NaI + AN		B ₂ CE6 + NaI + DMSO	
2.963	357.9	1.749	299.6	1.719	326.6
2.972	357.7	2.297	299.3	2.591	325.9
3.632	357.8	2.776	299.8	3.037	326.3
4.999	358.4	3.145	299.1	3.132	325.9
5.046	358.6	3.524	298.9	3.736	326.1
5.529	358.0	4.219	298.7	4.191	326.1
5.913	361.0	5.512	298.2	4.588	326.3
		6.164	297.9	5.081	326.0
B ₂ CE6 + CsI + AN		B ₂ CE6 + KI + DMSO		Cy ₂ CE6 + NaI + MeOH	
1.672	315.2	1.631	330.2	2.471	349.5
2.242	314.1	2.228	330.7	2.759	349.7
2.492	314.7	2.547	330.5	2.956	349.8
2.527	314.8	3.042	329.9	3.213	349.9
3.725	314.3	3.149	330.1	3.607	350.0
4.509	313.7	3.167	330.2	4.079	350.6
4.585	313.8	3.879	330.1	5.148	351.3
		4.427	329.5	6.078	351.8
Cy ₂ CE6 + KI + MeOH		Cy ₂ CE6 + CsI + MeOH		Cy ₂ CE6 + KI + AN	
2.029	354.4	2.655	359.5	2.114	360.4
2.181	354.5	2.723	360.6	2.751	360.9
3.006	354.8	3.743	359.8	3.055	361.2
4.069	355.2	4.129	360.2	4.166	361.4
4.656	355.3	5.016	361.1	4.899	363.8
6.364	355.8	5.526	361.4	5.402	363.9
7.338	356.5	6.926	361.8	6.459	366.3
		7.097	362.2		
Cy ₂ CE6 + CsI + AN		Cy ₂ CE6 + NaI + DMSO		Cy ₂ CE6 + KI + DMSO	
2.552	367.2	2.655	377.7	2.348	382.8
2.959	368.3	3.711	377.1	3.386	383.4
2.990	368.3	5.229	377.9	3.637	383.5
3.422	369.2	5.802	376.9	4.169	385.1
3.689	368.6	6.323	377.1	4.249	385.3
4.307	369.8	7.709	377.7	5.868	386.1
				6.321	386.9

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Cy₂CE6 + CsI + DMSO

1.811 396.4

3.355 396.5

3.671 394.7

4.586 394.9

6.473 394.9

6.885 395.9

9.335 396.7

^aUnits: mol-L⁻¹ ; ^bUnits: cm³-mol⁻¹

Table V. The Limiting Apparent Molar Volumes, V_{ϕ}^{∞} of the Crown Ether Complexes in MeOH, AN and DMSO, calculated from the data in Table IV using Equation (5).

Salt	V_{ϕ}^{∞} (MeOH)	V_{ϕ}^{∞} (AN)	V_{ϕ}^{∞} (DMSO)

CE5			
NaCl	190.7±0.6	-	-
NaI	208.4±0.9	211.1±0.9	*
KI	215.9±0.4	214.8±0.6	*
CsI	216.2±0.5	199.3±0.4	*
B ₂ CE6			
NaI	-	300.4±0.2	326.4±0.2
KI	-	308.9±0.2	331.0±0.3
CsI	-	315.6±0.3	339.1±0.4
Cy ₂ CE6			
NaI	347.8±0.1	355.6±0.9	377.9±0.4
KI	353.7±0.1	357.1±0.7	380.2±0.5
CsI	358.4±0.4	364.2±0.4	395.5±0.9

^aUnits: cm³-mol⁻¹; *Equilibrium constant is of the order of 10.

Table VI. Limiting Apparent Molar Volumes, V_{ϕ}^{∞} of the Metal Halide Salts at 25°C obtained from the literature. These values have been calculated from V_{ϕ} values given in Ref. (18).

Salt	$V_{\phi}^{\infty}(\text{cm}^3\text{-mol}^{-1})$		
	MeOH	AN	DMSO
NaCl	-7.9 (-5.5) ^a	-	-
NaI	9.2 (12.7) ^a	4.7 (4.7) ^c	34.1 (33.4) ^d
KI	20.2 (22.3) ^a	16.4 (15.6) ^c	40.8 (41.9) ^d
CsI	30.8 (33) ^b	27.7 (26) ^c	53.2 (53.5) ^d

Units: $\text{cm}^3\text{-mol}^{-1}$; ^aValue from Ref. 11; ^bValue from Ref. 15; ^cValue from Ref. 5; ^dValue from Ref. 16.

Table VII. Standard Volume Change for Complex Formation Between Alkali Metal Ions and the Three Crown Ethers, and a Comparison with Eq. (6).

Solvent	Ion	$\Delta V^\circ (\text{cm}^3\text{-mol}^{-1})$			B/r ⁺
		CE5	B ₂ CE6	Cy ₂ CE6	
MeOH	Na ⁺ (NaCl)	18	(9) ^a	-	18±2
	Na ⁺ (NaI)	15	(9) ^a	19	18±2
	K ⁺	11	(11) ^a	14	13±2
	Cs ⁺	1	(4) ^a	8	10±1
AN	Na ⁺	21	25	25	25±3
	K ⁺	13	22	16	18±2
	Cs ⁺	-13	17	11	14±2
DMSO	Na ⁺	*	4	-9	13±2
	K ⁺	*	2	-13	9±2
	Cs ⁺	*	-3	-10	7±1

*The equilibrium constant is of the order of 10; ^aValue from Ref. 5.