Phase equilibria in three component systems : alcohol–hydrocarbon–water

THESIS

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LIST OF SYMBOLS

x_1 : mole fraction of alkanol.

x_2 : mole fraction of aromatic compound.

x'_1 : mole fraction of alkanol in water–rich layer.

x'_2 : mole fraction of aromatic compound in water–rich layer.

x''_1 : mole fraction of alkanol in aromatic–rich layer.

x''_2 : mole fraction of aromatic compound in aromatic–rich layer.

$x_{1,p}$: mole fraction of alkanol at plait point.

$x_{2,p}$: mole fraction of aromatic compound at plait point.

$x_{1,min}$: minimum concentration (mole fraction) of alkanol which is soluble in any (water – aromatic compound) mixture.

ABSTRACT

The fuel industry in many parts of the world is blending alcohols with motor fuel either to extend the fuel or to improve its octane rating or both.

Unfortunately alcohols are hygroscopic and as a result, water becomes a component of the fuel. This can lead to phase separation and the formation of a water–rich layer which could have serious corrosion consequences.

In an attempt to understand the phase–splitting in alcohol–petrol–water blends, phase equilibria in ternary systems (alcohol–hydrocarbon–water) have been determined by experiment. The phase equilibria in these ternary systems are also discussed in terms of modern theories of liquid mixtures and the UNIQUAC theory is applied to the "ethanol + benzene + water" ternary system. The alcohols are all the C_1, C_2, C_3 and C_4 alcohols, and the hydrocarbons include those typically found in petrol, e.g.. cyclohexane, benzene and substituted benzenes.

1. INTRODUCTION

1.1 : WHY SOUTH AFRICA AND MANY PLACES IN THE WORLD ARE SEARCHING FOR ALTERNATIVE FUELS.

All of the fuel that is used in South Africa comes from either refined imported oil, or made from coal at Sasol. The supply of imported oil has frequently been threatened by international conflict. Example are the Arab–Israeli war of 1973 which precipitated the large price rise in oil ; the second was the Iranian revolution in 1979 which was followed by the invasion of Kuwait by Iraq in 1990.[1] These, together with the assessment that the world would exhaust its oil reserves within 60–100 years,[2] have created a worldwide interest in alternative energy sources and fuel extenders.

1.2 : ETHANOL IN FUEL

The use of alcohol as fuel sources and fuel extenders for motor vehicles in many parts of the world generated more interest in the 1990's than almost any other renewable energy source.[3] Ethanol has been the most popular alcohol used, either as a fuel–extender in ethanol–petrol blends or as pure ethanol. Its ready availability by fermentation of grains and its relatively good combustion characteristics in internal combustion engines accounts for its popularity both recently and also during the first half of the century.[4]

The invention of the four–cycle, internal combustion engine in 1877 by Otto and the two–cycle automobile engine by 1879 by Benz involved the testing of ethanol, other alcohols, and many other organic liquids as potential fuels. Another factor that played an important role in the development of ethanol fuel was the passage of laws that permitted the production of tax–free ethanol for industrial use : in the United Kindgom in 1855, the Netherlands in 1865, France in 1872, Germany in 1879 and later in the United States. By 1935 over 430 million litres were used in Europe alone.[5]

More recently, Brazil introduced its "*Proalcoal Programme*" in 1975, when annual ethanol production was 500 million litres. Zimbabwe and Malawi both produce 15 to 20 percent ethanol–petrol blends where the ethanol is produced from sugar cane.[6] In South Africa, Sasol has been blending in a mixture of alcohol up to 12% in petrol, where ethanol constitutes around 60% of the alcohol used.[7]

1.3 : METHANOL IN FUEL

Methanol is also used in the motor fuel industry. It is relatively easy to manufacture from coal and from wood extract. By the early 1930s, when synthetic methanol process technology was well established and comprised *ca* 75% of the methanol market in the United States, methanol was considered a possible alternative for petrol.[8] Since then, the use of methanol as a petrol extender has been widely tested in vehicle trials in the United States of America, New Zealand and Germany.[9] The general conclusion from these trials was that petrol blends containing up to 15% methanol (M15) could be introduced without modifying existing vehicles.[9] In the late 1970s, AECI began testing a fleet of vehicles on M15 fuel under South African conditions. These were essentially standard production vehicles and the trial did not reveal any significant problems at the time. [9]

At present, the coal–based methanol produced at Modderfontein is also used as a booster for aircraft operating from high altitude airports such as Johannesburg. The potential for using methanol as a transport fuel is considerable.[9] It is particularly suitable for an Otto engine, by virtue of its clean burning properties and high octane number [9]. Operating on pure methanol (M100), engines can employ higher compression ratios and operate with a leaner fuel mixture than on petrol, which enables the energy efficiency of the engine to be increased by 20 – 30%.[9] After World War I, car racing teams began to use alcohol–fuel blends formulated with aviation petrol. Ethanol–benzene–aviation petrol blends generally ranged from volumetric ratios of *ca* 20:20:60 to 80:10:10 [10]. After World War II, engine compression ratios were increased, and the racing community shifted to pure methanol and methanol–nitro paraffin blends. With the exception of some racing events, pure methanol is now used almost exclusively.

1.4 : C_3 AND HIGHER ALCOHOLS IN FUEL

Many oil companies in the United States of America have blended C_3 and higher alcohols, e.g. 2–propanol and 2–methyl–1–propanol, in petrol as anti–icing additives but not as primary fuel components [10]. The higher alcohols are more expensive to produce. Also 2–methyl–2–propanol and blends of 2–methyl–2–propanol with methanol are marketed as octane boosters in the United States.[10]

1.5 : OPERATING PROBLEMS

Although using alcohol–fuel blends as transport fuels has its advantages, many problems have been experienced with these blends.

These problems relate to

(i) Materials compatibility. For example, there are problems related to plastic pipes, and metal–alcohol reactions (especially true for methanol), in petrol tanks and carburettor.

(ii) Water tolerance and the phase separation of the alcohol–petrol blends into a water–rich layer and a petrol–rich layer. Phase separation results from the hygroscopic nature of the alcohol. The amount of water that the blend can tolerate before separation occurs depends on many factors including the type of alcohol and its concentration, petrol composition and the effect of the other co–solvents, e.g. higher alcohols in the blend.[11] The water–rich layer resulting from the phase separation can be a layer of almost pure water which has a great potential for corrosion, especially in carburettors where more than one metal is in contact with the fuel.[12]

1.6 : AREA OF RESEARCH COVERED IN THIS THESIS

In this work the phase equilibrium properties of alcohol–hydrocarbon–water ternary systems have been determined. The alcohols are all the C_1, C_2, C_3 and C_4 alcohols, that is, methanol, ethanol, 1–propanol, 2–propanol, 1–butanol, 2–butanol, 2–methyl–1–propanol and 2–methyl–2–propanol, and the hydrocarbons are cyclohexane and the aromatic compounds benzene, o–, m– and p–xylene, toluene and mesitylene. Other hydrocarbons such as n–hexane and n–heptane have been investigated by other workers. All these compounds are present in petrol. The research carried out in this project is aimed at finding the effect on alcohol–hydrocarbon–water phase equilibria of the

(i) type of alcohol ; and
(ii) the type of hydrocarbon component in petrol.

Attempts at predicting phase equilibria from modern theories of liquid mixtures are also included. In this work the general approach is given and a test done using the well known UNIQUAC theory using the programme ESTM from the Technical University of Denmark.

2. EXPERIMENTAL TECHNIQUE

2.1 : MATERIALS

The methanol, ethanol and the two propanols were obtained from Merck (AR grade). These were purified and dried by refluxing with magnesium and iodine, followed by distillation. The four butanols were also supplied by Merck (AR grade). These were dried by the addition of anhydrous potassium carbonate and purified by distillation. The benzene, toluene, p–xylene, o–xylene, m–xylene and mesitylene were supplied by BDH and used without further purification. The purity of each of the components was determined by glc and was never less than 99.6 mole percent.

2.2 : METHOD USED IN THIS WORK

The "*method of titration*" has been used to determine the ternary liquid–liquid equilibrium data.[13] In this method the binodal curve is first established and then the tielines are drawn. This is the method used in this work. To establish the binodal curve, binary mixtures of two compounds, e.g. a hydrocarbon and an alcohol, were prepared accurately by weighing. The mixtures were left to equilibrate in a water bath set at 25° ± 0.1 °C, for an hour. The third component, water, in this case, was added dropwise, from a pre–weighed gas–tight syringe, until the mixtures turned cloudy. The syringe was weighed again to determine the mass of the component added. A drop of the alcohol was then added to the cloudy mixture to make it clear again, and the refractive index of the clear mixture was measured using an 1T Atago refractometer set at 25.5°C. The slightly elevated temperature was used to ensure that phase separation did not occur. This composition was used to draw the binodal curve.[14] At the water–rich end of the binodal curve the binary mixture was made up of water and an alcohol, and the third component was the hydrocarbon.

To determine tielines three–component mixtures were prepared by mass in the two–phase region of the phase diagram. The mixtures were left in a water bath, set at 25° ± 0.1 °C for 24 hours to separate into two phases. Two gas–tight glass syringes were then used to draw samples of the two phases into two small glass containers that had been kept warm at 26° C, and analysed as soon as possible so as to overcome the effects of evaporation. Two methods were then used to analyse the mixtures. These are the Karl Fischer [15] titration method and the refractive index method.[16]

In the Karl Fischer method, a Karl Fischer reagent is used to titrate against the water in each phase. In this manner the water content of each phase is determined. These two concentrations are then located on the binodal curve and the tieline drawn.

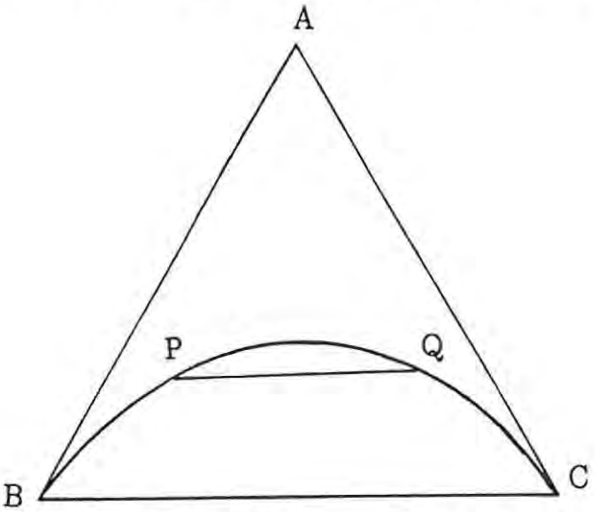


FIGURE 2.1 : The Karl Fischer method for drawing tielines.

P is mass percent of water in water–rich layer and Q is mass percent of water in hydrocarbon–rich layer. PQ is drawn to form the tieline. A, B and C refer to the three components of the mixture.

The other method, the refractive index method, makes use of a "*calibration curve*" to draw the tielines. To draw the calibration curve, perpendicular lines are dropped from each point on the binodal curve to the hydrocarbon axis. The refractive index corresponding to each point on the binodal curve is then plotted against the corresponding point on the hydrocarbon axis. In this way a graph of refractive index versus percent hydrocarbon (the calibration curve) is drawn, as shown in the following figure :

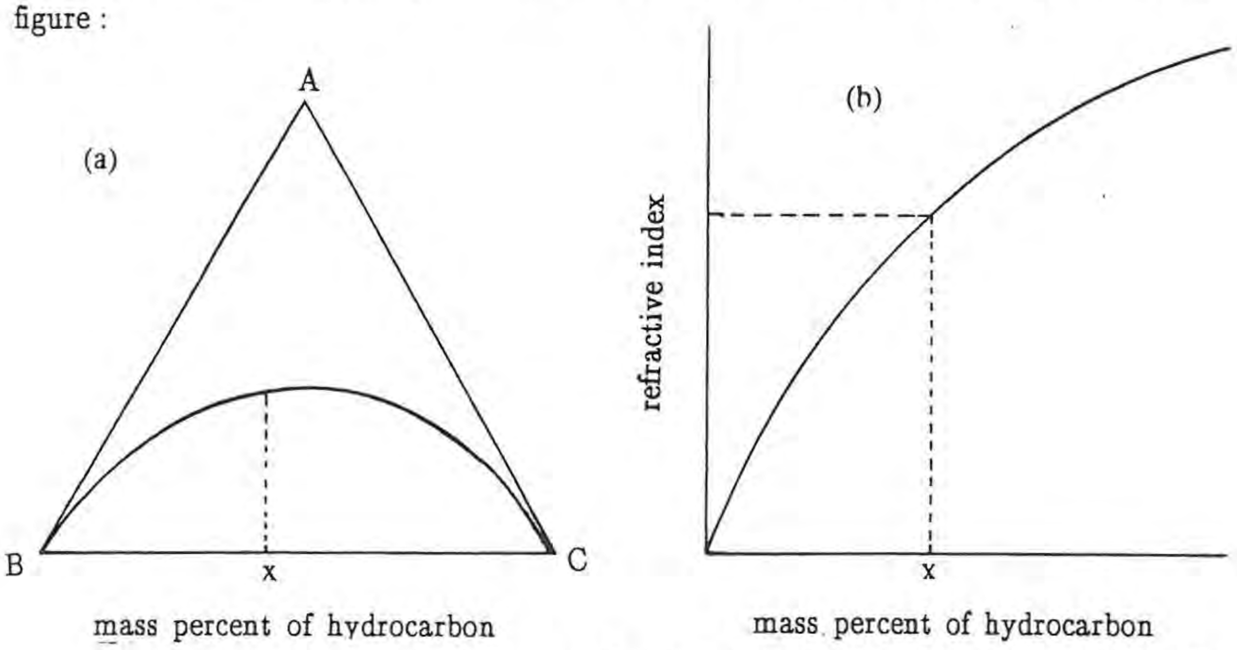


FIGURE 2.2 : The refractive index method for drawing tielines using (a) the binodal curve and (b) the calibration curve.

2.3 OTHER METHODS

Many other workers have measured binodal curves and tielines. The basic method of establishing the binodal curve and the tielines used by these workers is similar to the refractive index method[16] described above. The only difference is in the instrumentation. Instead of using many flasks, each containing a different composition, one vessel, fitted with a stirrer is sometimes used. The concentration of components one and two is changed at intervals and component three subsequently added to arrive at the *"haze"* point[17]. With this type of instrumentation, samples are not weighed directly, but are measured by volume. The advantage is that the sytem is compact. The weighing method used in the work of this thesis is significantly more accurate than the volume method.

Gas chromatography is often used to determine tielines.[18] The composition of each of the two phases is determined by peak area comparison. When using this method, there is therefore no need to determine the binodal curve first, as is done in this project. The tielines are thus determined directly, and the binodal curve can be drawn through the tielines. Attempts in this thesis have shown the glc method to be inferior because of the difficulty of accurately relating peak height ratios to mass ratios or mole ratios.

3. CORRELATION OF THE TIELINES AND DETERMINATION OF PLAIT POINTS

The use of tielines in a ternary solubility systen has considerable application in determining the quantitative distribution of the solute between two conjugate phases. While the tieline method of representation has the advantage of easily yielding the weight ratios of the two conjugate phases separating from a mixture of known composition, it possesses the rather serious disadvantage of requiring considerable data for the entire range of concentrations – there are indeed an infinite number of tielines per system. It becomes necessary to interpolate between adjacent tielines if the composition of a mixture for which distribution data is required, does not coincide exactly with a tieline. Except for systems for which a considerable number of tielines have been determined, the interpolation of tielines or ternary co–ordinates is unsatisfactory. [19]

The Bachman method [20] of tieline correlation is an attempt at providing an answer to this. Bachman studied the results of Branker, Hunter and Nash [21], and found a method of plotting by which tielines in many ternary liquid systems exhibit a straight–line relation if the proper functions of the concentrations at the extremes of the tielines are chosen as the dependent and independent variables. He found that if A and B are the nonconsolute components and C is the consolute component of a ternary liquid system, a plot of mass percent A in the A–rich layer against mass percent B in the B–rich layer will produce a line which has as its equation : $a_1 + kb_1 = ma_1b_2$. a_1, b_1 and c_1 are the respective mass fractions of A, B and C in the A–rich layer, a_2, b_2 and c_2 are the corresponding mass fractions in the B–rich layer, and m and k are constants. Dividing the equation by b_2 ,

$$a_1/b_2 = ma_1 - k.$$

Accordingly, a plot of a_1 against a_1/b_2 will yield a straight line.

In addition to the use of this method for correlating tieline data, it can also be used to find the plait point, as described by Heric *et al.* [22]

The main disadvantage of this method is that it applies to cases where liquids A and B are immiscible. When there is some miscibility the lines show a noticeable degree of curvature. This results in an inaccurate determination of the plait point, especially if only a few tielines have been determined.

This is of critical importance in the systems investigated in this work, because the alcohols are partially miscible in the hydrocarbons. It therefore becomes necessary to complement this method with another which takes into account this partial miscibility.

The Hand [23] method is an attempt to overcome the problem experienced with partially miscible systems. Hand introduced a successful empirical method of plotting ternary liquid equilibrium data, based on the equation,

$$\frac{W_1''}{W_2''} = k\left(\frac{W_1'}{W_3'}\right)^n$$

where the concentrations are in mass fractions. W_1'' is the mass fraction of component 1 in component 2–rich phase, W_2'' the mass fraction of component 2 in component 2–rich phase, W_1' the mass fraction of component 1 in component 3–rich phase and W_3' the mass fraction of component 3 in component 3–rich phase. This is a type of distribution curve, where n is introduced to account for mutual solubility of the solvents. A log–log plot of $\frac{W_1''}{W_2''}$ against $\frac{W_1'}{W_3'}$ results in a good straight line for most systems, the slopes of which equal n.

Treybal[24] rearranged this equation to the form :

$$\frac{x_2''}{x_2''} = k'\left(\frac{x_1'}{x_3'}\right)^n$$

where the concentrations are in mole fractions where n is a constant. The n values for the two plots (Hand and Treybal) are the same, and the coefficients are related :

$$k = k'\left(\frac{MW_3}{MW_1}\right)\left(\frac{MW_2}{MW_3}\right)^n$$

MW refers to molecular weight and subscripts 1, 2 and 3 refer to compounds 1, 2 and 3 respectively. In addition, Treybal discussed a method for finding plait points.

As an example, consider the ethanol–toluene–water ternary system (figure 3). In both the Bachman and Treybal methods the plait point is the point of intersection of the straight line and the curve (see graphs below).

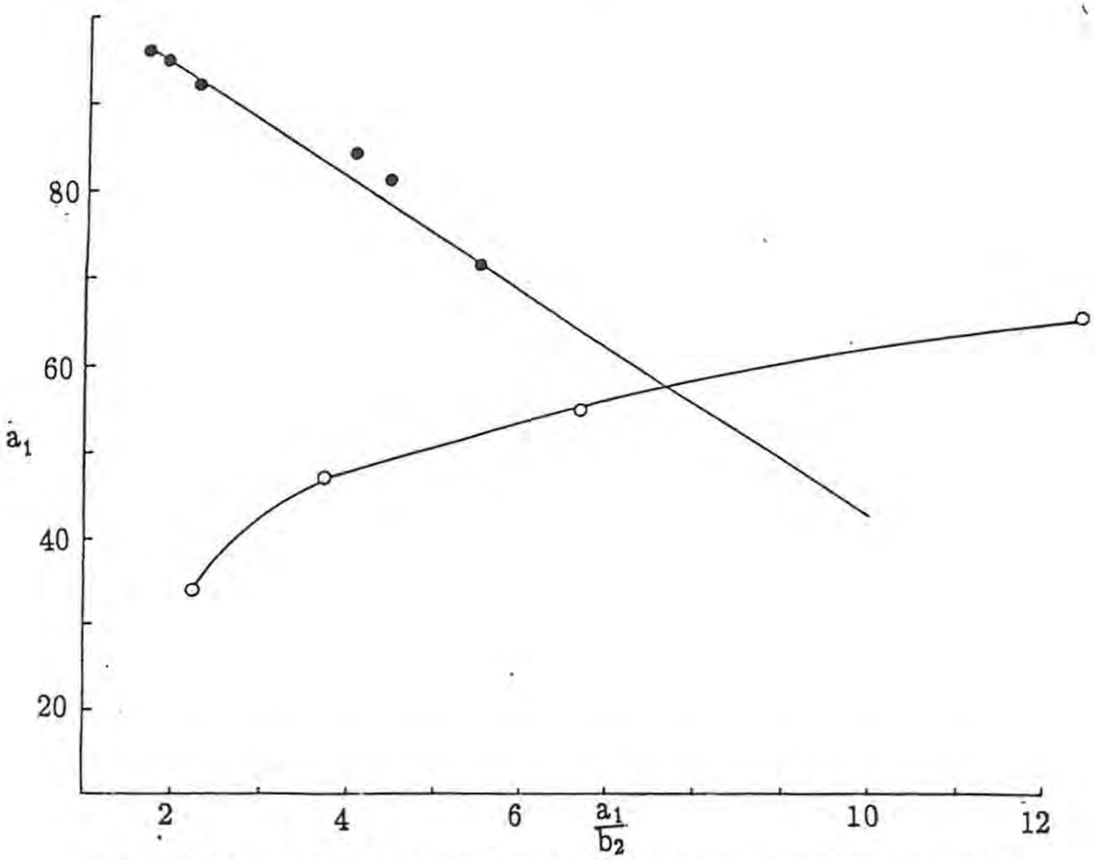


FIGURE 3(a) : Bachman Method : The ethanol—toluene—water ternary system.

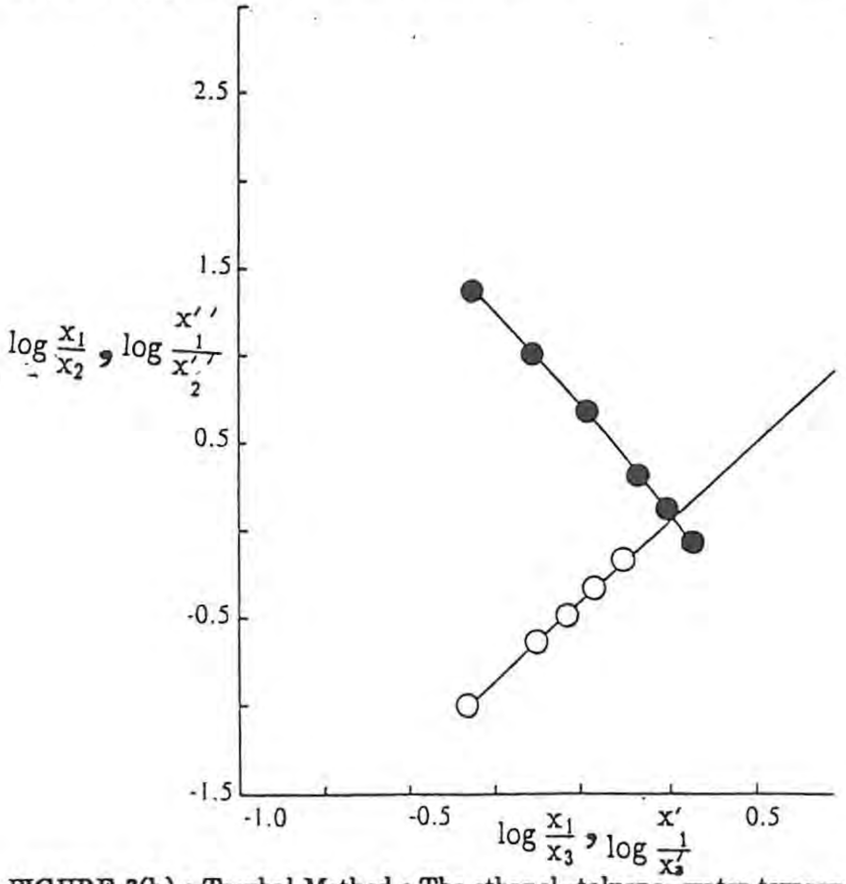


FIGURE 3(b) : Treybal Method : The ethanol—toluene—water ternary system.

In the Treybal method the straight line is a result of a plot of $\log \dfrac{x_1''}{x_2''}$ vs $\log \dfrac{x_1'}{x_3'}$ where x_1'' is the mole fraction of alcohol in toluene–rich phase, x_2'' is the mole fraction of toluene in toluene–rich phase, x_1' the mole fraction of alcohol in the water–rich phase and x_3' the mole fraction of water in the water–rich phase. The curve results from a plot of $\log \frac{x_1}{x_2}$ vs $\log \frac{x_1}{x_3}$ where x_1, x_2 and x_3 are mole fractions of alcohol, toluene and water respectively for a point on the binodal curve.

In the Bachman method a straight line results from a plot of a_1 vs $\frac{a_1}{b_2}$, where a_1 is the mass percent of toluene in toluene–rich phase and b_2 is the mass percent of water in water–rich phase. A graph of a_1 vs a_1/b_2 has been plotted to get the curve, where a and b are the mass percentages of toluene and water respectively, for a point on the binodal curve.

In the Treybal method, for the ethanol–toluene–water ternary system, the line intersects the curve at

$$\log \frac{x_1''}{x_2''} = \log \frac{x_1}{x_2} = 0.061, \;\; \log \frac{x_1'}{x_3'} = \log \frac{x_1}{x_3} = 0.258.$$

From this we can determine the composition of the plait point to be :

$$x_1 = 0.413, \;\; x_2 = 0.359, \;\; x_3 = 0.228.$$

For the Bachman method the two plots intersect at :

$$a_1 = a = 58, \;\; \frac{a_1}{b_2} = 7.72 \;\; \therefore \;\; b_2 = b = 7.51 \;\; \therefore \;\; c = 34.49.$$

Changing these mass percentages to mole fractions we get :

$$x_1 = 0.417, \;\; x_2 = 0.351, \;\; x_3 = 0.222.$$

From the above it can be noticed that both the Bachman and Treybal methods give similar plait points for the ethanol–toluene–water ternary systems. This is true for most of the systems that have been investigated.

Plait points have been determined for all the systems discussed in this work. Both the Treybal and Bachman methods were used to determine the plait points, although only the Treybal method has been shown. The plait points (in mole fractions) are given in Table 6.6(a).

The Othmer and Tobias [19] method is often used to correlate tieline data. This method also gives straight lines in a ternary system where two solvents are partially miscible. This method is a combination of the Bachman and Hand methods, and it was not used in this work.

4:FITTING MATHEMATICAL EQUATIONS TO BINODAL CURVE DATA

Until recently, the equation of Hlavaty[25] has been the only succesful method in fitting an equation to binodal curve data for systems involving one pair of immiscible liquids. In Hlavaty's equation the mole fraction of the species (1), is given by :

$$x_1 = A_1 x_A \ln x_A + A_2 \ln x_B + A_3 x_A x_B, \qquad (4.1)$$

$$x_A = (x_2 + {}^1/_2\, x_1 - x_2^0) \,/\, (x_{22}^0 - x_2^0), \qquad (4.2)$$

$$x_B = (x_{22}^0 - x_2 - {}^1/_2\, x_1) \,/\, (x_{22}^0 - x_2^0) \qquad (4.3)$$

where x_{22}^0 and x_2^0 are values of x_2 on the binodal curve which cuts $x_1 = 0$ axis. Species (1) is miscible with both species (2) and species (3).

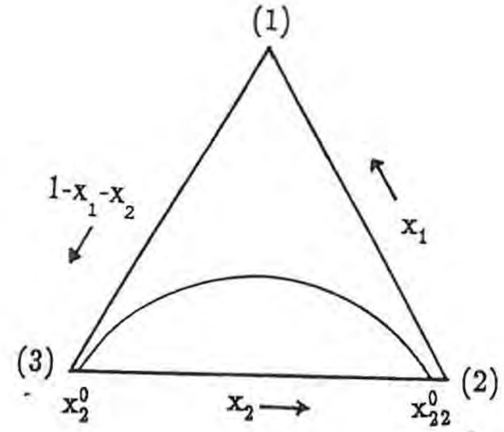


FIGURE 4(a) : **Graphical illustration of symbols used in the Hlavaty equation.**

Unfortunately, the independent variables are highly correlated and slight changes in binodal curve data produce large changes in the magnitudes of the coefficients A_1, A_2 and A_3. A very much better equation, proposed by T. Letcher, P.M. Siswana, S. Radloff and P. van der Watt in a recent paper[13], which does not suffer from this disadvantage is the Beta density function equation :

$$x_1 = B_1(1 - \ln x_A)^{B_2}\, x_A^{B_3} \qquad (4.4)$$

Yet another equation that has been proposed by the same workers (26), which also does not suffer the disadvantage of being highly corralative, is

$$x_1 = C_1(-\ln x_A)^{C_2}\, x_A^{C_3} \qquad (4.5)$$

This is known as the logarithmic–gamma equation. The equation was chosen because the binodal curves are similar in shape to the densities of logarithmic–gamma distribution which have been found by Schultz and Crouse[27] to describe the distribution of mass fractions of a body subjected to successive random divisions of its randomly divided parts.

The parameters A_j of equation (4.1) (Hlavaty's equation) and B_j of equation (4.4) and C_j of equation (4.5) can be estimated by two different methods.

In method 1, a simple least–squares regression is performed with x_1 as the dependent variable and x_A and x_B as independent variables for Hlavaty's equation, and with $\ln(x_1)$ as the dependent variable and x_A and x_B (where $x_B = 1 - x_A$) as independent variables for the Beta and for logarithmic–gamma equations.

Fitting these equations by least–squares is extremely difficult because the dependent variable x_1 appears in both the left and right hand sides of the equations to be fitted. To illustrate the difficulty, consider the normal equation for estimating A_1 in Hlavaty's equation. This equation is obtained by attempting to minimise

$$s^2 = \sum_{i=1}^{n} [x_{1i}(\mathrm{exp}) - x_{1i}(\mathrm{calc})]^2$$

with respect to A_1 where n is the number of experimentally observed pairs (x_{1i}, x_{2i}) and $x_{1i}(\mathrm{calc})$ is the calculated value of x_{1i} based on the least squares fit. Then :

$$x_{1i}(\mathrm{calc}) = A_1 x_A \ln x_A + A_2 x_B \ln x_B + x_A x_B A_3 \quad \text{where}$$

$$x_A = [x_{2i} + 0.5x_{1i}(\mathrm{calc}) - x_2^0] \,/\, (x_{22}^0 - x_2^0)$$

$$\text{and} \qquad x_B = [x_{22}^0 - x_{2i} - 0.5x_{1i}(\mathrm{Calc})] \,/\, (x_{22}^0 - x_2^0)$$

hence

$$dx_{1i}(\mathrm{calc})/dA_1 = (x_A \ln x_A) \,/\, [1–0.5\, A_1(1 + \ln x_A) + 0.5A_2 \\ (1 + \ln x_B) + 0.5A_3(2x_A - 1)]$$

where the numerator and coefficients A_1, A_2 and A_3 are only known once $x_{1i}(\mathrm{Calc})$ is known.

The normal equation for A_1 is :

$$ds^2/dA_1 = 0$$

which implies

$$\sum_{i=1}^{n} d/dA_1\,[x_{1i} - x_{1i}(\text{calc})]^2 = 0$$

and also

$$\sum_{i=1}^{n} [x_{1i} - x_{1i}(\text{calc})]\; dx_{1i}(\text{calc})/dA_1 = 0$$

but the equation cannot be written down explicitly since the x_{1i}(calc) cannot be expressed as functions of the unknowns A_1, A_2 and A_3 and the known (x_{1i},x_{2i}) alone. To overcome this difficulty x_{1i}(calc) is replaced by the appropriate function with x_{1i} substituted for x_{1i}(Calc), and evaluating $[dx_{1i}(\text{Calc})]/dA_1$ at x_{1i} rather than at x_{1i}(Calc). As initial estimates of A_1, A_2 and A_3, the least–squares estimates obtained by regressing the observed x_{1i} as dependent variables, are used.

The same is done for B_1, B_2 and B_3 and for C_1, C_2 and C_3, using a least–squares regression of ln x_{1i} as dependent variable on x_A and x_B as independent variables.

Method (2) involved estimating A_j, B_j and C_j by solving the equations,

$$\sum_{i=1}^{n} [x_{1i} - f(x_{1i},x_{2i})](dx_{1i}/dA_j) = 0 \quad \text{for } j = 1,2 \text{ and } 3,$$

$$\sum_{i=1}^{n} [x_{1i} - g(x_{1i},x_{2i})](dx_{1i}/dB_j) = 0 \quad \text{for } j = 1,2 \text{ and } 3$$

and

$$\sum_{i=1}^{n} [x_{1i} - h(x_{1i},x_{2i})](dx_{1i}/dB_j) = 0 \quad \text{for } j = 1,2 \text{ and } 3$$

where f, g and h are the right–hand sides of the Hlavaty's equation, the Beta function equation and the logarithmic–gamma fu/ction equation respectively. The above equations differ from the usual least–squares regression equations in that f, g and h and the derivatives are evaluated at x_{1i}(exp) and not x_{1i}(calc). The equations are then solved using DNEQNF sub–routine of IMSL[27], with the solutions of A_j, B_j and C_j obtained in method (1) as initial guesses.

The coefficients A_j of equation (4.1), B_j of equation (4.4) and C_j of equation (4.5) are given in Tables 6.1(c), 6.2(e), 6.3(c), 6.4(c) and 6.5(c) together with the respective root mean square errors, calculated from

$$\sigma = \sqrt{\Sigma[x_1(\text{calc}) - x_1(\text{exp})]^2 \ / \ (n-3)}$$

where x_1(calc) is calculated from the fitted equations (4.1), (4.4) and (4.5) and the corresponding value of x_2.

To illustrate the application of these equations the results for ethanol–toluene–water ternary system are given here. In the following diagram (Figure 4(b)), x_1 has been plotted against x_2, where x_1 and x_2 are the values observed from experiment, from the Hlavaty equation, from the Beta function equation and from the logarithmic–gamma equation. The values are those obtained for the ethanol–toluene–water ternary system.

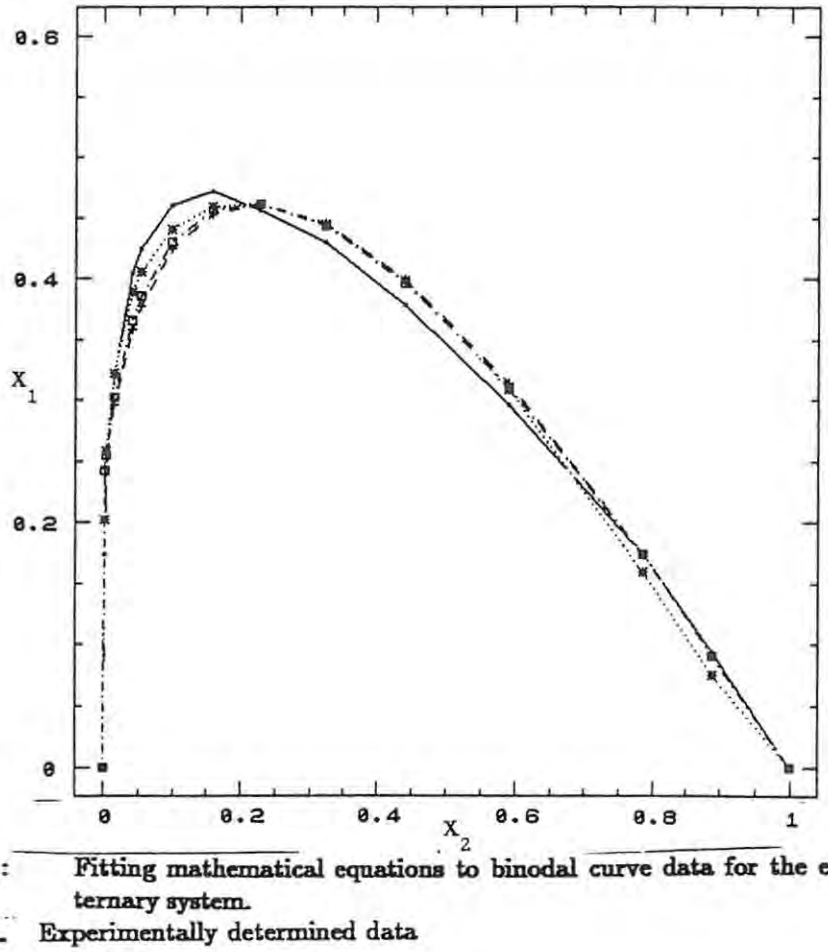


FIGURE 4(b) : **Fitting mathematical equations to binodal curve data for the ethanol–toluene–water ternary system.**

—— Experimentally determined data

·✱·· Hlavaty equation

–+– Beta function equation

–□– Logarithmic–gamma function equation.

5 : PREDICTION OF TERNARY LIQUID—LIQUID EQUILIBRIA

5.1 : INTRODUCTION

Phase equilibrium thermodynamics serves as the mathematical framework for providing information on phase equilibria. The following figure illustrates schematically the sort of problems that can be solved by equilibrium thermodynamics :

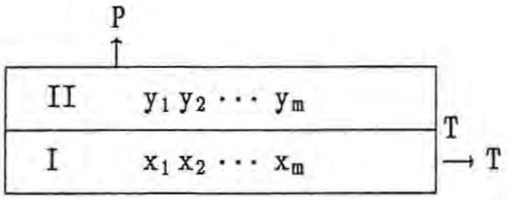


FIGURE 5.1(a) Schematic representation of a thermodynamics problem.

We are given a mixture with M components and two phases, and we suppose that the two phases have reached an equilibrium state. If we know the mole fractions in phase I $(x_1, x_2, \cdots, x_m)$ and the temperature T, what are the mole fractions in phase II $(y_1, y_2, \cdots, y_m)$ and the pressure P[28] ?

Application of thermodynamics to phase equilibra in multicomponent systems is shown schematically in the figure below.[28]

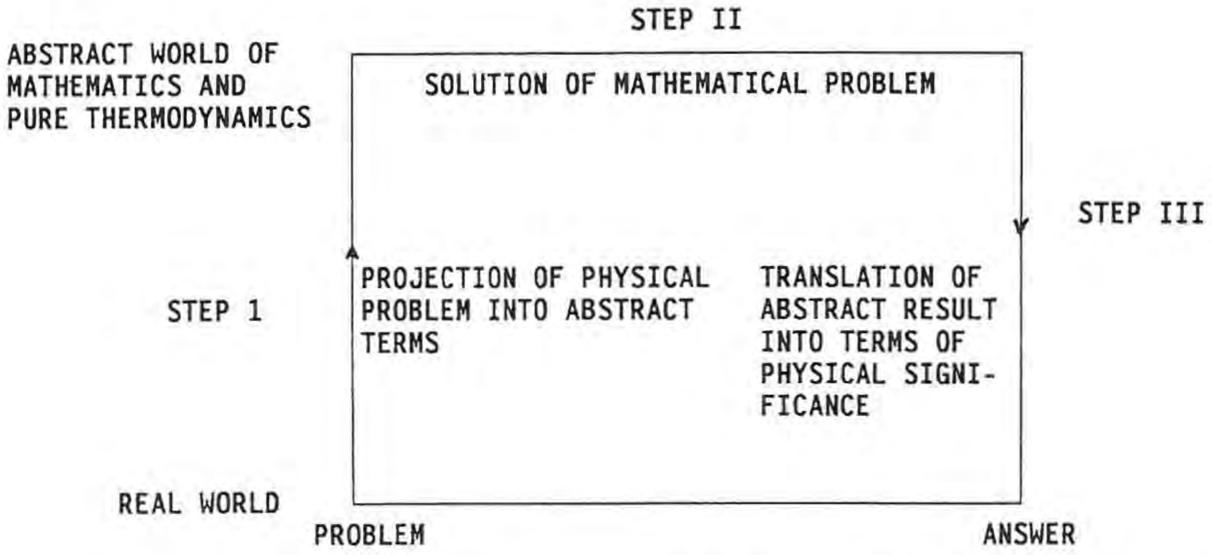


FIGURE 5.1(b) : **Schematic representation of the solution of thermodynamics problems.**

The real world and the real problem are represented by the lower horizontal line, while the upper horizontal line represents the world of abstraction. The three–step application of thermodynamics to a real problem consists of an indirect mental process, instead of attempting to solve the real problem within the world of physically realistic variables, the indirect process first projects the problem into the abstract world, then seeks a solution within that world, and finally projects this solution back into physical reality. The solution of a phase–equilibrium problem using thermodynamics require three steps : In step I, the real problem is translated into an abstract, mathematical problem ; in step II a solution is found to the mathematical problem ; and in step III the mathematical solution is translated back into physically meaningful terms.

The essential feature of step I is to define appropriate and useful mathematical functions to facilitate step II. The profound insight of Gibbs, who, in 1875, defined such a function – the chemical potential – made it possible to achieve the goal of step II ; the mathematical solution to the phase–equilibrium problem is given by the simple result that at equilibrium, the chemical potential of each component must be the same in every phase i.e. $\mu_i^I = \mu_i^{II}$, for some component i, where μ is the chemical potential.

Since the chemical potential does not have an immediate equivalent in the physical world, it is therefore desirable to express the chemical potential in terms of some auxiliary function which might be more easily identified with physical reality. Such an auxiliary function is supplied by the concept of fugacity.[28]

In attempting to simplify the abstract equation of chemical equilibrium, G.N. Lewis first considered the chemical potential for a pure, ideal gas and then generalised to all systems the result he obtained for the ideal case. We have that $d\mu_i = -s_i\, dT + v_i\, dP$ where s_i is the molar entropy and v_i the molar volume.

Therefore
$$\frac{\partial u}{\partial p} = v_i$$

the ideal–gas equation,

$$v_i = \frac{RT}{P},$$

and integrating at constant temperature,

$$\mu_i = \mu_i^0 + RT \ln \frac{P}{P^0}$$

The essential value of the above equation is that it relates a mathematical abstraction to a common, intensive property of the real world (the pressure). However, the equation is valid only for pure, ideal gases ; to generalise it, Lewis defined a function f, called the fugacity, by writing for an isothermal change for any system whether solid, liquid or gas, pure or mixed, ideal or not,

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_i^0} \qquad (5.1)$$

While either μ_i^0 or f_i^0 is arbitrary, both may not be chosen independently ; when one is chosen, the other is fixed. Lewis called the ratio f/f^0 the activity, designated by the symbol α. The fugacity provides a convenient transformation of the fundamental equation of phase equilibrium, $\mu_i^I = \mu_i^{II}$; for phases I and II respectively we have {by equation (5.1)} that :

$$\mu_i^I = \mu_i^{0I} + RT \ln \frac{f_i^I}{f_i^{0I}} \qquad (5.2)$$

and

$$\mu_i^I = \mu_i^{0II} + RT \ln \frac{f_i^{II}}{f_i^{0II}} \qquad (5.3)$$

By using the equilibrium relation we have the result that

$$f_i^I = f_i^{II} \qquad (5.4)$$

The result tells us that the equilibrium condition in terms of chemical potentials can be replaced without loss of generality by an equation which says that for any species i, the fugacities must be the same in all phases. If phase I is vapour and phase II is liquid, equation (5.4) is rewritten in terms of the vapour phase fugacity coefficient ψ_i, the liquid phase activity coefficient γ_i, and the liquid phase reference fugacity f_i^0 :

$$\psi_i y_i P = \gamma_i x_i f_i^0 \quad i = 1,2,\cdots,M \qquad (5.5)$$

If both phases are liquid (mole fractions given by x_i^I , x_i^{II}) equation (5.5) becomes :

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad i = 1,2,\cdots,M$$

At pressure up to a few atmospheres, the fugacity coefficients and reference fugacities are readily calculated using the virial equation in conjunction with second virial coefficients obtained from experimental information or generalized correlations. Indeed, at these low pressures ψ_i is often nearly unity and f_i^0 is often nearly the pure–component vapour pressure at the same temperature as the mixture.[28]

To answer the question in connection with the phase equilibrium problem stated on page 16, we are often left with the problem of establishing a relation for the activity coefficients as functions of compositions x_i and temperature T.

Many equations have been proposed for the calculation of activity coefficients and prediction of liquid–liquid equilibria. In these models liquids are considered either to be gas–like, that is, to be dense and highly nonideal gases whose properties can be described by some equation of state of which van der Waals' is the best known example, or to be solid–like, in a quasicrystalline state, where the molecules do not translate fully in a chaotic manner as in a gas, but where each molecule tends to stay in a small region, a more or less fixed position in space about which it vibrates back and forth. The quasicrystalline picture of the liquid state supposes molecules to sit in a regular array in space, called a lattice, and therefore theories of liquids and liquid mixtures based on this simplified picture are called lattice theories.[29]

A very brief discussion of equations used to calculate activity coefficients follows below. The UNIQUAC equation is discussed in some detail since it has been used in this work. All of these equations are based on the lattice theory of fluids.[29]

5.2 : THE FLORY – HUGGINS EQUATION

One of the most useful applications of the lattice theory of fluids is to liquid mixtures wherein the molecules of one component are very much larger than those of the other component. A common example of such mixtures is provided by solutions of polymers in liquid solvents.

The Gibbs energy of mixing consists of an enthalpy term and an entropy term. In the theory of regular solutions for molecules of similar size it is assumed that the entropy term corresponds to that for an ideal solution and attention is focussed on the enthalpy of mixing ; however, when considering solutions of molecules of different size, it has been found advantageous to assume, at least at first, that the enthalpy of mixing is zero and to concentrate on the entropy. Solutions with zero enthalpy of mixing are called athermal solutions because their components mix with no liberation or absorption of heat. It is customary to write the thermodynamic mixing properties as the sum of two parts [29] :

(1) A combinatorial contribution which appears in the entropy (and therefore in the Gibbs energy and in the Helmholtz energy) but not in the enthalpy or in the volume of mixing, and

(2) a residual contribution, determined by differences in intermolecular forces and in free volumes between the components. For the entropy of mixing,, for example, we write : $\Delta S_{mixing} = \Delta S^C + S^R \cdots$ (5.6) where the superscript C stands for combinatorial and the superscript R stands for residual.[29]

Using the concept of a quasicrystalline lattice as a model for a liquid, and expression for the combinatorial entropy of mixing was derived independently by Flory and by Huggins for flexible molecules that differ significantly in size. The derivation, based on statistical arguments and several well defined assumptions, is not reproduced here. It is presented in several references.[30] Only a brief discussion will be given, along with the result.

We consider a mixture of two liquids 1 and 2. Molecules of type 1 (solvent) are small and spherically symmetric. Molecules of type 2 (polymer) are assumed to behave like flexible chains i.e. as if they consist of a large number of mobile segments, each having the same size as a solvent molecule. Furthermore, it is assumed that each site of the quasilattice is occupied by either a solvent molecule or a polymer segment and that adjacent segments occupy adjacent sites. Let there by N_1 molecules of solvent and N_2 molecules of polymer and let there be r segments in a polymer molecule. The total number of lattice sites is $(N_1 + rN_2)$. The fractions Φ_1^* and Φ_2^* of sites occupied by the solvent and by the polymer are given by :

$$\Phi_1^* = \frac{N_1}{N_1 + r\ N_2} \text{ and } \Phi_1^* = \frac{r\ N_1}{N_1 + r\ N_2} \qquad (5.7)$$

Flory and Huggins[30] have shown that if the amorphous (i.e. non crystalline) polymer and the solvent mix without any energetic effects (i.e. athermal behaviour), the change in Gibbs energy and entropy of mixing are given by the remarkably simple expression :

$$\frac{\Delta G^c}{RT} = \frac{\Delta S^c}{R} = -N_1 \ln \Phi_1^* - N_2 \ln \Phi_2^* \qquad (5.8)$$

To apply the theoretical result of Flory and Huggins to real polymer solutions, i.e. to solutions which are not athermal, it has become common practice to add to the combinatorial part of the Gibbs energy, a semiempirical part for the residual contribution. In other words, we add a term which, if there is no difference in free volume, is given by the enthalpy of mixing.[29]

The excess enthalpy is set proportional to the volume of the solution and to the product of the volume fractions. The Flory–Huggins[30] equation for real polymer solutions then becomes :

$$\frac{\Delta G_{\text{mixing}}}{RT} = \frac{\Delta G^c}{RT} + \frac{G^R}{RT} = N_1 \ln \Phi_1^* + N_2 \ln \Phi_2^* + \chi \, \Phi_1^* \, \Phi_2^* \, (N_1+N_2). \tag{5.9}$$

The activity of the solvent is given by :

$$\ln \alpha_1 = \ln(1-\Phi_2^*) + (1-\tfrac{1}{r})\Phi_2^* + \chi \, {\Phi_2^*}^2 \tag{5.10}$$

and the corresponding equation for the activity coefficient of the solvent is

$$\ln \gamma_1 = \ln\,[1-(1-\tfrac{1}{r})\Phi_2^*] + (1-\tfrac{1}{r})\Phi_2^* + \chi \, {\Phi_2^*}^2 \tag{5.11}$$

5.3 : WILSON'S EQUATION

About twenty years after the work of Flory and Huggins, Wilson[31] considered the case where the components in a mixture differ not only in molecular size but also in intermolecular forces. Wilson's point of departure was equation (5.8) which he used as a basis for an *ad hoc* extension.[29]

To derive Wilson's equation, we first consider a binary solution of components 1 and 2. If we focus attention on a central molecule of type 1, the probability of finding a molecule of type 2, relative to finding a molecule of type 1, about this central molecule, is expressed in terms of the overall mole fractions and two Boltzmann factors :

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \; \exp(-\lambda_{21}/RT)}{x_1 \; \exp(-\lambda_{11}/RT)} \tag{5.12}$$

Equation (5.12) says that the ratio of the number of molecules of type 2 to the molecules of type 1 about a central molecule 1 is equal to the ratio of the overall mole fractions of 2 and 1 weighted by the Boltzmann factors $\exp(-\lambda_{21}/RT)$ and $\exp(-\lambda_{11}/RT)$. The parameters λ_{21} and λ_{11} are, respectively, related to the potential energies of a 1–2 and 1–1 pair of molecules. An equation analogous to equation 5.12 can be written for the probability of finding a molecule of type 1, relative to find a molecule of type 2, about a central molecule 2. The equation is :

$$\frac{x_{12}}{x_{22}} = \frac{x_2 \; \exp(-\lambda_{12}/RT)}{x_1 \; \exp(-\lambda_{22}/RT)} \tag{5.13}$$

Wilson now defines local volume fractions using equations (5.12) and (5.13). The local volume fraction of component 1, designated by ξ_1, is defined by

$$\xi_1 = \frac{v_1 x_{11}}{v_1 x_{11} + v_2 x_{21}} \tag{5.14}$$

where v_1 and v_2 are the molar liquid volumes of components 1 and 2.

Substitution gives

$$\xi_1 = \frac{v_1 x_1 \exp(-\lambda_{11}/RT)}{v_1 x_1 \ \exp(-\lambda_{11}/RT) + v_2 x_2 \ \exp(-\lambda_{21}/RT)} \tag{5.15}$$

Similarly, the local volume fraction of compound 2 is

$$\xi_2 = \frac{v_2 x_2 \exp(-\lambda_{22}/RT)}{v_2 x_2 \ \exp(-\lambda_{22}/RT) + v_1 x_1 \ \exp(-\lambda_{12}/RT)} \tag{5.16}$$

Wilson proposes to use the local fractions ξ_1 and ξ_2 rather than the overall fraction Φ_1^* abd Φ_2^* in the expression of Flory and Huggins (Equation (5.8)). That is, he writes for the molar excess Gibbs energy of a binary system :

$$\frac{g^E}{RT} = x_1 \ln \frac{\xi_1}{x_1} + x_2 \ln \frac{\xi_2}{x_2} \tag{5.17}$$

To simplify notation, it is convenient to define two new parameters Λ_{12} and Λ_{21} in terms of the molar volumes v_1 and v_2 and the energies λ_{11}, λ_{22} and λ_{12}. (We assume $\lambda_{12} = \lambda_{21}$). These definitions are

$$\Lambda_{12} \equiv \frac{v_2}{v_1} \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT}\right] \tag{5.18}$$

$$\Lambda_{21} \equiv \frac{v_1}{v_2} \exp\left[-\frac{\lambda_{12} - \lambda_{22}}{RT}\right] \tag{5.19}$$

Wilson's modification of the Flory–Huggins equation then becomes :

$$\frac{g^E}{RT} = x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(\Lambda_{21} x_1 + x_2)$$

The activity coefficients derived from this equation are given by

$$\ln \gamma_1 = -\ln(\alpha_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right] \tag{5.20}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right] \tag{5.21}$$

5.4 : THE NRTL EQUATION

The basic idea in Wilson's derivation follows from the concept of local composition. This concept was also used by Renon[32] in his derivation of the NRTL (non–random, two–liquid) equation ; however, Renon's equation, unlike Wilson's, is applicable to partially miscible as well as completely miscible systems. The NRTL equation for the excess Gibbs energy is

$$\frac{g^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right] \qquad (5.22)$$

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (5.23)$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (5.24)$$

The significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation, g_{ij} is an energy parameter characteristic of the i–j interaction. The parameter α_{12} is related to the nonrandomness in the mixture ; when α_{12} is zero, the mixture is completely random. The NTRL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from 0.20 to 0.47 ; when experimental data is scarce, the value of α_{12} can often be set arbitrarily ; a typical choice is $\alpha_{12} = 0.3$. From equation (5.22) the activity coefficients are

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \qquad (5.25)$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \qquad (5.26)$$

For the multicomponent case equation 5.25 becomes :

$$\ln\gamma_i = \frac{\overset{j}{\Sigma}\,\tau_{ji}\,G_{ji}\,x_j}{\overset{\ell}{\Sigma}\,G_{\ell}\,x_{\ell}} + \sum^{j}\frac{x_j\,G_{ij}}{\overset{\ell}{\Sigma}\,G_{\ell}\,x_{\ell}}\left[\tau_{ij} - \frac{\overset{r}{\Sigma}x_r\,\tau_{rj}\,G_{rj}}{\overset{\ell}{\Sigma}\,G_{\ell}\,x_{\ell}}\right] \qquad (5.27)$$

i, j, ℓ and r = 1,2 $\cdots$,M where M is number of components in the mixture.

$$\tau_{ji} \equiv \frac{g_{ji} - g_{ii}}{RT} ; (g_{ji} = g_{ij} ; \tau_{ji} \neq \tau_{ij}) \tag{5.28}$$

$$G_{ji} = \exp(-\alpha_{ji}\, \tau_{ji}),(\alpha_{ji} = \alpha_{ij}) \tag{5.29}$$

The parameters $(g_{ji} - g_{ii})$ and $\alpha_{ji}(= \alpha_{ij})$ can be obtained from binary data. For each possible binary pair in a mixture, three parameters are needed.

5.5 : THE UNIQUAC EQUATION [33]

A critical examination of the derivation of the NRTL equation shows that this equation is more suitable for h^E than g^E. Further, since experimental data for typical binary parameters are usually not sufficiently plentiful or precise to yield three meaningful binary parameters, attempts were made to derive a two–parameter equation for g^E which retains at least some of the advantages of the Wilson without, however, being restricted to completely miscible mixtures. Abrams, a South African student working with Prausnitz, derived an equation which, in a sense, extends the quasichemical theory of Guggenheim for nonrandom mixtures to solution containing molecules of different size. This extension was therefore called the universal quasi–chemical theory, or in short, UNIQUAC.

The local composition concept introduced by Wilson is again utilized.

5.5.1 : PARTITION FUNCTION FOR A BINARY MIXTURE

Following Guggenheim (1952), Abrams and Prausnitz postulated that a liquid can be represented by a three–dimensional lattice of equi–spaced lattice sites ; the volume in the immediate vicinity of a site is called a cell. Each molecule in the liquid is divided into attached segments such that each segment occupies a cell. The total number of cells is equal to the total number of segments. [A possible refinement where some cells are unoccupied (holes) is not used]. The configurational partition function Z is given by

$$Z = Z_{\text{lattice}} \cdot Z_{\text{cell}}. \tag{5.30}$$

where Z_{lattice} refers to the situation where the centre of every segment is coincident with a lattice and where Z_{cell} provides those contributuions to Z which are caused by motions of a segment about this central position.

In mixtures of nonelectrolyte liquids removed from critical conditions, we assume that for each component Z_{cell} is independent of composition. For a binary mixture containing N_1 molecules of component 1 and N_2 molecules of component 2, the Helmholtz energy of mixing is then given by

$$\Delta A = -kT \ln \frac{Z_{lattice}(N_1,N_2)}{Z_{lattice}(N_1,0) Z_{lattice}(0,N_2)} \tag{5.31}$$

where k is the Boltzmann's constant. The molar excess Gibbs energy g^E is given by

$$g^E \simeq a^E = \frac{\Delta A}{n_1 + n_2} - RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{5.32}$$

where R is the gas constant, x stands for mole fraction, and n for the number of moles. Following Guggenheim, the lattice partition function is given by

$$Z_{lattice} = \sum_{all\ \theta} \omega(\theta) \exp[-U_0(\theta)/kT] \tag{5.33}$$

where ω is the combinatorial factor (number of ways that the molecules can be arranged in space) and U_0 is the potential energy of the lattice, that is, the energy required to remove all molecules from the lattice ; U_0 is closely related to the energy of isothermal vaporization from the liquid to the ideal–gas state. Bothe ω and U_0 depend on the molecular configuration of the mixture, designated by θ. The summation in equation (5.33) is over all possible values of θ which are permitted within the constraints of the overall stoichiometry.

Since Guggenheim was concerned with mixtures of spherical molecules having the same size, he used for θ the quantity N_{12} which is the number of nearest neighbours, where one neighbour is a molecule of component 1 and the other a molecule of component 2. For mixtures of polysegmented molecules differing in size and shape, N_{12} is not an appropriate variable for describing the micro–composition of the lattice. For such mixtures the local area fraction is used.

5.5.2 : LOCAL AREA FRACTION

A molecule of component 1 is represented by a set of bonded segments, the number of segments per molecule is r_1. While all segements, by definition, have the same size, they differ in their external contact area.

For a molecule of component 1, the number of external nearest neighbours is given by zq_1 where z is the co–ordination number of the lattice and q_1 is a parameter proportional to the molecule's external surface area. Similarly, for molecule of component 2, we have structure parameters r_2 and q_2.

Let us focus attention on the composition of a region in the immediate vicinity of a molecule 1. The local area fraction θ_{21} is the fraction of external sites around molecule 1 (molecule of component 1) which are occupied by segments of molecule 2 (molecule of component 2). Similarly, local area fraction θ_{11} is the fraction of external sites around molecule 1 which are occupied by segmemnts of another molecule 1. When attention is focused on the composition in the immediate vicinity of a molecule 2, similar definitions hold for θ_{12} and θ_{22}. For a binary mixture, therefore, we have four local area fractions which describe the microstructure of the lattice ; however, only two of these are independent because

$$\theta_{11} + \theta_{21} = 1. \tag{5.34}$$

$$\theta_{12} + \theta_{22} = 1 \tag{5.35}$$

The lattice energy U_0 is the sum of all interaction energies between pairs of nonbonded segments.

$$-U_0 = (z/2)q_1 N_1(\theta_{11} U_{11} + \theta_{21} U_{21}) + (z/2)q_2 N_2(\theta_{22} U_{22} + \theta_{12} U_{12}) \tag{5.36}$$

where U_{ij} characterizes the energy of interaction between sites i and j. For convenience let $U_{ij} = (z/2)U_{ij}$. Equation (5.36) then becomes

$$-U_0 = q_1 N_1(\theta_{11} U_{11} + \theta_{21} U_{21}) + q_2 N_2(\theta_{22} U_{22} + \theta_{12} U_{12}) \tag{5.36(a)}$$

The minus sign on the left–hand side of equation (5.36) and (5.36(a)) follows from the convention that the potential energy of the ideal–gas state (infinite separation between molecules) is taken as zero. In a given molecule, all segments are not necessarily chemically identical. Energy parameters U_{ij}, therefore, represent averages since subscripts i and j refer to components, that is molecules of type i and j.

5.5.3 : COMBINATORIAL FACTOR

For a given set of local area fractions, we must calculate the number of possible configurations. We assume that

$$\omega = \omega_1 \omega_2 \, h(N_1,N_2) \tag{5.37}$$

where ω_i refers to the number of configurations associated with a site occupied by a segment of molecule i (i = 1,2). The function h depends on N_1 and N_2 ; it is introduced as a normalization factor to ensure that the combinatorial factor ω satisfies a physically reasonable boundary condition. The number of distinguishable configurations ω_1 and ω_2 are approximated by

$$\omega_1 = \frac{(q_1N_1\theta_{11} + q_2N_2\theta_{12})!}{(q_1N_1\theta_{11})\,!\,(q_1N_1\theta_{21})!} \tag{5.38}$$

$$\omega_2 = \frac{(q_2N_2\theta_{22} + q_1N_1\theta_{21})!}{(q_2N_2\theta_{22})\,!\,(q_2N_2\theta_{12})!} \tag{5.39}$$

Co–ordination number z does not appear in equations (5.38) and (5.39) because it is not possible to permute independently all of the nearest neighbours about a lattice site.

To find h, we consider the athermal case (all $U_{ij} = 0$ and therefore $U_0 = 0$). The maximum term in summation (equation 5.13) is found by separate differentiations with respect to θ_{11} and θ_{22} and by setting the results equal zero.

The average local area fractions for an athermal mixture are given by

$$\theta_{11}^{(0)} = \frac{q_1N_1}{q_1N_1 + q_2N_2} \tag{5.40}$$

$$\theta_{11}^{(0)} = \frac{q_2N_2}{q_1N_1 + q_2N_2} \tag{5.41}$$

The superscript (0) denotes zero th approximation (that is, athermal mixture). Mass balance constraints give

$$\theta_{12}^{(0)} = \theta_{11}^{(0)} = \theta_1 \equiv \frac{q_1N_1}{q_1N_1 + q_2N_2} \tag{5.42}$$

$$\theta_{21}^{(0)} = \theta_{22}^{(0)} = \theta_2 \equiv \frac{q_2N_2}{q_1N_1 + q_2N_2} \tag{5.43}$$

In the zero th approximation, therefore, the average local area fractions are the same as the average area fractions denoted by θ_1 and θ_2.

The normalization factor h can now be found by substituting equations (5.38) to (5.41) into equation (5.37) yielding

$$h(N_1,N_2) = \frac{\omega^{(0)}(q_1N_1\theta_{11}^{(0)})!\,(q_1N_1\theta_{21}^{(0)})!\,(q_2N_2\theta_{22}^{(0)})!\,(q_2N_2\theta_{12}^{(0)}}{(q_1N_1\theta_{11}^{(0)} + q_2N_2\theta_{12}^{(0)})!(q_2N_2\theta_{22}^{(0)} + q_1N_1\theta_{22}^{(0)})!} \tag{5.44}$$

where $\omega^{(0)}$ is the combinatorial factor given by Staverman. [57]

Having found h as outlined above, we now proceed to find the next approximation for the average local fraction for the nonathermal case, that is, where $U_{ij} \neq 0$.

5.5.4 : AVERAGE LOCAL AREA FRACTIONS IN NONATHERMAL MIXTURES

The summation in equation (5.33) is replaced by its maximum form. Equation (5.37), (5.38) and (5.39) are used again but in this approximation U_0 (equation (5.36)) is not set equal to zero. Equation (5.44) is retained.

The resulting expression for Z_{lattice} is separately differentiated with respect to θ_{11} and θ_{22} and the results are set equal to zero. Again using the constraining equations (5.34) and (5.35) but omitting mathematical details, we now find that the average local area fractions are given by

$$\theta_{11}^{(1)} = \frac{\theta_1}{\theta_1 + \theta_2 \exp(-(U_{21}-U_{11})/RT)} \tag{5.45}$$

and

$$\theta_{22}^{(1)} = \frac{\theta_2}{\theta_2 + \theta_1 \exp(-(U_{12}-U_{22})/RT)} \tag{5.46}$$

where U_{ij} is expressed in units of calories per mole and where superscript (1) denotes first approximation and θ_1 and θ_2 are average area fractions defined by equations (5.42) and (5.34). In mixtures that are not athermal, therefore, the average local area fractions are not the same as the average area fractions.

Substituting equation (5.31), (5.33),(5.36(A)), (5.37) to (5.39), and (5.44) to (5.35) into equation (5.32) we obtain the desired result.

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \tag{5.47}$$

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + (z/2)(q_1 x_1 \ln \frac{\Phi_1}{x_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \tag{5.48}$$

and

$$\frac{g^E(\text{residual})}{RT} = q_1 x_1 \ln[\theta_1 + \theta_2 \tau_{21}] - q_2 x_2 \ln[\theta_2 + \theta_1 \tau_{12}] \tag{5.49}$$

where

$$\tau_{21} \equiv \exp\left\{ -\left[\frac{U_{21}-U_{11}}{RT} \right], \tau_{12} \equiv \exp\left[\frac{U_{12}-U_{22}}{RT} \right] \right\} \tag{5.50}$$

in equation (5.48) Φ is the average segment fraction :

$$\Phi_1 \equiv \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \text{ and } \Phi_2 \equiv \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \tag{5.51}$$

Equations (5.47) to (5.49) contain pure–component structural parameters r_1, r_2, q_1 and q_2; these are evaluated from bond angles and bond distances.

The expression for g^E(combinatorial) contains two composition variables : the average area fraction θ and the average segment fraction Φ. However, the expression g^E(residual) contains only one composition variable : the average area fraction θ. There are no adjustable binary parameters in equation (5.48), but there are two adjustable binary parameters in equation (5.49) : $(U_{21}-U_{11})$ and $(U_{12}-U_{22})$. From the derivation of equations (5.47) to (5.49) it follows that $U_{21} = U_{12}$.

Activity coefficients are readily found by differentiation. For a binary mixture, activity coefficient γ_1 is given by

$$\begin{aligned}\ln \gamma_1 = \quad & \ln \Phi_1/x_1 + (z/2)q_1 \ln \Phi_1/\theta_1 + \Phi_2(\ell_1 - (r_1/r_2)\ell_2) \\ & - q_1 \ln(\theta_1 + \theta_2 r_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} \right)\end{aligned} \qquad (5.52)$$

where $\ell_1 = (z/2)(r_1-q_1) - (r_1-1)$; $\ell_2 = (z/2)(r_2-q_2) - (r_2-1)$.

For compound 2, γ_2 can be found by interchanging subscripts 1 and 2. The derivation of equation (5.47) is readily extended to mixtures of three or more components without additional assumption.

For the multicomponent case equation (5.48) and (5.49) become

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_i x_i \ln \frac{\Phi_i}{x_i} + z/2 \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \qquad (5.48(a))$$

$$\frac{g^E(\text{residual})}{RT} = \sum_i q_i x_i \ln(\sum_i \theta_j \tau_{ji}) \qquad (5.49(a))$$

where

$$\tau_{ij} \equiv \exp -\left\{ \left[\frac{U_{ji} - U_{ii}}{RT} \right] \right\} \qquad (5.50(a))$$

and the activity coefficient for component i becomes

$$\begin{aligned}\ln \gamma_i = \quad & \ln \frac{\Phi_i}{x_i} + (z/2)q_i \ln \frac{\theta_i}{x_i} + \ell_i - \frac{\Phi_i}{x_i}\sum_j x_i \ell_j \\ & - q_i \ln(\sum_j \theta_j \tau_{ji}) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}\end{aligned} \qquad (5.51(a))$$

where

$$\ell_j \equiv (z/2)(r_j - q_j) - (r_j - 1\,). \qquad (5.52(a))$$

and where the average area fraction θ and the average segment fraction Φ are defined by

$$\theta_i \equiv \frac{q_i N_i}{\sum_j q_j N_j} = \frac{q_i x_i}{\sum_j q_j N_j} \qquad (5.53)$$

$$\theta_i \equiv \frac{r_i N_i}{\sum_j r_j N_j} = \frac{r_i x_i}{\sum_j r_j x_j} \qquad (5.54)$$

where x is the mole fraction.

5.5.5 : APPLICATION OF THE UNIQUAC EQUATION TO DETERMINE LIQUID–LIQUID PHASE EQUILIBRIA IN TERNARY MIXTURES [34]

UNIQUAC equation can be used to predict where one or two phases exist at equilibrium for a known composition. Provided that the binary parameters are known, the activity coefficient can be calculated from equations 5.51(a) for each component on any composition. The molar Gibbs energy of mixing can then be calculated at any composition from

$$G^{E}_{mix} = RT \sum_i x_i \ln \gamma_i x_i. \qquad (5.55)$$

For a ternary system the mole fraction of component 1 (x_1) is held constant and G^{E}_{mix} is calculated from knowledge of activity coefficients and is then plotted as a function of the mole fraction of component 2 (x_2).

The condition for equilibrium is that the total free energy can be minimised, if the free energy of the system can be reduced by separation into two phases, then phase separation will take place.

This is seen in the following diagram.

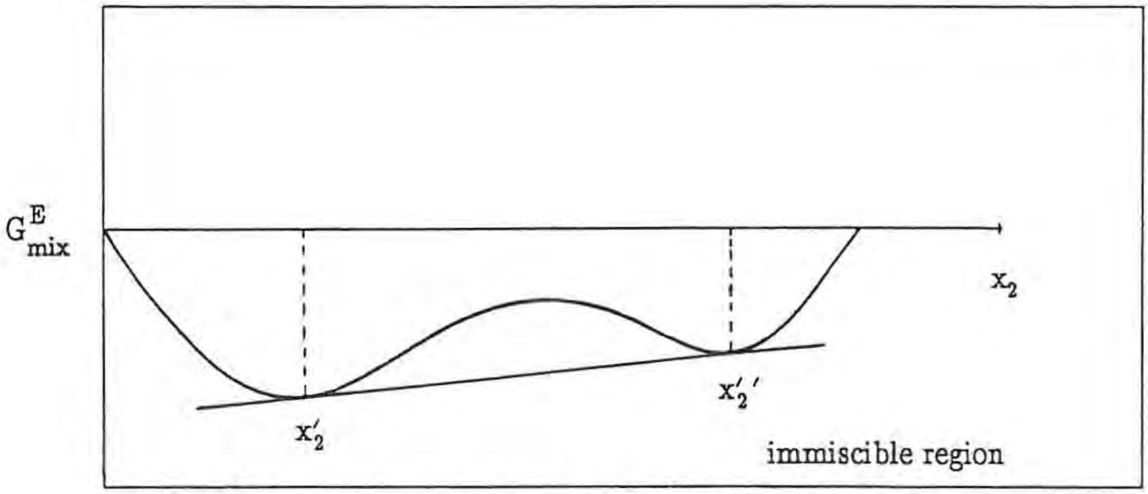


FIGURE 5.5.5(a):Gibbs energy function for a partially miscible liquid mixture.

The mathematical condition for phase separation is that a straight line can be placed in such a way that it is simultaneously congruent to the free energy curve at two points x'_2 and $x'_2{}'$. Any intermediate point on this straight line represents a lower free energy than a point on the unstable one phase curve, and a mixture having such a composition will separate into two phases having compositions x'_2 and $x'_2{}'$.

From each curve of G^E_{mix} plotted as a function of x_2, for constant x_1, the two points with a common tangent define two points on the ternary phase diagram. By varying x_1 the whole phase diagram can be determined.

The use of the UNIQUAC equation for prediction of liquid–liquid equilibria data is illustrated using the ethanol–benzene–water ternary system. It was picked because the interaction parameters were known for this system. The computer program used was obtained from Professor Aage Fredenslund of the Technical University of Denmark. The interaction parameters were not known for the other systems so attempts to apply this predictive proceedure was restricted to this one system. The input and output files used in Professor Fredenslund's programme are given in Appendices A and B. The experimental binodal curve and tie line data are given in Table 6.4(a). The data required to apply the UNIQUAC equations 5.51(a) and 5.55 is given in Table 5.1 and Table 5.2. The calculated tie lines predicted by the UNIQUAC equation are given in Table 5.3. .A summary of the result is given in Figure 5.5.5(b) where the experimental and predicted phase equilibria and tie lines are plotted. A detailed set of results are given in tabulated form in Appendices C and D.

TABLE 5.1 : PURE–COMPONENT STRUCTURAL PARAMETERS

Component	UNIQUAC r	UNIQUAC q
Water	0.92	1.4
Ethanol	2.11	1.97
Benzene	3,19	2.4

TABLE 5.2 : BINARY PARAMETERS

Component I	Component J	τ_{ij}	τ_{ji}
Water	Ethanol	380.68	– 64.560
Water	Benzene	115.13	2057.4
Ethanol	Benzene	–128.88	997.41

TABLE 5.3 : CALCULATED TIELINES IN MOLE PERCENT

ethanol		benzene	
Phase 1 (x'_1)	Phase 2 (x''_1)	Phase 1 (x'_2)	Phase 2 (x''_2)
0.0000	0.0000	0.1832	98.1147
6.0629	2.5574	0.4371	95.0177
11.6333	4.9925	0.8667	91.9919
15.2091	6.6632	1.2909	89.8823
20.3080	9.3007	2.1920	86.4800
25.0142	12.1691	3.4858	82.6662
30.5214	16.5153	5.9786	76.6180
35.8483	23.2206	10.6517	66.4428
39.3205	33.4404	19.1795	47.3295
38.9387	38.9379	30.3840	30.3848

TABLE 5.4 : DEVIATION BETWEEN CALCULATED AND EXPERIMENTAL CONCENTRATIONS IN MOLE PERCENT.

	ethanol		benzene	
	Phase 1 (x_1')	Phase 2(x_1'')	Phase 1(x_2')	Phase 2(x_2'')
Exp. tieline	6.9000	3.5000	0.1000	96.1000
Calculated tieline	6.4370	2.7178	0.4608	94.8127
Calc.–Exp.	–0.4630	–0.7822	0.3608	–1.2873
Exp. tieline	14.6000	6.7000	0.2000	92.5000
Calculated tieline	13.6323	5.9139	1.0883	90.8321
Calc.–Exp.	–0.9677	–0.7861	0.8883	–1.6679
Exp. tieline	25.5000	10.0000	1.5000	87.4000
Calculated tieline	23.0457	10.9090	2.8825	84.3560
Calc.–Exp.	–2.4543	0.9090	1.3825	–3.0440
Exp. tieline	30.4000	16.6000	2.5000	77.6000
Calculated tieline	29.0638	15.2181	5.1787	78.4598
Calc.–Exp.	–1.3362	–1.3819	2.6787	0.8598
Exp. tieline	37.8000	24.4000	7.9000	65.4000
Calculated tieline	35.9070	23.3334	10.7363	66.2576
Calc.–Exp.	–1.8930	–1.0666	2.8363	0.8576
Calc.–Exp. Root Mean Square	1.5839	1.0103	1.9000	1.7424

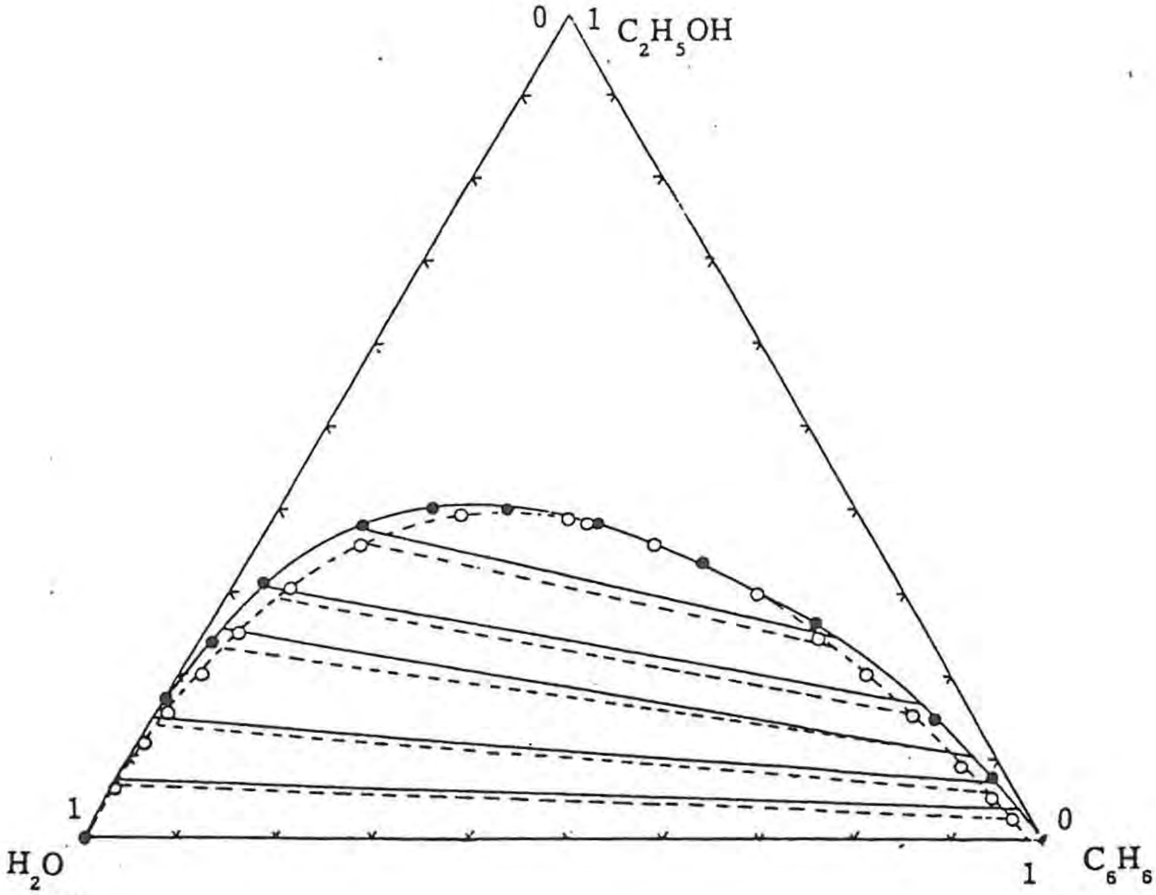


FIGURE 5.5.5(b) : The ethanol—benzene—water ternary system in mole fractions.

- - - - - - - UNIQUAC

———————— EXPERIMENTAL

The experimental and the UNIQUAC binodal curves are very similar. The two curves coincide at the region of the plait point. The tieline slopes are also very similar for both the experimental and UNIQUAC data.

6 : RESULTS

The experimental phase equilibrium results have been presented in the following order :

6.1 Alcohol–mesitylene–water ternary system ;
6.2 Alcohol–xylene–water ternary system ;
6.3 Alcohol–toluene–water ternary system ;
6.4 Alcohol–benzene–water ternary system ; and
6.5 Alcohol–cyclohexane–water ternary system.

For each section, tables of results for binodal curve data, tieline data and coefficients of the fitted equations have been drawn. Ternary phase diagrams, Treybal plots and distribution curves have also been drawn. Finally a table of plait points has also been included.

6.1 : THE ALCOHOL–MESITYLENE–WATER TERNARY SYSTEM AT 298.2K.

TABLE 6.1(a) : The composition of points on the coexistence curve for mixtures $\{x_1C_mH_{2m+1}OH + x_2C_6H_3(CH_3)_3 + (1 - x_1 - x_2)H_20\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH		C_2H_5OH		C_3H_7OH		$CH_3CH(OH)CH_3$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.360	0,001	0.322	0.004	0.070	0.000	0.069	0.000
0.457	0,002	0.367	0.007	0.114	0,001	0.113	0.001
0.565	0.005	0.416	0.012	0.165	0.006	0.166	0.005
0.734	0.022	0.452	0.019	0.179	0.008	0.229	0,014
0.788	0.043	0.554	0.053	0.220	0.016	0.326	0.044
0.796	0.053	0.599	0.101	0.295	0.037	0.389	0.093
0.807	0.092	0.596	0,152	0.379	0.081	0.410	0.138
0.792	0.141	0.569	0.218	0.424	0.141	0.415	0.207
0.747	0.202	0.522	0.300	0.435	0.218	0.403	0.303
0.682	0.273	0.457	0.409	0.420	0.333	0.370	0.433
0.595	0.370	0.359	0.553	0.381	0.444	0.297	0.595
0.471	0.503	0.215	0.743	0.300	0.601	0.174	0.783
0.292	0.690	0.119	0.858	0.175	0.789	0.093	0.888
0.163	0.826	0.000	0.999	0.092	0.880	0.000	0.999
0.000	0.999			0.000	0.999		

TABLE 6.1(a) (Continued)

C_4H_9OH		$CH_3CH(OH)CH_2CH_3$		$CH(CH_3)_2CH_2OH$		$C(CH_3)_3OH$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.019	0.000	0.051	0.000	0.021	0.000	0.115	0.003
0.488	0.000	0.312	0.000	0.546	0,000	0.164	0.011
0.493	0.002	0.392	0.018	0.560	0.021	0.224	0.022
0.530	0.034	0.435	0.033	0.577	0.089	0.304	0,047
0.546	0.083	0.482	0.074	0.568	0.150	0.375	0.099
0.541	0.143	0.504	0.134	0.549	0.226	0.413	0.170
0.496	0.306	0.505	0,208	0.504	0.311	0.425	0.262
0.436	0.404	0.479	0.295	0.445	0.413	0.401	0.371
0.365	0.525	0.431	0.399	0.368	0.531	0.349	0.504
0.269	0.664	0.369	0.520	0.271	0.670	0.267	0.660
0.146	0.814	0.269	0.663	0.149	0.825	0.149	0.827
0.077	0.902	0.142	0.828	0.077	0.906	0.000	0.999
0.000	0.999	0.077	0.913	0.000	0.999		
		0.000	0.999				

TABLE 6.1(b) : The compositions of the conjugate solutions x'_1, x'_2, x''_1 and x''_1 for $\{x_1C_mH_{2m+1}OH + x_2C_6H_3(CH_3)_3 + (1 - x_1 - x_2)H_2O\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH				C_2H_5OH			
x'_1	x'_2	x''_1	x''_2	x'_1	x'_2	x''_1	x''_2
water–rich		**mesitylene–rich**		**water–rich**		**mesitylene–rich**	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.533	0.001	0.090	0.905	0.282	0.000	0.050	0.940
0.663	0.010	0.140	0.852	0.356	0,006	0.073	0.914
0.755	0.023	0.200	0.790	0.440	0.017	0.101	0.879
0.800	0.056	0.208	0.717	0.513	0.035	0.151	0.820
0.795	0.135	0.408	0.573	0.580	0.070	0.245	0.705
				0.581	0.193	0.410	0.480

C_3H_7OH				$CH_3CH(OH)CH_3$			
x'_1	x'_2	x''_1	x''_2	x'_1	x'_2	x''_1	x''_2
water–rich		**mesitylene–rich**		**water–rich**		**mesitylene–rich**	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.055	0.000	0.177	0.782	0.188	0.008	0.187	0.763
0.070	0.000	0.289	0.615	0.270	0,027	0.270	0.640
0.087	0.000	0.352	0.503	0.332	0.047	0.330	0.525
0.098	0.001	0.422	0.320	0.390	0.096	0.387	0.380
0.105	0.001	0.434	0.256				
0.117	0.002	0.425	0.159				
0.135	0.003	0.380	0.090				

TABLE 6.1(b) : (CONTD.)

C_4H_9OH				$CH_3CH(OH)CH_2CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		mesitylene–rich		water–rich		mesitylene–rich	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.007	0.000	0.361	0.530	0.010	0.000	0.133	0.836
0.010	0.000	0.491	0.315	0.020	0.000	0.320	0.591
0.015	0.000	0.545	0.070	0.035	0.000	0.495	0.253
0.019	0.000	0.488	0.000	0.051	0.000	0.312	0.000
$CH(CH_3)_2CH_2OH$				$C(CH_3)_3OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		mesitylene–rich		water–rich		mesitylene–rich	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.007	0.000	0.205	0.752	0.030	0.000	0.290	0.615
0.011	0.000	0.382	0.509	0.038	0.000	0.381	0.430
0.016	0.000	0.503	0.312	0.055	0.000	0.421	0.228
0.021	0.000	0.546	0.000	0.080	0.001	0.362	0.088
				0.100	0.002	0.282	0.041

TABLE 6.1(c) : The coefficients A_i, B_i and C_i in equations (4.1), (4.4) and (4.5) respectively for $C_mH_{2m+1}OH$ + $x_2C_6H_3(CH_3)_3$ $(1 - x_1 - x_2)H_2O$ together with the standard deviation σ. The standard errors are given in parenthesis.

CH_3OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = 1.7387$ (0.31) $A_2 = 1.9316$ (0.28) $A_3 = 8.1931$ (0.81) $\sigma = 0.033$	$B_1 = 5.7282$ (0.54) $B_2 = 1.4664$ (0.05) $B_3 = 1.4390$ (0.07) $\sigma = 0.036$	$C_1 = 5.2080$ (0.44) $C_2 = 1.4294$ (0.05) $C_3 = 2.0091$ (0.08) $\sigma = 0.035$
C_2H_5OH		
$A_1 = 0.0419$ (0.20) $A_2 = 0.8017$ (0.20) $A_3 = 3.4424$ (0.55) $\sigma = 0.024$	$B_1 = 2.6891$ (0.21) $B_2 = 1.2291$ (0.04) $B_3 = 1.0303$ (0.05) $\sigma = 0.034$	$C_1 = 2.4737$ (0.17) $C_2 = 1.1976$ (0.04) $C_3 = 1.5036$ (0.06) $\sigma = 0.031$
C_3H_7OH		
$A_1 = -0.2157$ (0.04) $A_2 = 0.1722$ (0.05) $A_3 = 1.6842$ (0.13) $\sigma = 0.009$	$B_1 = 1.8318$ (0.61) $B_2 = 1.0986$ (0.02) $B_3 = 0.9548$ (0.01) $\sigma = 0.010$	$C_1 = 1.5751$ (0.45) $C_2 = 1.0369$ (0.02) $C_3 = 1.3073$ (0.02) $\sigma = 0.007$
$CH_3CH(OH)CH_3$		
$A_1 = -0.3634$ (0.08) $A_2 = 0.0724$ (0.09) $A_3 = 1.2701$ (0.22) $\sigma = 0.022$	$B_1 = 1.6538$ (0.07) $B_2 = 1.0401$ (0.02) $B_3 = 0.9154$ (0.02) $\sigma = 0.024$	$C_1 = 1.4384$ (0.04) $C_2 = 0.9855$ (0.01) $C_3 = 1.2504$ (0.02) $\sigma = 0.016$
C_4H_9OH		
$A_1 = -1.0177$ (0.14) $A_2 = 0.2792$ (0.11) $A_3 = 1.0679$ (0.36) $\sigma = 0.007$	$B_1 = 2.7938$ (0.19) $B_2 = 1.2817$ (0.04) $B_3 = 1.0578$ (0.03) $\sigma = 0.049$	$C_1 = 2.2273$ (0.08) $C_2 = 1.1927$ (0.02) $C_3 = 1.4109$ (0.02) $\sigma = 0.021$

TABLE 6.1(c) (CONTD.)

$CH_3CH(OH)CH_2CH_3$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = 0.4535$ (0.11) $A_2 = 0.2773$ (0.11) $A_3 = 1.7416$ (0.30) $\sigma = 0.014$	$B_1 = 2.2071$ (0.15) $B_2 = 1.1246$ (0.04) $B_3 = 0.9944$ (0.03) $\sigma = 0.036$	$C_1 = 1.8885$ (0.08) $C_2 = 1.0670$ (0.02) $C_3 = 1.3479$ (0.03) $\sigma = 0.021$
$CH(CH_3)_2CH_2OH$		
$A_1 = -1.2323$ (0.20) $A_2 = 0.1996$ (0.14) $A_3 = 0.7531$ (0.48) $\sigma = 0.009$	$B_1 = 2.7735$ (0.19) $B_2 = 1.2377$ (0.04) $B_3 = 1.0584$ (0.03) $\sigma = 0.041$	$C_1 = 2.2771$ (0.10) $C_2 = 1.1636$ (0.03) $C_3 = 1.4092$ (0.03) $\sigma = 0.024$
$CH(CH_3)_3OH$		
$A_1 = -0.2765$ (0.05) $A_2 = -0.0018$ (0.06) $A_3 = 1.3058$ (0.16) $\sigma = 0.008$	$B_1 = 1.5711$ (0.05) $B_2 = 0.9832$ (0.02) $B_3 = 0.9040$ (0.02) $\sigma = 0.012$	$C_1 = 1.3991$ (0.03) $C_2 = 0.9338$ (0.01) $C_3 = 1.2349$ (0.01) $\sigma = 0.007$

TABLE 6.1(d) : Plait points for the alcohol–mesitylene–water ternary systems, in mole fractions. The plait points have been given in the form (x_1,x_2) where x_1 = mole fraction of alcohol and x_2 = mole fraction of mesitylene.

System	Plait Points
Methanol	(0.5, 0.47)
Ethanol	(0.5, 0.35)
1–Propanol	(0.2, 0.01)
2–Propanol	(0.42,0.22)
t–Butanol	(0.19,0.01)

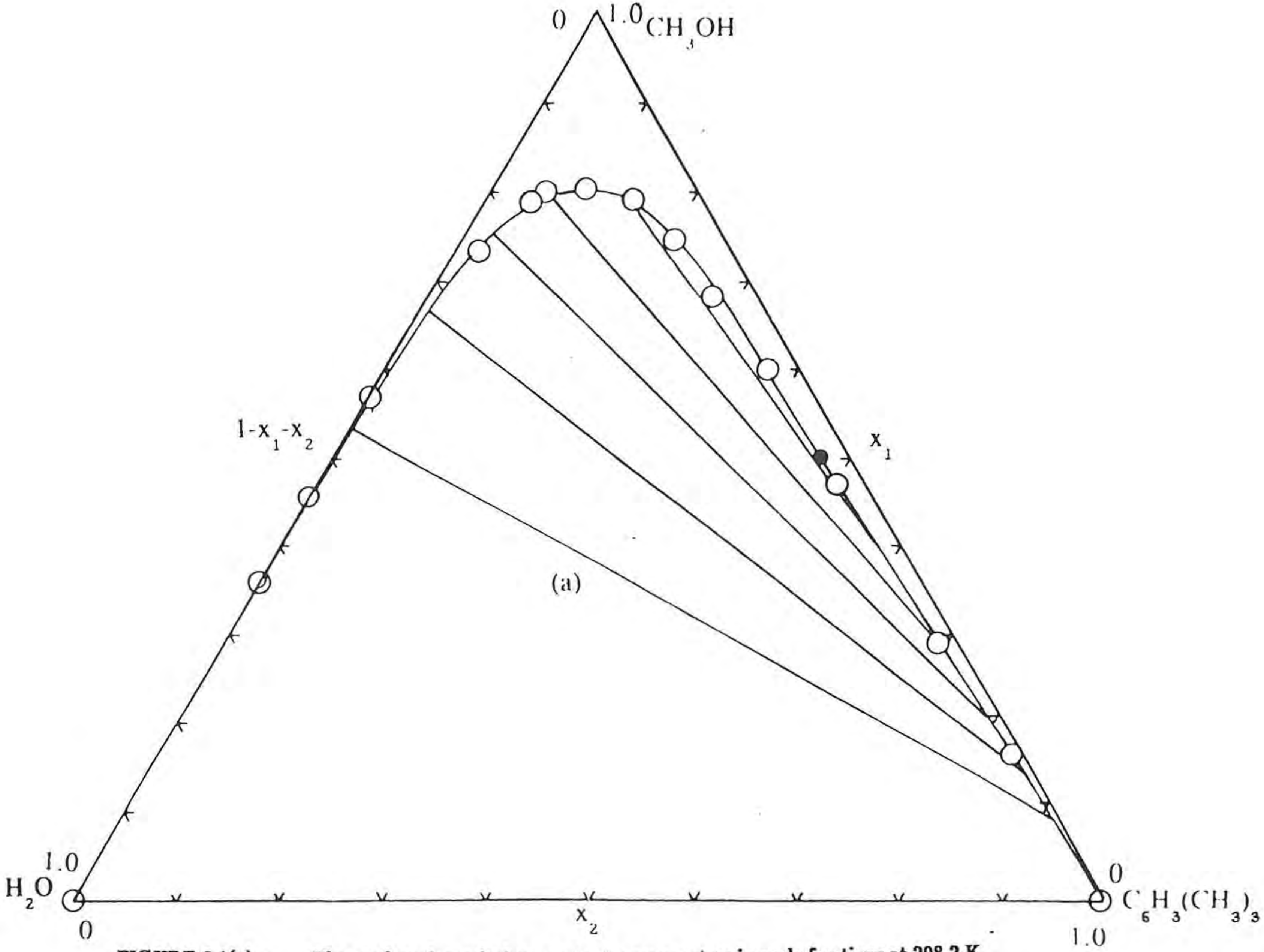


FIGURE 6.1(a) : The methanol–mesitylene–water ternary system in mole fractions at 298.2 K

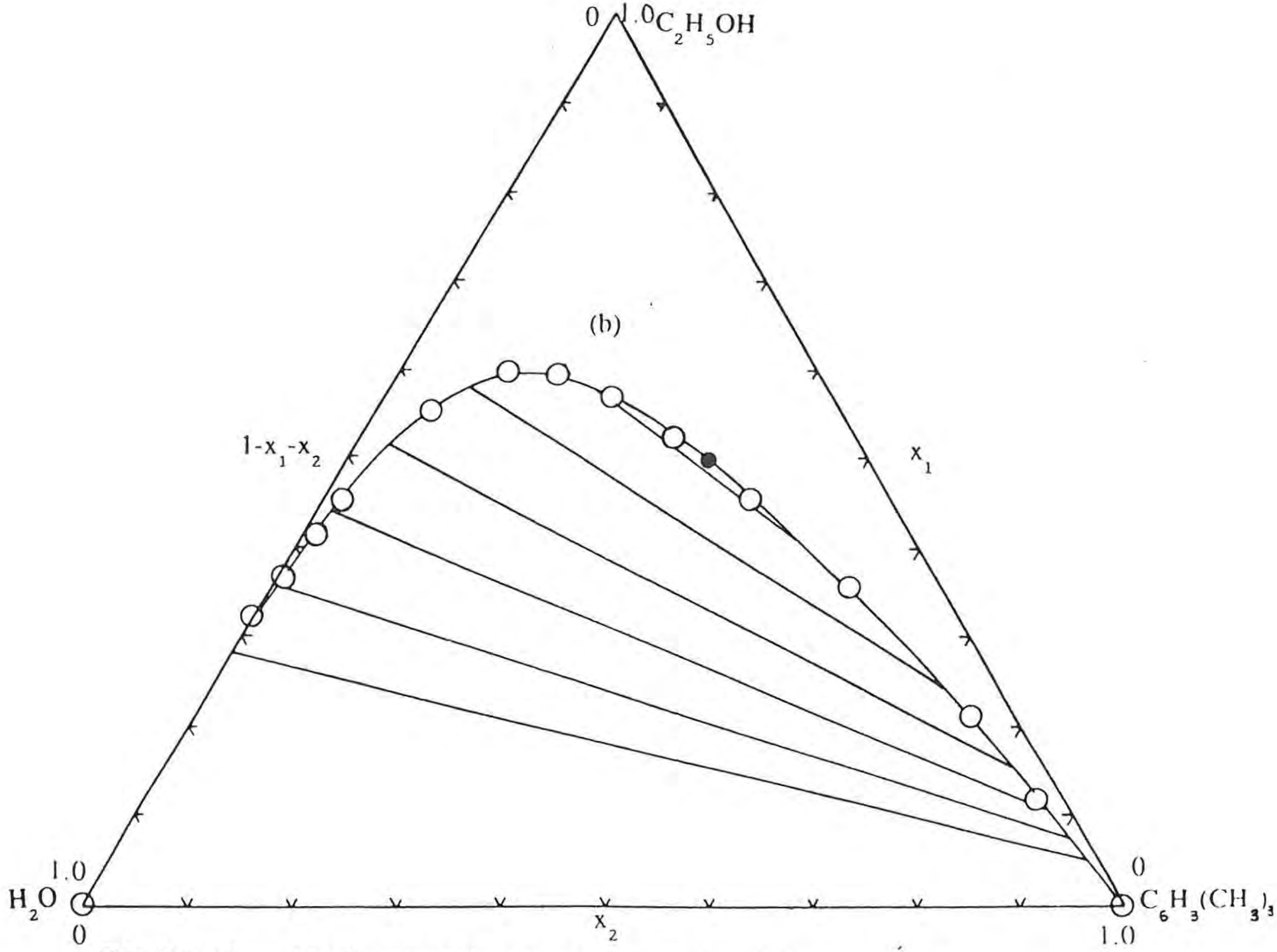


FIGURE 6.1(b) : **The ethanol—mesitylene—water ternary system in mole fractions at 298.2 K**

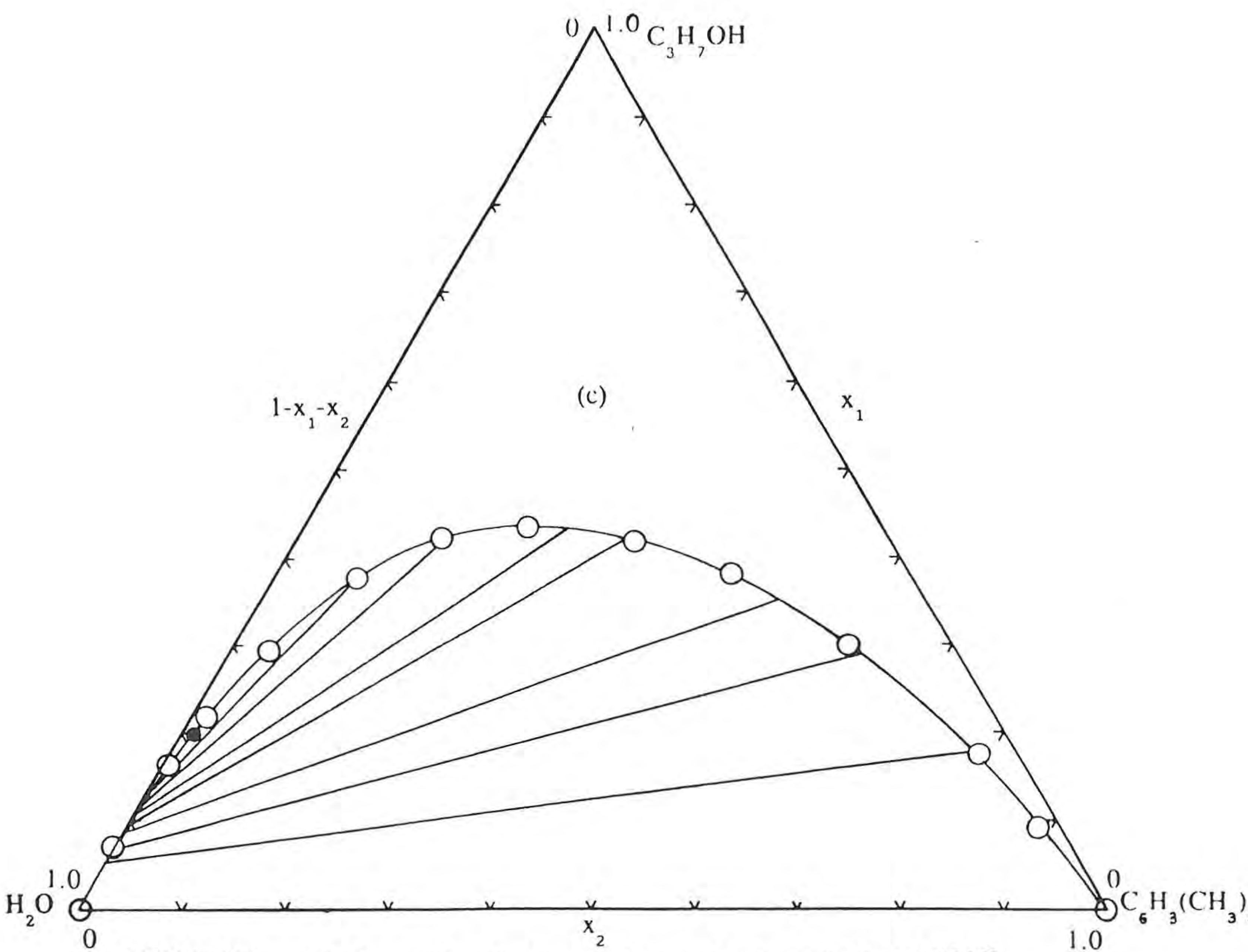


FIGURE 6.1(c) : The 1–propanol–mesitylene–water ternary system in mole fractions at 298.2 K

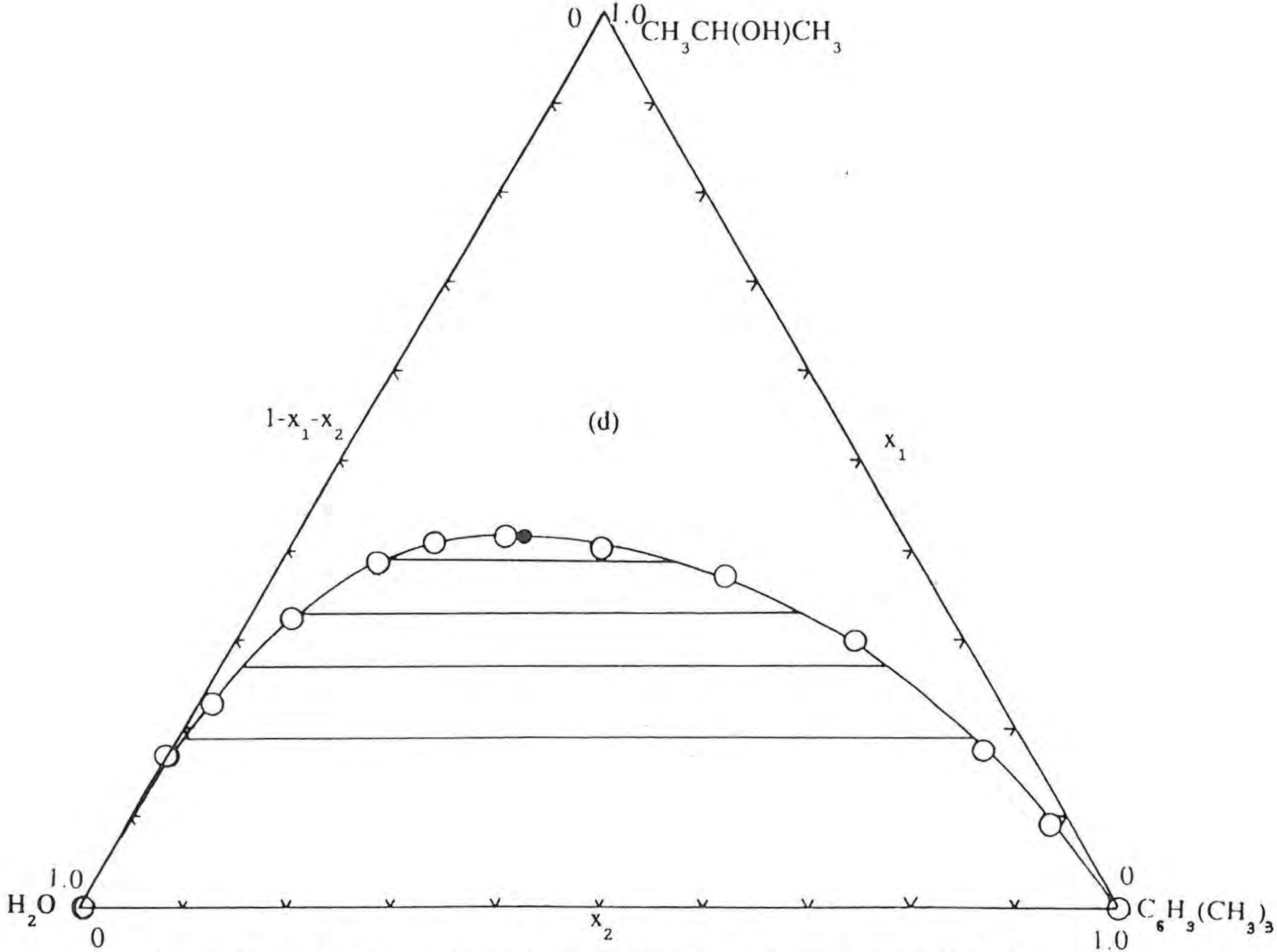


FIGURE 6.1(d) : **The 2–propanol–mesitylene–water ternary system in mole fractions at 298.2 K**

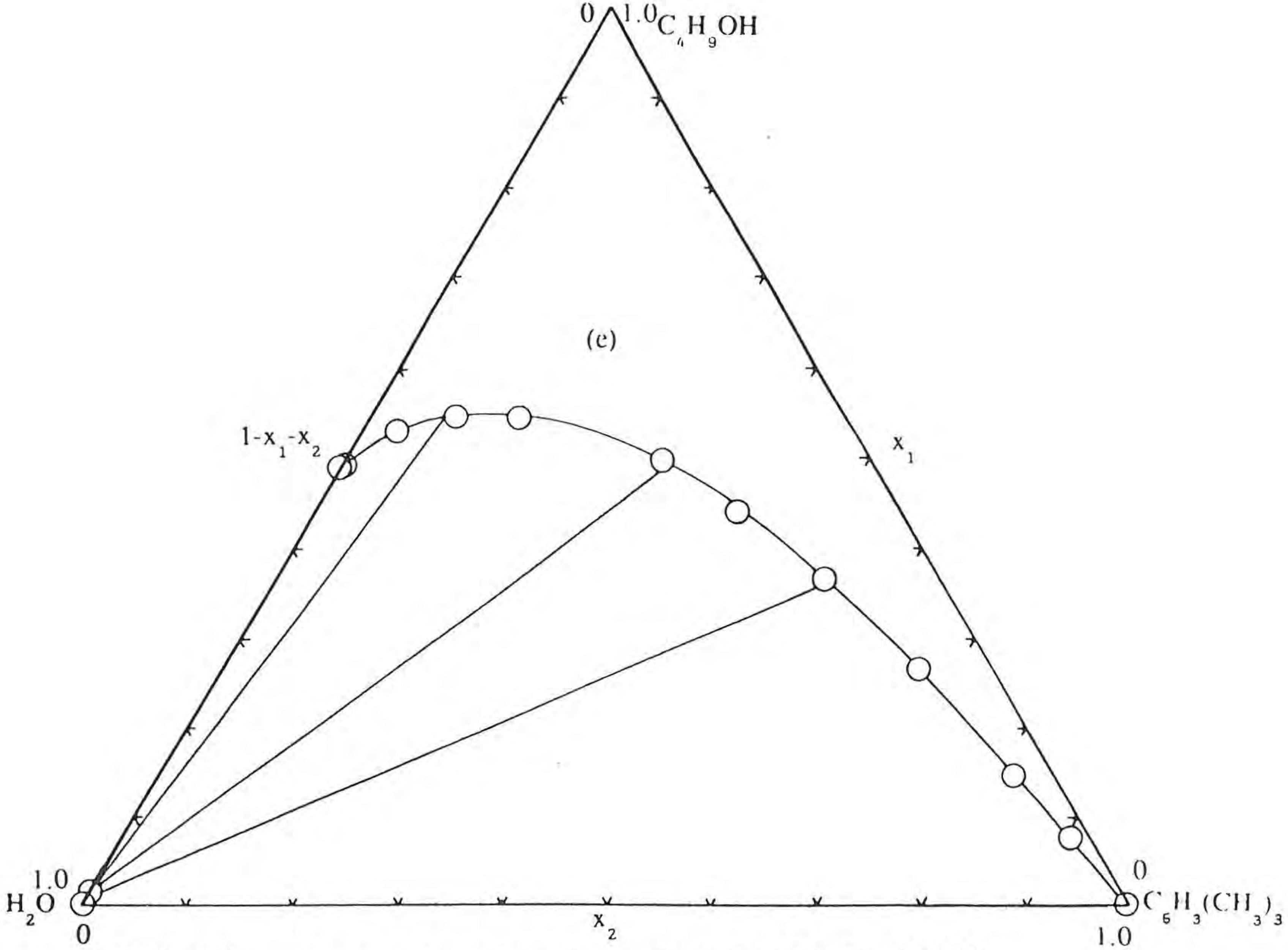


FIGURE 6.1(e) : **The 1–butanol–mesitylene–water ternary system in mole fractions at 298.2 K**

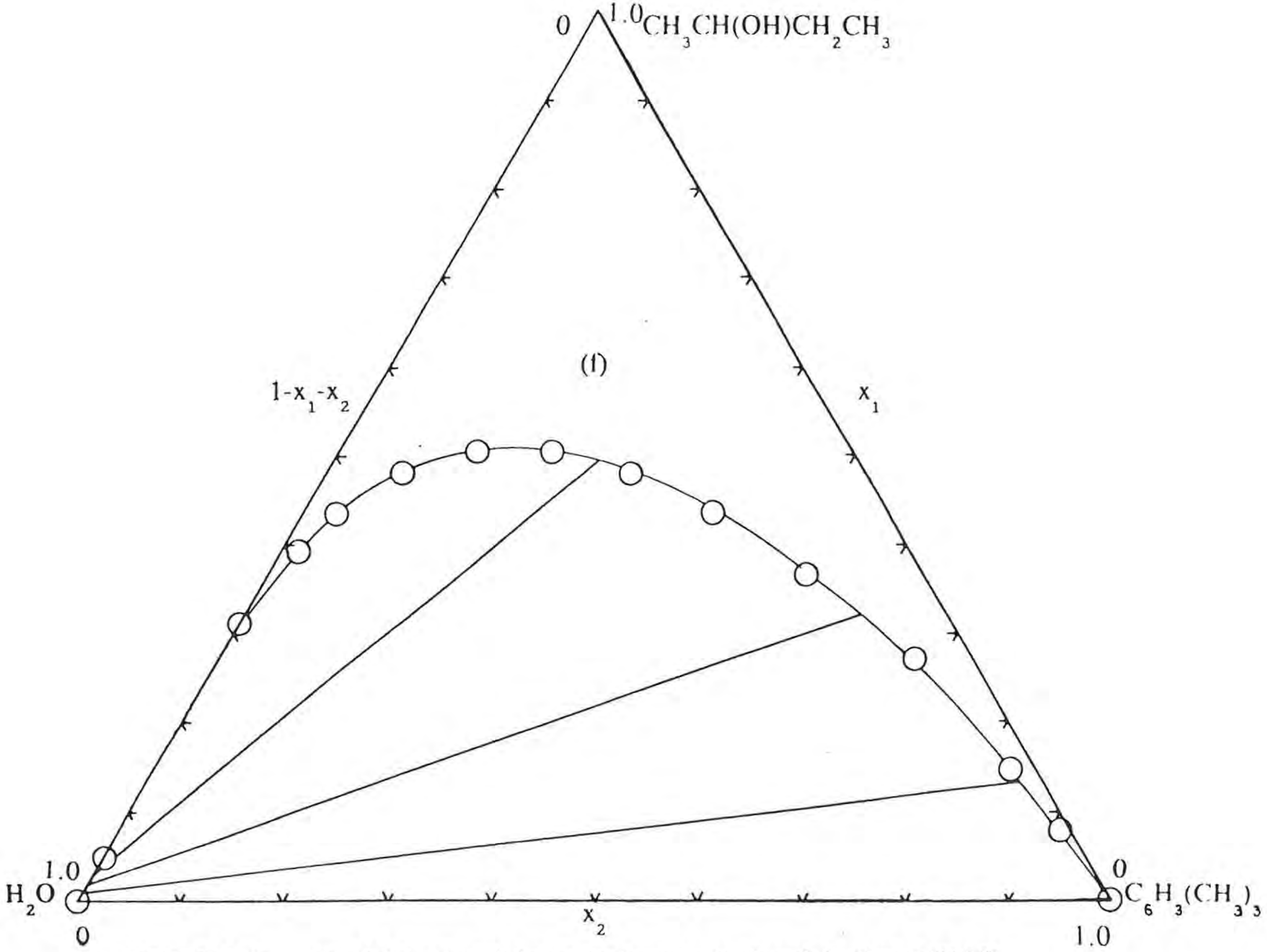


FIGURE 6.1(f) : **The 2–butanol–mesitylene–water ternary system in mole fractions at 298.2 K**

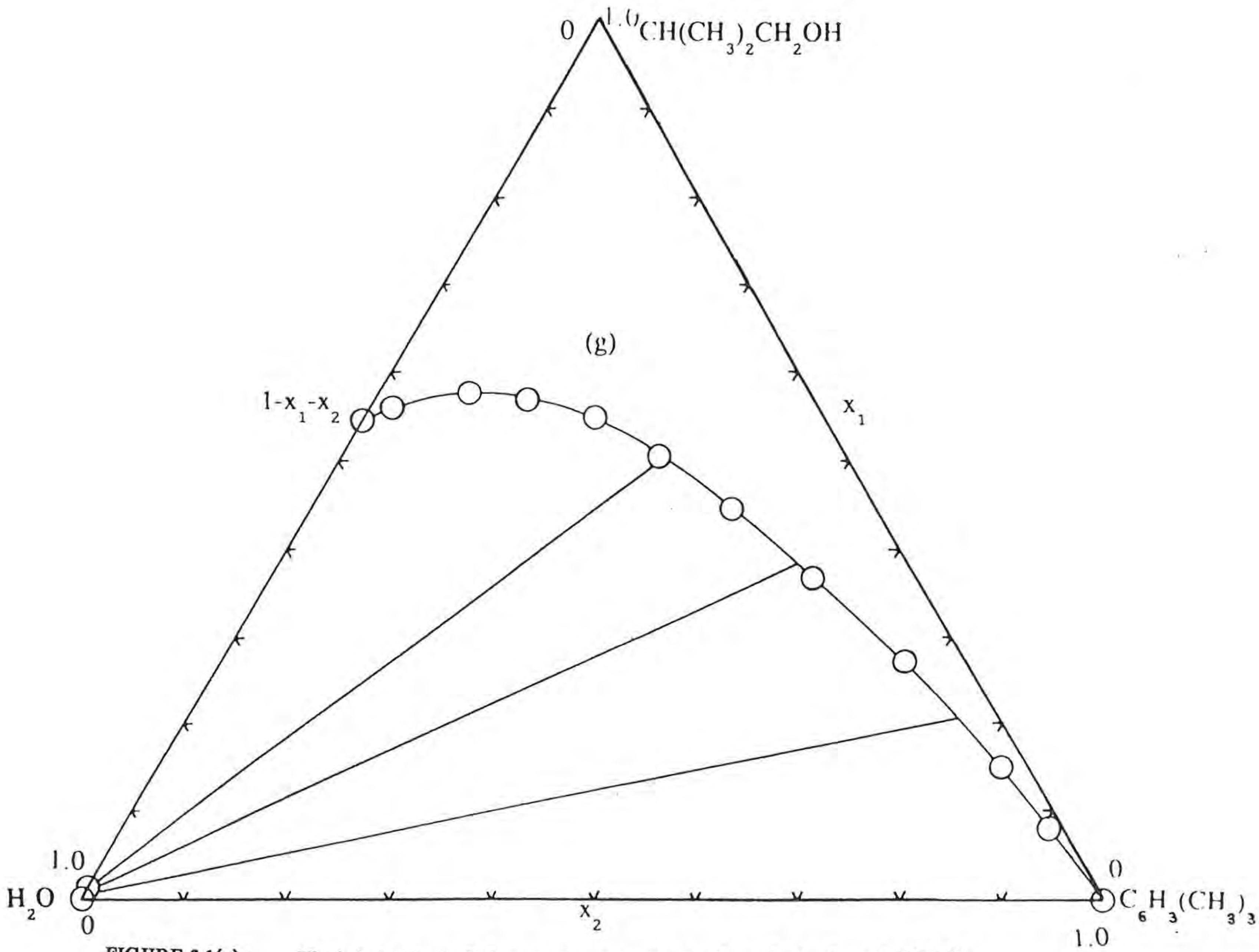


FIGURE 6.1(g) : **The i–butanol–mesitylene–water ternary system in mole fractions at 298.2 K**

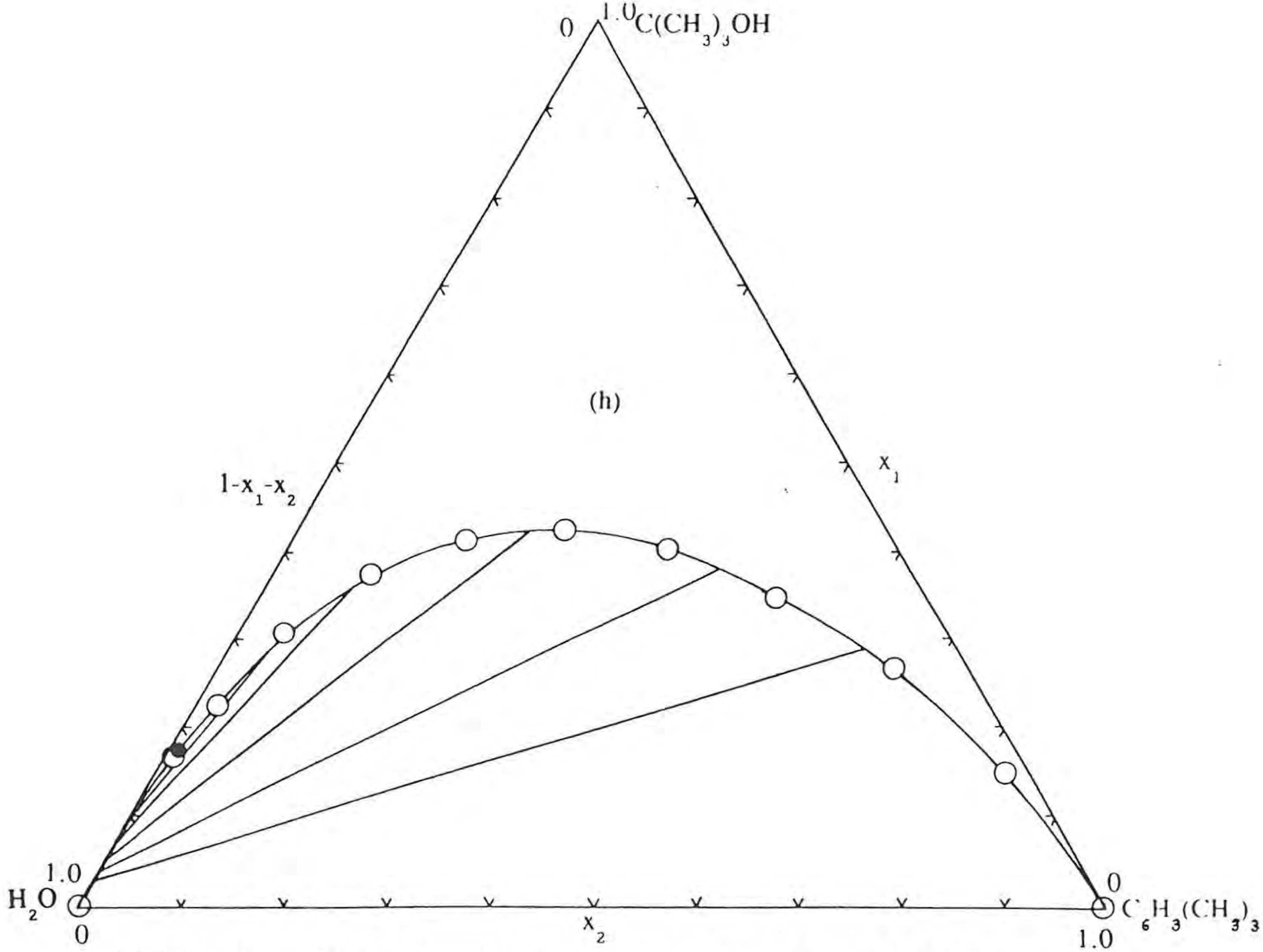
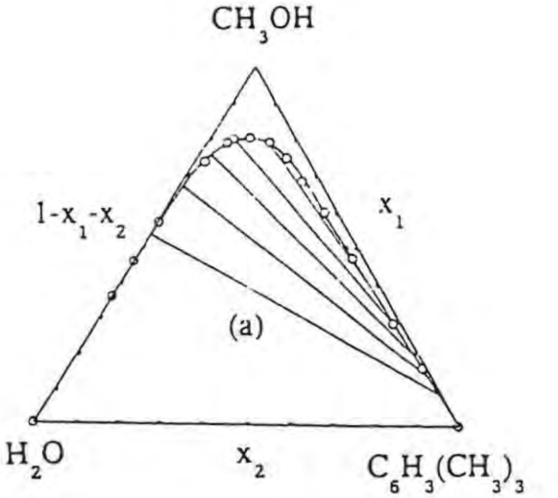
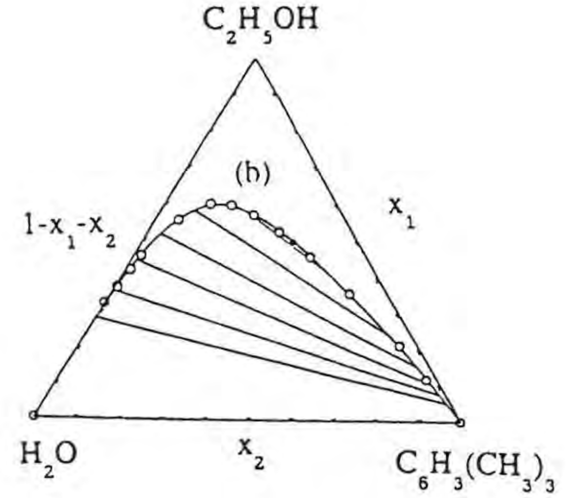
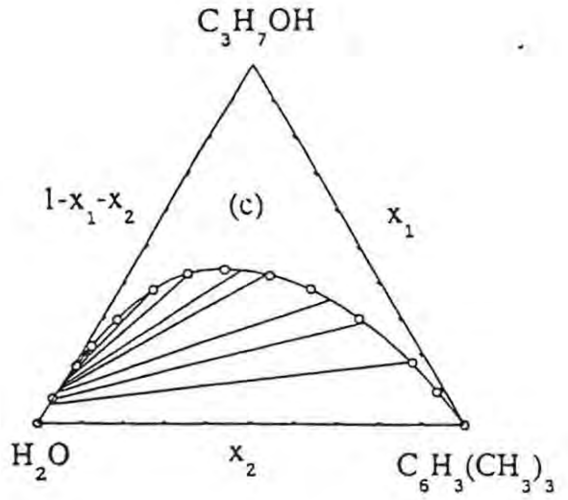
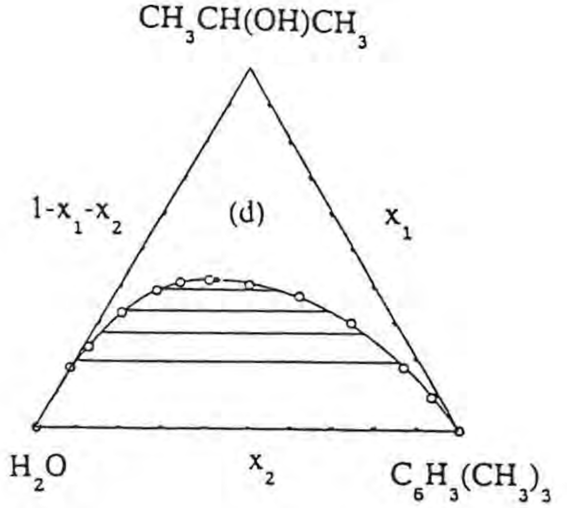


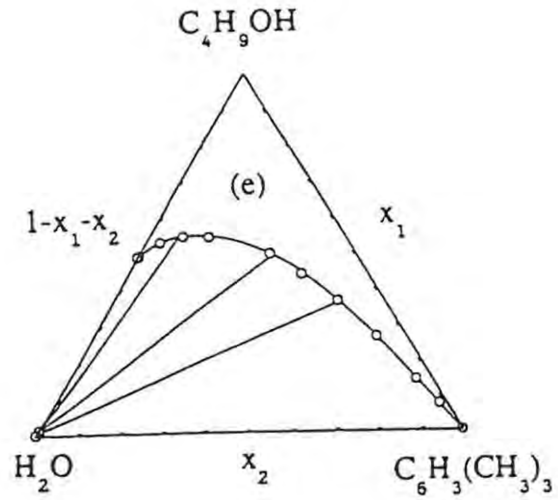
FIGURE 6.1(h) : The t–butanol–mesitylene–water ternary system in mole fractions at 298.2 K

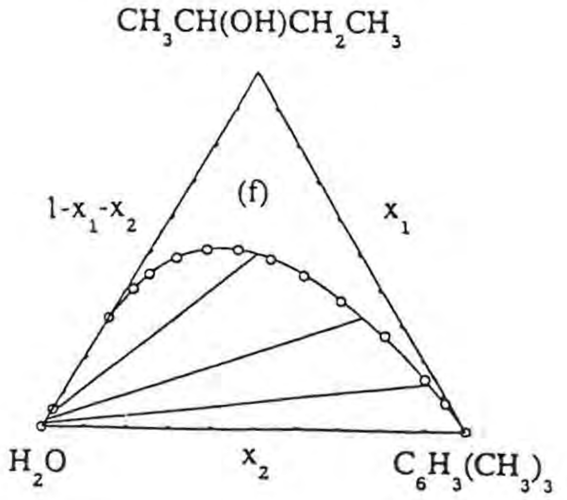

CH_3OH
$1-x_1-x_2$
x_1
(a)
H_2O
x_2
$C_6H_3(CH_3)_3$


C_2H_5OH
(b)
$1-x_1-x_2$
x_1
H_2O
x_2
$C_6H_3(CH_3)_3$


C_3H_7OH
$1-x_1-x_2$
(c)
x_1
H_2O
x_2
$C_6H_3(CH_3)_3$


$CH_3CH(OH)CH_3$
$1-x_1-x_2$
(d)
x_1
H_2O
x_2
$C_6H_3(CH_3)_3$


C_4H_9OH
(e)
$1-x_1-x_2$
x_1
H_2O
x_2
$C_6H_3(CH_3)_3$


$CH_3CH(OH)CH_2CH_3$
(f)
$1-x_1-x_2$
x_1
H_2O
x_2
$C_6H_3(CH_3)_3$

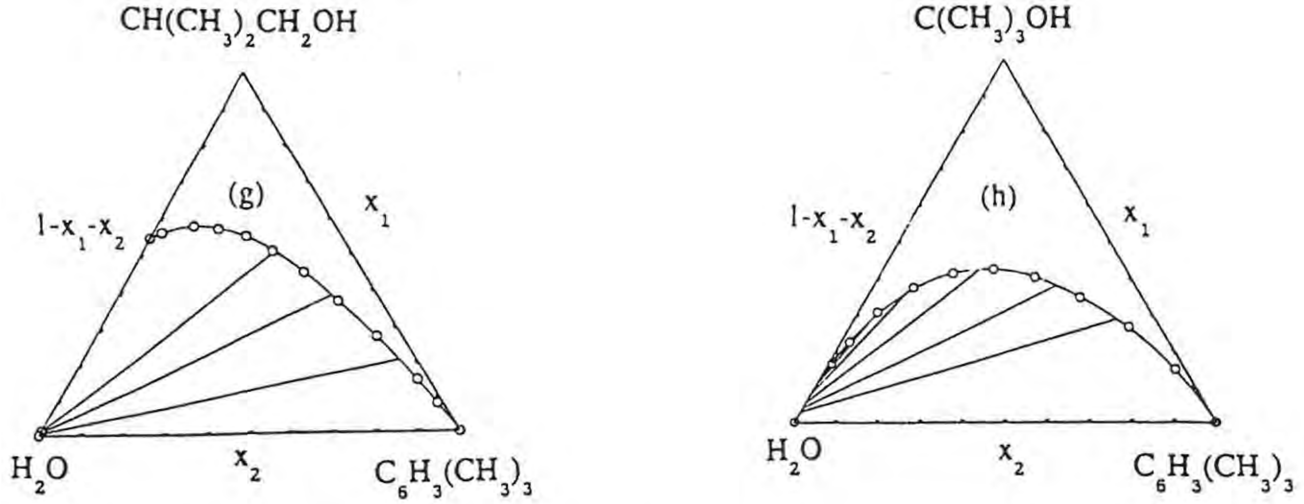


FIGURE 6.1(a–h) : **Summary of liquid–liquid equilibrium curves and tielines for $\{x_1C_mH_{2m+1}OH + x_2C_6H_3(CH_3)_3 + (1-x_1-x_2)H_2O\}$ at 298.2 K.**

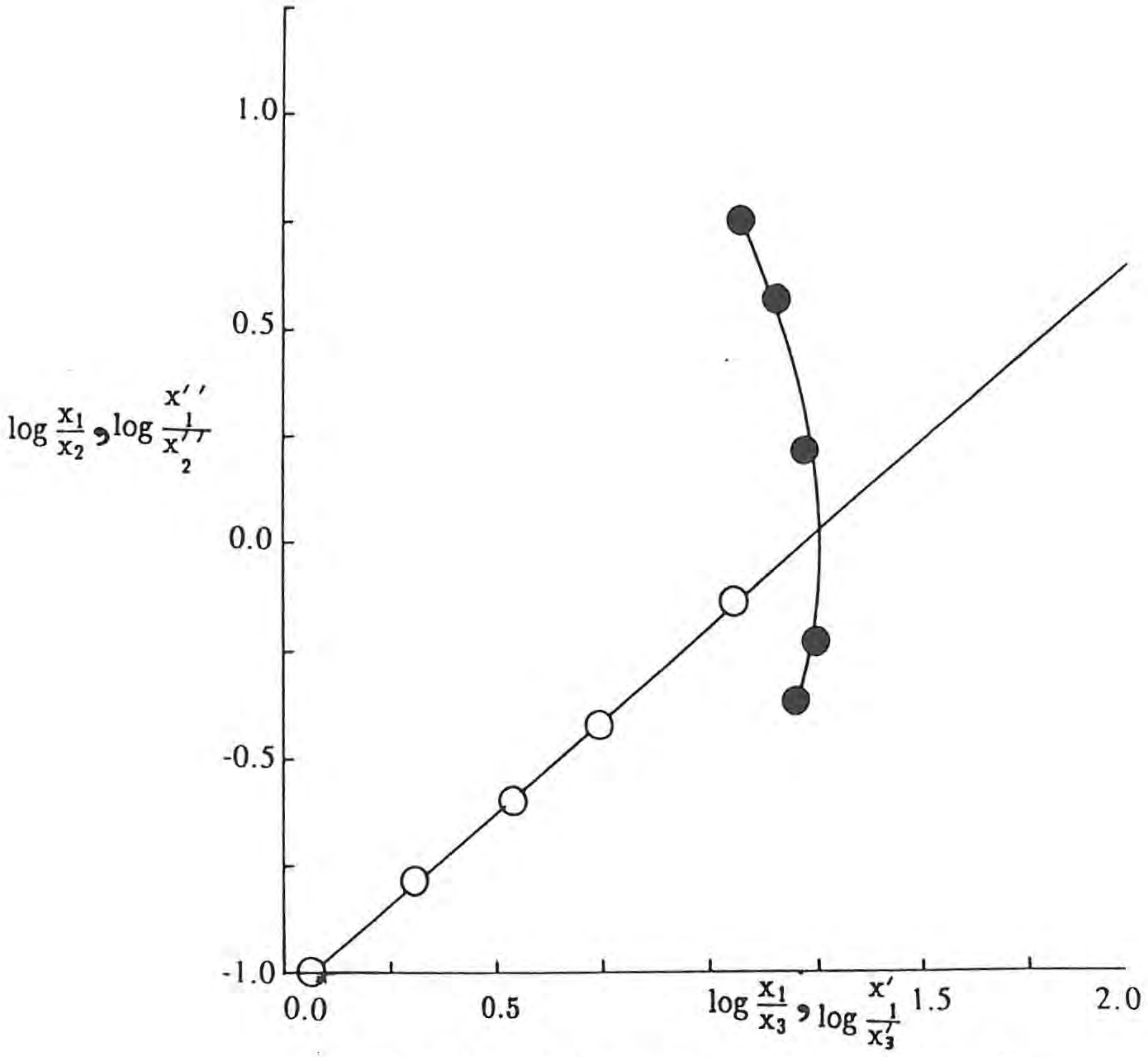


FIGURE 6.1(i) : Determination of plait point {Treybal method} : The methanol–mesitylene–water ternary system.

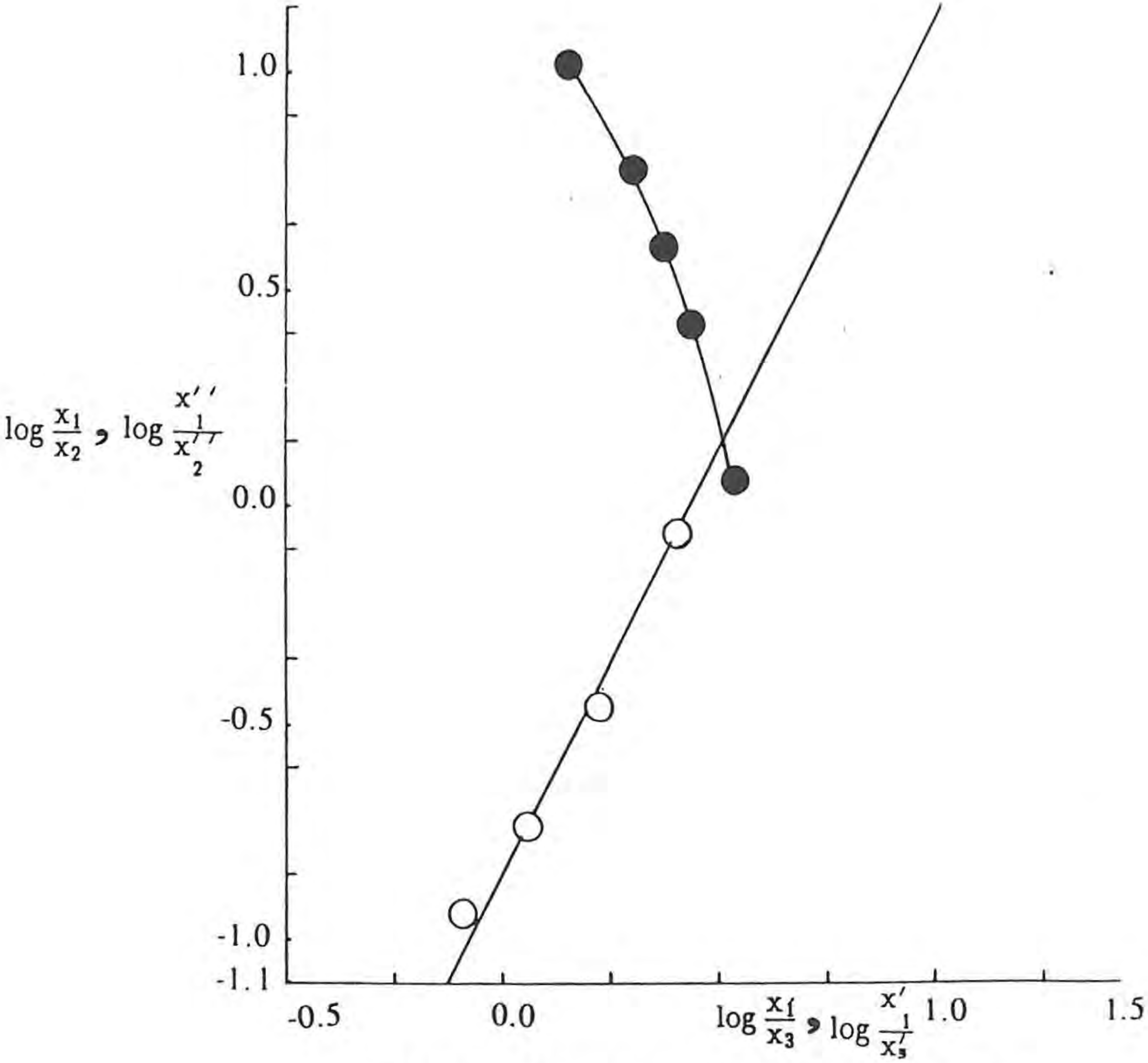


FIGURE 6.1(j) : Determination of plait point {Treybal method} : The ethanol–mesitylene–water ternary system.

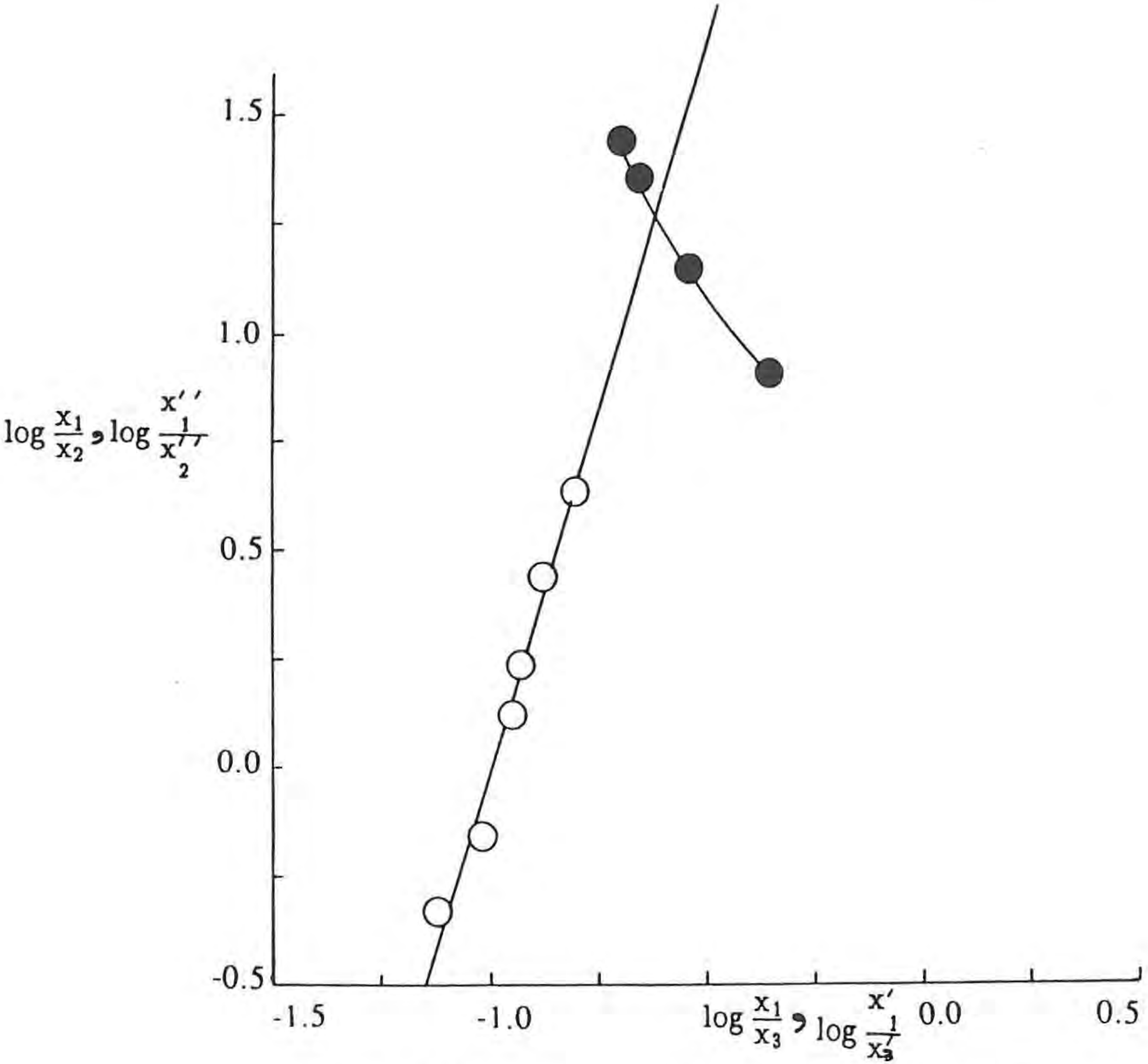


FIGURE 6.1(k) : **Determination of plait point {Treybal method} :**
The 1–propanol–mesitylene–water ternary system.

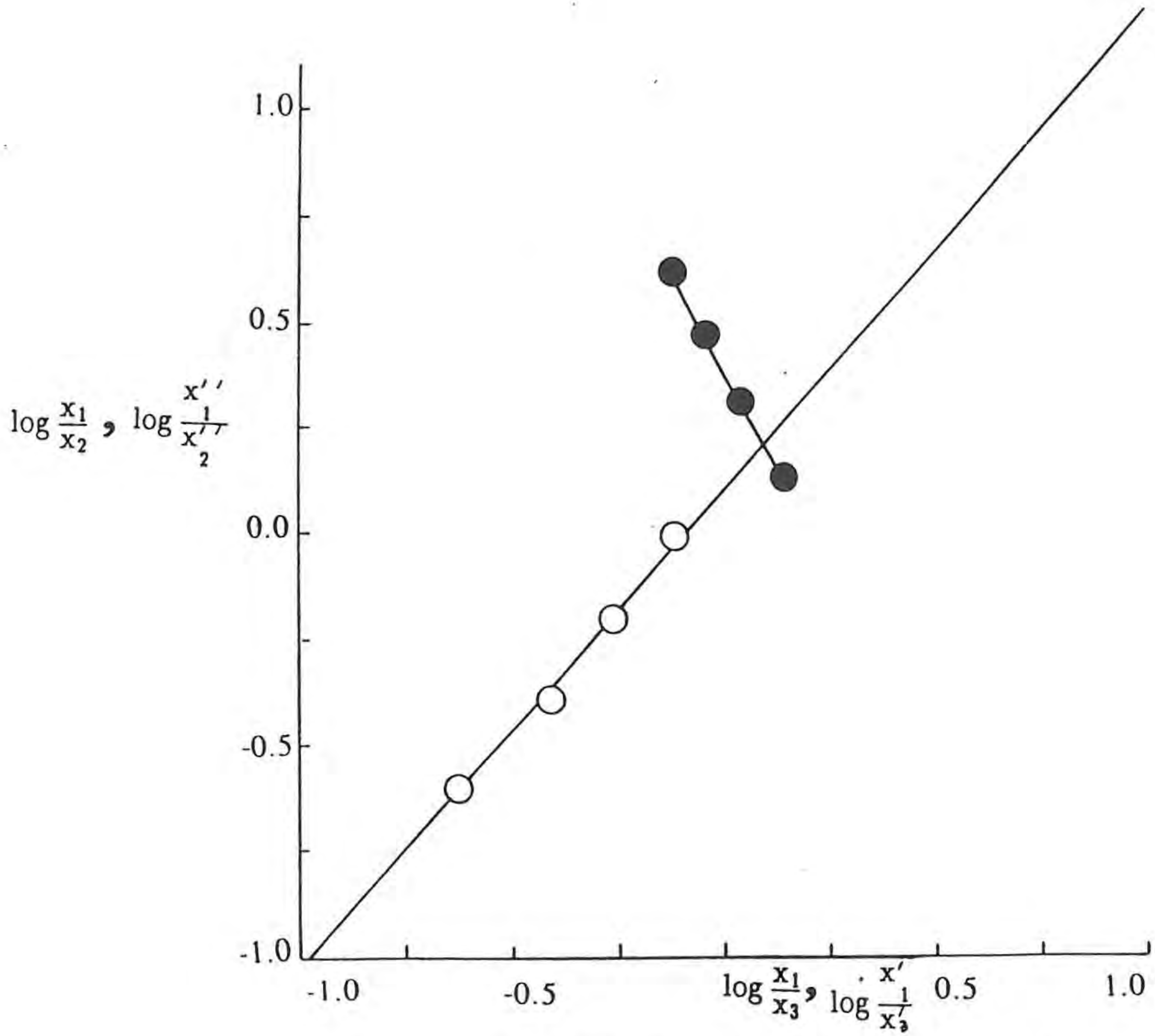


FIGURE 6.1(l) : Determination of plait point {Treybal method} : The 2–propanol–mesitylene–water ternary system.

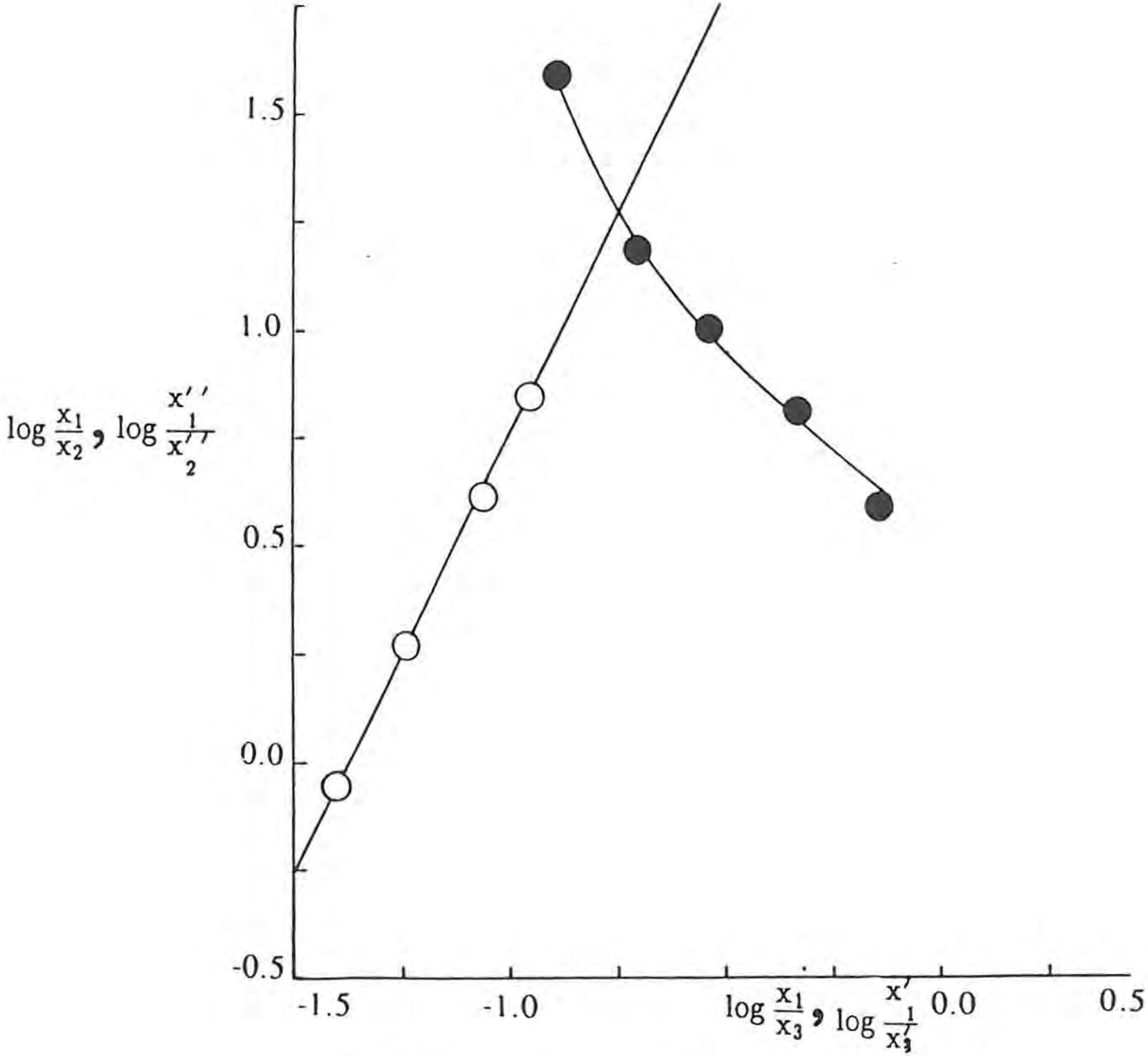


FIGURE 6.1(m) : Determination of plait point {Treybal method} : The t–butanol–mesitylene–water ternary system.

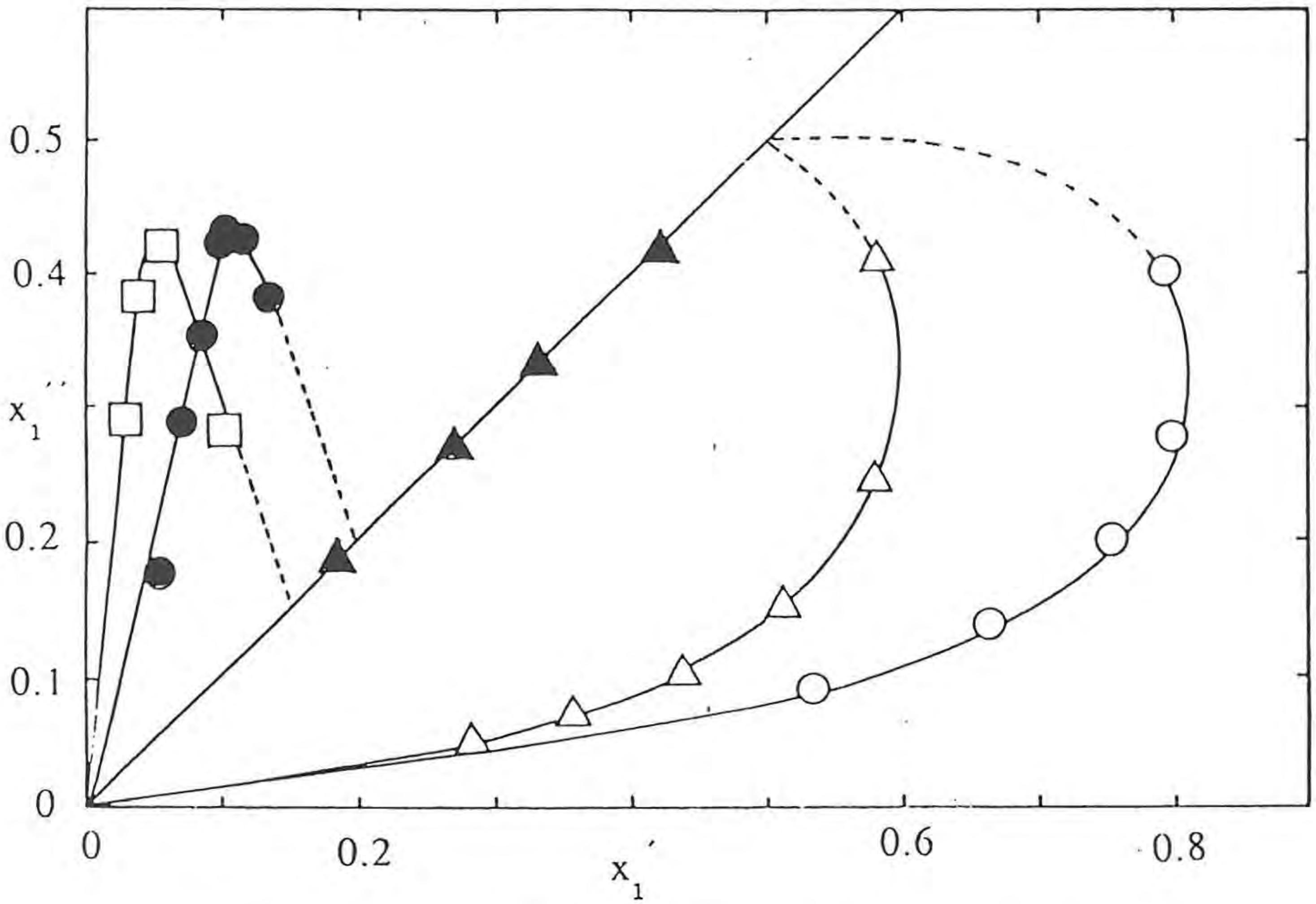


FIGURE 6.1(n) : A plot of x_1'' against x_1', showing the relative solubilities of the alkanol in the mesitylene–rich and water–rich layers.
○, CH_3OH; △, C_2H_5OH; ●, C_3H_7OH; ▲, $CH_3CH(OH)CH_3$; □, $C(CH_3)_3OH$.

6.2 : THE ALCOHOL–p–XYLENE–WATER TERNARY SYSTEM AT 298.2K.

TABLE 6.2(a): The composition of points on the binodal curve for $\{x_1C_mH_{2m+1}OH + x_2p\text{–}C_8H_{10} + (1 - x_1 - x_2)H_2O\}$ at 298.2 K.

CH_3OH		C_3H_7OH		C_4H_9OH		$CH(CH_3)_2CH_2OH$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.998	0.000	0.998	0.000	0.998	0.000	0.998
0.150	0.840	0.083	0.889	0.070	0.915	0.069	0.916
0.263	0.716	0.157	0.798	0.133	0,837	0.135	0.843
0.433	0.523	0.277	0.625	0.248	0.691	0.249	0.695
0.548	0.385	0.358	0.474	0.341	0.557	0.345	0.561
0.629	0.285	0.413	0.351	0.415	0.434	0.422	0.444
0.686	0.207	0.441	0.251	0.474	0.330	0.530	0.247
0.721	0.145	0.442	0,167	0.514	0.239	0.558	0.167
0.730	0.095	0.408	0.099	0.534	0.093	0.571	0.105
0.707	0.053	0.315	0.045	0.539	0.070	0.572	0.011
0.615	0.021	0.260	0.028	0.491	0.003	0.548	0.000
0.508	0.005	0.194	0.014	0.488	0.000	0.021	0.000
0.407	0.003	0.138	0.006	0.020	0.000		
0.315	0.001	0.050	0.000				
0.224	0.001	0.000	0.000				
0.090	0.000						
0.000	0.000						

C_2H_5OH		$CH_3CH(OH)CH_3$		$CH_3CH(OH)CH_2CH_3$		$C(CH_3)_3OH$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.998	0.000	0.998	0.000	0.998	0.000	0.998
0.107	0.875	0.083	0.892	0.070	0.916	0.070	0.915
0.196	0.763	0.158	0.806	0.134	0,842	0.133	0.837
0.328	0.572	0.277	0.627	0.248	0.693	0.243	0.680
0.418	0.424	0.354	0.468	0.341	0.555	0.327	0.533
0.479	0.312	0.391	0.332	0.412	0.431	0.385	0.403
0.516	0.224	0.394	0.223	0.462	0.322	0.412	0.287
0.534	0.157	0.366	0,138	0.494	0.231	0.411	0.191
0.528	0.098	0.321	0.078	0.503	0.150	0.369	0.111
0.465	0.050	0.273	0.039	0.486	0.085	0.310	0.054
0.410	0.023	0.259	0.032	0.414	0.021	0.224	0.023
0.320	0.008	0.195	0.011	0.360	0.006	0.164	0.012
0.241	0.003	0.129	0.002	0.330	0.002	0.115	0.005
0.174	0.001	0.050	0.001	0.322	0.000	0.041	0.003
0.065	0.000	0.000	0.000	0.051	0.000	0.000	0.000

TABLE 6.2(b) : The composition of points on the binodal curve for the mixtures
$x_1CH_3CH(OH)CH_3 + x_2o\text{–}C_6H_4(CH_3)_2$
or $x_2m\text{–}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)H_2O\}$
where x_1 and x_2 refer to mole fractions

$o\text{–}C_6H_4(CH_3)_2$		$m\text{–}C_6H_4(CH_3)_2$	
x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000
0.091	0.001	0.091	0.001
0.139	0.003	0.139	0.002
0.195	0.011	0.195	0.010
0.260	0.031	0.261	0.028
0.319	0.077	0.322	0.078
0.356	0.134	0.367	0.139
0.386	0.219	0.391	0,221
0.386	0.328	0.390	0.330
0.351	0.463	0.353	0.466
0.274	0.620	0.276	0.625
0.158	0.804	0.157	0.806
0.084	0.899	0.085	0.899
0.000	0.999	0.000	0.997

TABLE 6.2(c) : The composition of the conjugate solutions x_1', x_2', x_1'', x_2'' for $\{x_1C_mH_{2m+1}OH + x_2p\text{–}C_8H_{10} + (1-x_1-x_2)H_2O\}$ at 298.2 K.

CH_3OH				C_4H_9OH			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.728	0.115	0.310	0.660	0.488	0.000	0.020	0.000
0.695	0.039	0.144	0.842	0.542	0.140	0.015	0.000
0.620	0.019	0.058	0.916	0.399	0.463	0.010	0.000
0.419	0.005	0.021	0.970	0.170	0.788	0.005	0.000
0.199	0.000	0.005	0.985	0.000	0.998	0.000	0.000
C_2H_5OH				$CH_3CH(OH)CH_2CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.508	0.252	0.415	0.433	0.322	0.000	0.051	0.000
0.532	0.147	0.275	0.650	0.490	0.230	0.040	0.000
0.514	0.074	0.168	0.795	0.385	0,480	0.026	0.000
0.391	0.022	0.066	0.919	0.130	0.843	0.015	0.000
0.292	0.007	0.031	0.960	0.000	0.998	0.000	0.000
0.168	0.001	0.011	0.985				
C_3H_7OH				$CH_3C(CH_3)CH_2OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.314	0.039	0.142	0.009	0.548	0.000	0.021	0.000
0.426	0.123	0.078	0.004	0.510	0.282	0.014	0.000
0.439	0.250	0.052	0.003	0.257	0,685	0.008	0.000
0.385	0.418	0.038	0.002	0.000	0.998	0.000	0.000
0.228	0.702	0.024	0.001				
$CH_3CH(OH)CH_3$				$C(CH_3)_3OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.345	0.102	0.220	0.017	0.246	0.030	0.123	0.009
0.399	0.268	0.178	0.010	0.382	0.131	0.055	0.002
0.349	0.480	0.128	0.005	0.409	0,305	0.030	0.001
0.265	0.648	0.075	0.002	0.367	0.444	0.018	0.001
0.165	0.797	0.043	0.000	0.332	0.522	0.015	0.000
				0.212	0.723	0.005	0.000

TABLE 6.2(d) : The composition of the conjugate solutions x_1', x_2', x_1'', x_2'' for $\{x_1CH_3CH(OH)CH_3 + x_2o\text{–}C_6H_4(CH_3)_2$ or $x_2m\text{–}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)H_2O\}$ where x_1 and x_2 refer to mole fractions.

$o\text{–}C_6H_4(CH_3)_2$				$m\text{–}C_6H_4(CH_3)_2$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		o–xylene–rich		water–rich		m–xylene–rich	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.086	0.001	0.046	0.938	0.089	0.001	0.031	0.953
0.118	0.002	0.098	0.867	0.129	0.002	0.134	0.823
0.206	0.014	0.293	0.577	0.192	0.009	0.286	0.588
0.208	0.034	0.364	0.422	0.234	0.020	0.366	0.407
0.335	0.092	0.381	0.204	0.322	0.072	0.383	0.207

TABLE 6.2(e): The coefficients A_i, B_i and C_i in equations (4.1), (4.4) and (4.5) respectively for $x_1C_mH_{2m+1}OH$ + $x_2P–C_8H_{10}$ + $(1 - x_1 -.x_2)H_2O$ together with the standard deviation σ. The standard errors are given in parenthesis

CH_3OH		
Hlavaty	**Beta**	**Log–Gamma**
A_1 = 0.8730 (0.18) A_2 = 1.3009 (0.20) A_3 = 5.8030 (0.52) σ = 0.066	B_1 = 3.8347 (0.22) B_2 = 1.2856 (0.04) B_3 = 1.2076 (0.03) σ = 0.080	C_1 = 3.3313 (0.20) C_2 = 1.2368 (0.04) C_3 = 1.6478 (0.04) σ = 0.079
CH_3CH_2OH		
Hlavaty	**Beta**	**Log–Gamma**
A_1 = –0.1230 (0.14) A_2 = 0.5680 (0.16) A_3 = 2.6730 (0.40) σ = 0.049	B_1 = 2.3566 (0.14) B_2 = 1.1655 (0.04) B_3 = 1.0213 (0.03) σ = 0.040	C_1 = 2.0408 (0.08) C_2 = 1.1173 (0.02) C_3 = 1.4071 (0.03) σ = 0.032
$CH_3CH_2CH_2OH$		
Hlavaty	**Beta**	**Log–Gamma**
A_1 = –0.1559 (0.06) A_2 = 0.3425 (0.07) A_3 = 2.0083 (0.18) σ = 0.028	B_1 = 1.9035 (0.05) B_2 = 1.1384 (0.01) B_3 = 0.9767 (0.01) σ = 0.011	C_1 = 1.6303 (0.04) C_2 = 1.0857 (0.01) C_3 = 1.3422 (0.01) σ = 0.021
$CH_3(CH)(OH)CH_3$		
Hlavaty	**Beta**	**Log–Gamma**
A_1 = –0.3617 (0.04) A_2 = –0.0174 (0.05) A_3 = 1.0671 (0.13) σ = 0.028	B_1 = 1.6199 (0.08) B_2 = 1.0498 (0.03) B_3 = 0.9254 (0.02) σ = 0.023	C_1 = 1.3829 (0.05) C_2 = 0.9945 (0.02) C_3 = 1.2523 (0.02) σ = 0.015

TABLE 6.2(e) (CONTD.) :

C_4H_9OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -1.3118$ (0.06) $A_2 = 0.0568$ (0.04) $A_3 = 0.2955$ (0.14) $\sigma = 0.005$	$B_1 = 2.5538$ (0.20) $B_2 = 1.2088$ (0.05) $B_3 = 1.0358$ (0.03) $\sigma = 0.026$	$C_1 = 1.5420$ (0.03) $C_2 = 1.0211$ (0.01) $C_3 = 1.0586$ (0.02) $\sigma = 0.004$
$CH_3CH_2CH(OH)CH_3$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.6191$ (0.08) $A_2 = 0.1747$ (0.08) $A_3 = 1.3305$ (0.22) $\sigma = 0.014$	$B_1 = 1.7612$ (0.06) $B_2 = 1.0435$ (0.02) $B_3 = 0.8168$ (0.02) $\sigma = 0.014$	$C_1 = 1.6711$ (0.05) $C_2 = 1.0369$ (0.01) $C_3 = 1.2304$ (0.03) $\sigma = 0.011$
$CH(CH_3)_2CH_2OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -1.7629$ (0.06) $A_2 = -0.0530$ (0.03) $A_3 = -2.3774$ (0.12) $\sigma = 0.002$	$B_1 = 2.4356$ (0.16) $B_2 = 1.1666$ (0.04) $B_3 = 1.0372$ (0.02) $\sigma = 0.034$	$C_1 = 1.5620$ (0.08) $C_2 = 1.0166$ (0.02) $C_3 = 0.9993$ (0.06) $\sigma = 0.009$
$C(CH_3)_3OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.2293$ (0.04) $A_2 = 0.1031$ (0.05) $A_3 = 1.4808$ (0.12) $\sigma = 0.030$	$B_1 = 1.7051$ (0.07) $B_2 = 1.0481$ (0.02) $B_3 = 0.9639$ (0.02) $\sigma = 0.021$	$C_1 = 1.4989$ (0.03) $C_2 = 0.0108$ (0.01) $C_3 = 1.3095$ (0.01) $\sigma = 0.012$

TABLE 6.2(f) : Plait points for the alcohol–p–xylene–water ternary systems in mole fractions. The plait points have been given in the form (x_1,x_2) where x_1 = mole fraction of alcohol and x_2 = mole fraction of p–xylene.

System	Plait Points
Methanol	(0.54,0.49)
Ethanol	(0.46,0.35)
1–Propanol	(0.26,0.01)
2–Propanol	(0.28,0.07)
t–Butanol	(0.17,0.01)

System	Plait Point
2–Propanol–o–xylene	(0.36,0.13)
2–Propanol–m–xylene	(0.36,0.12)

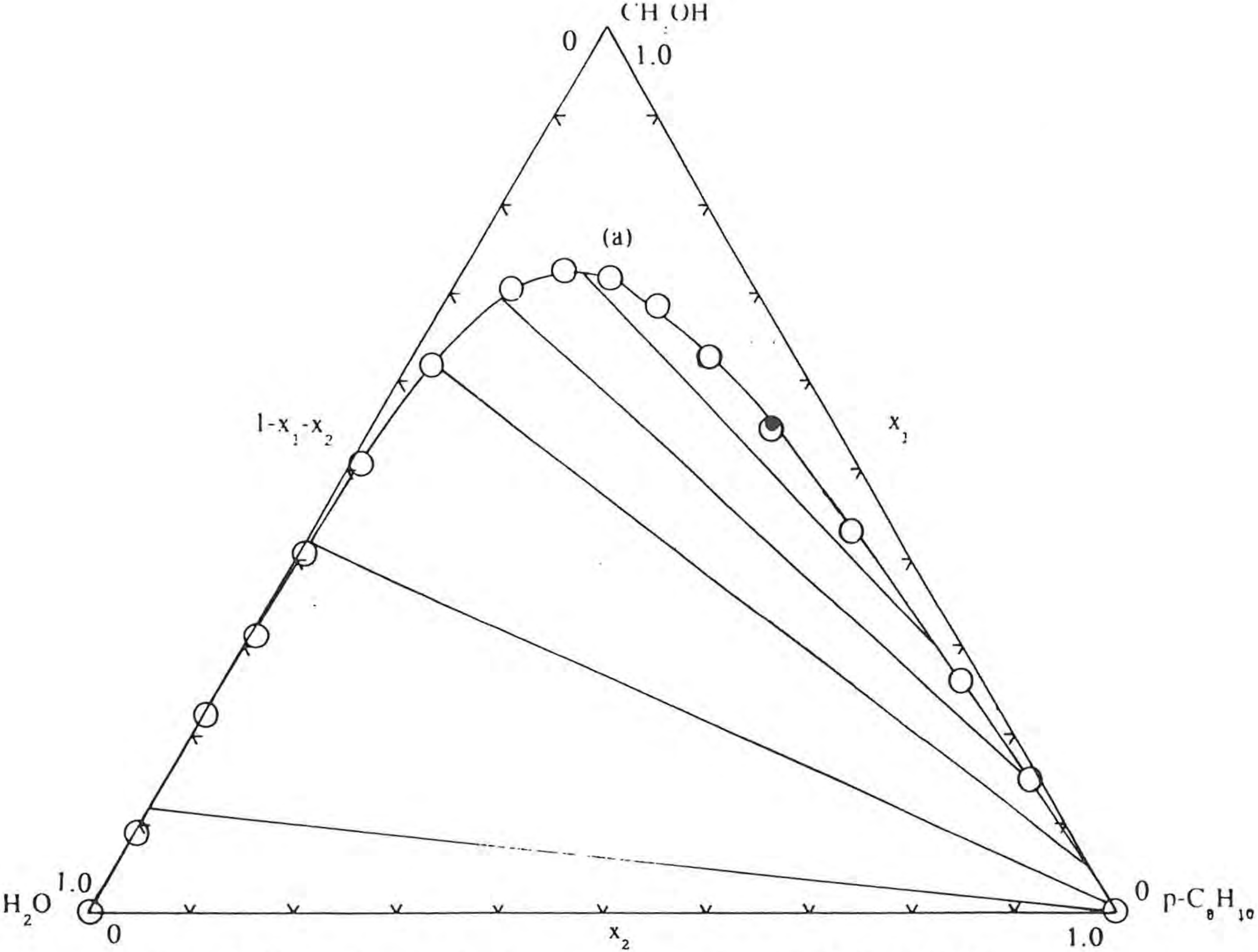


FIGURE 6.2(a) : The methanol—p—xylene—water ternary system in mole fractions at 298.2 K

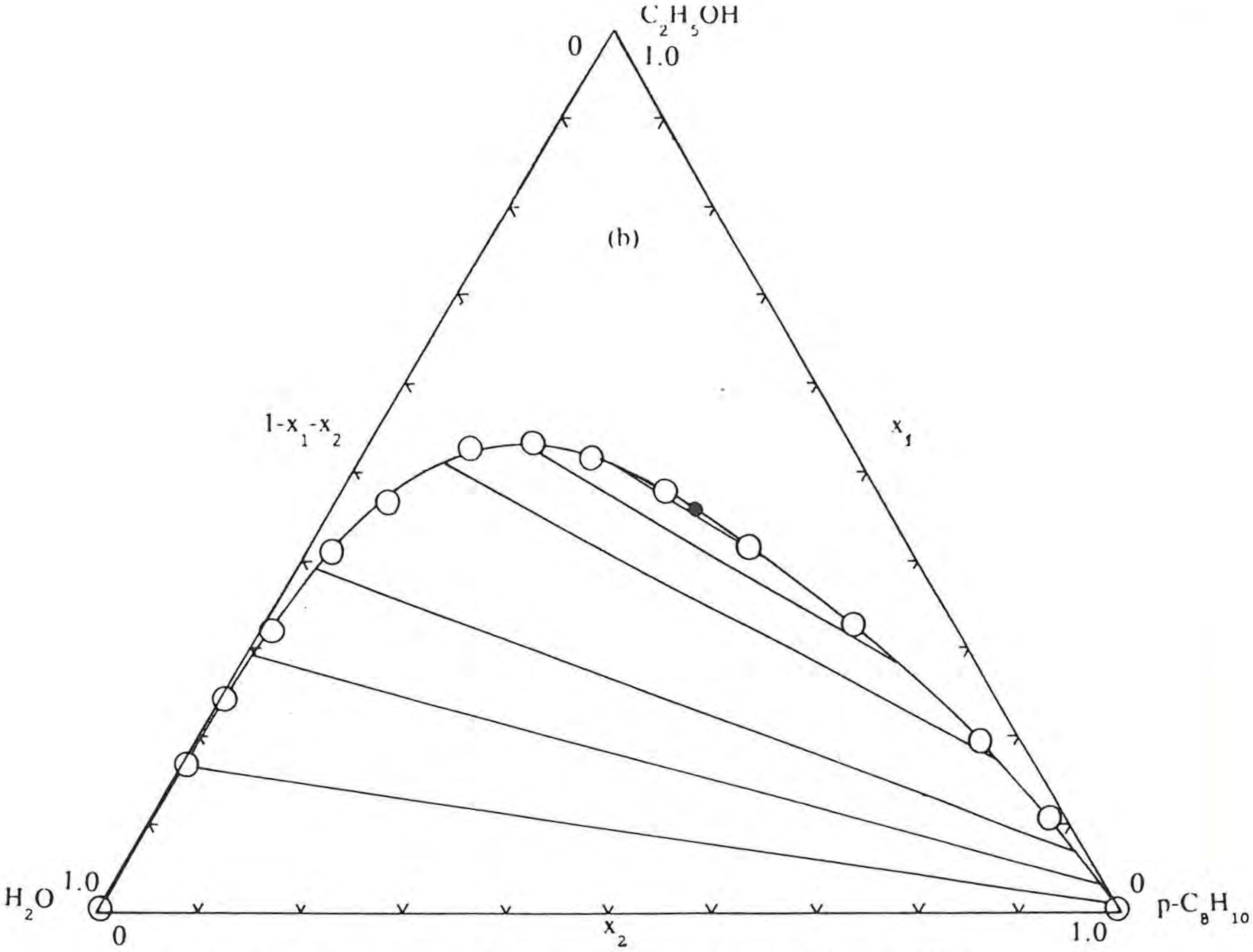


FIGURE 6.2(b) : The ethanol–p–xylene–water ternary system in mole fractions at 298.2 K

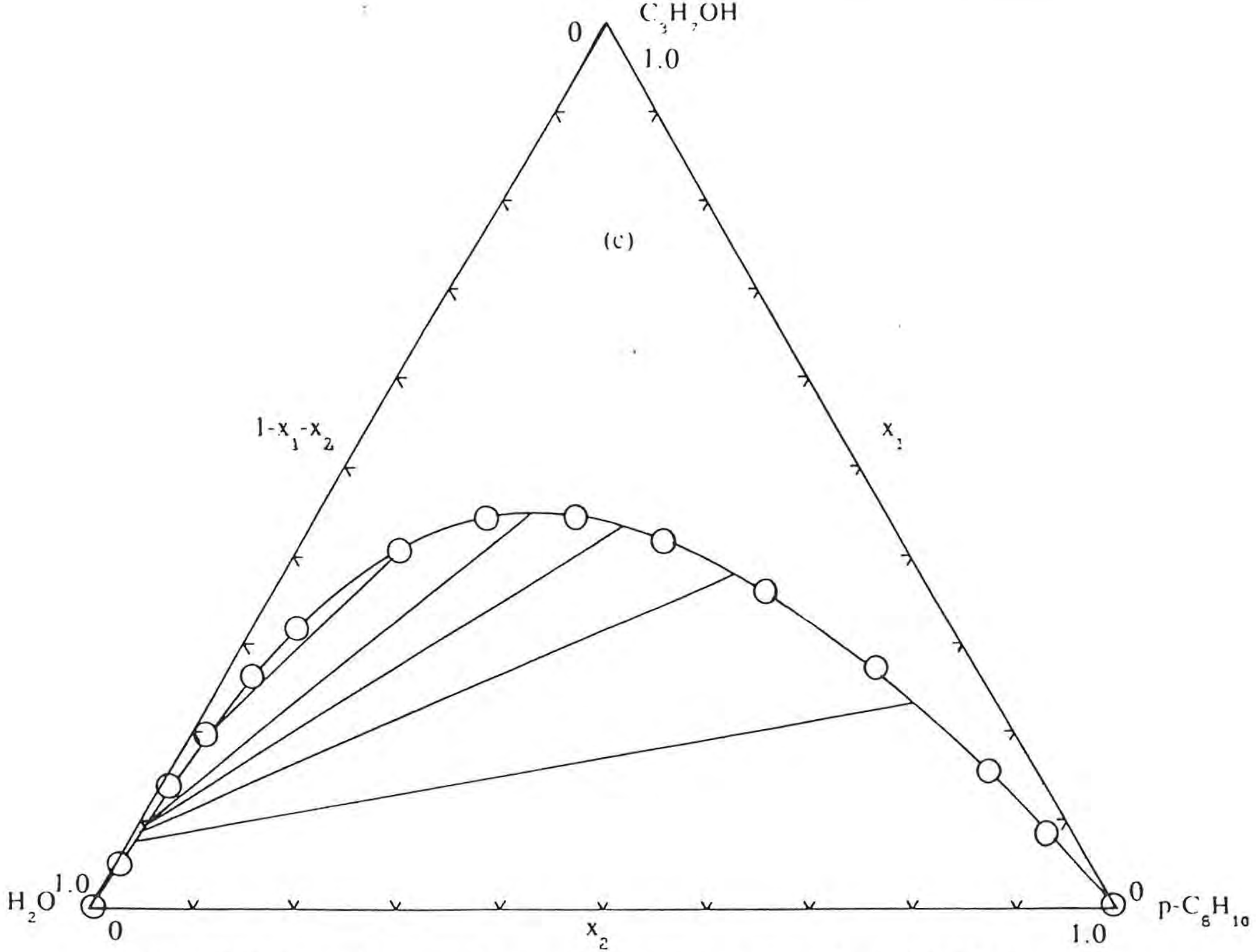


FIGURE 6.2(c) : The 1–propanol–p–xylene–water ternary system in mole fractions at 298.2 K

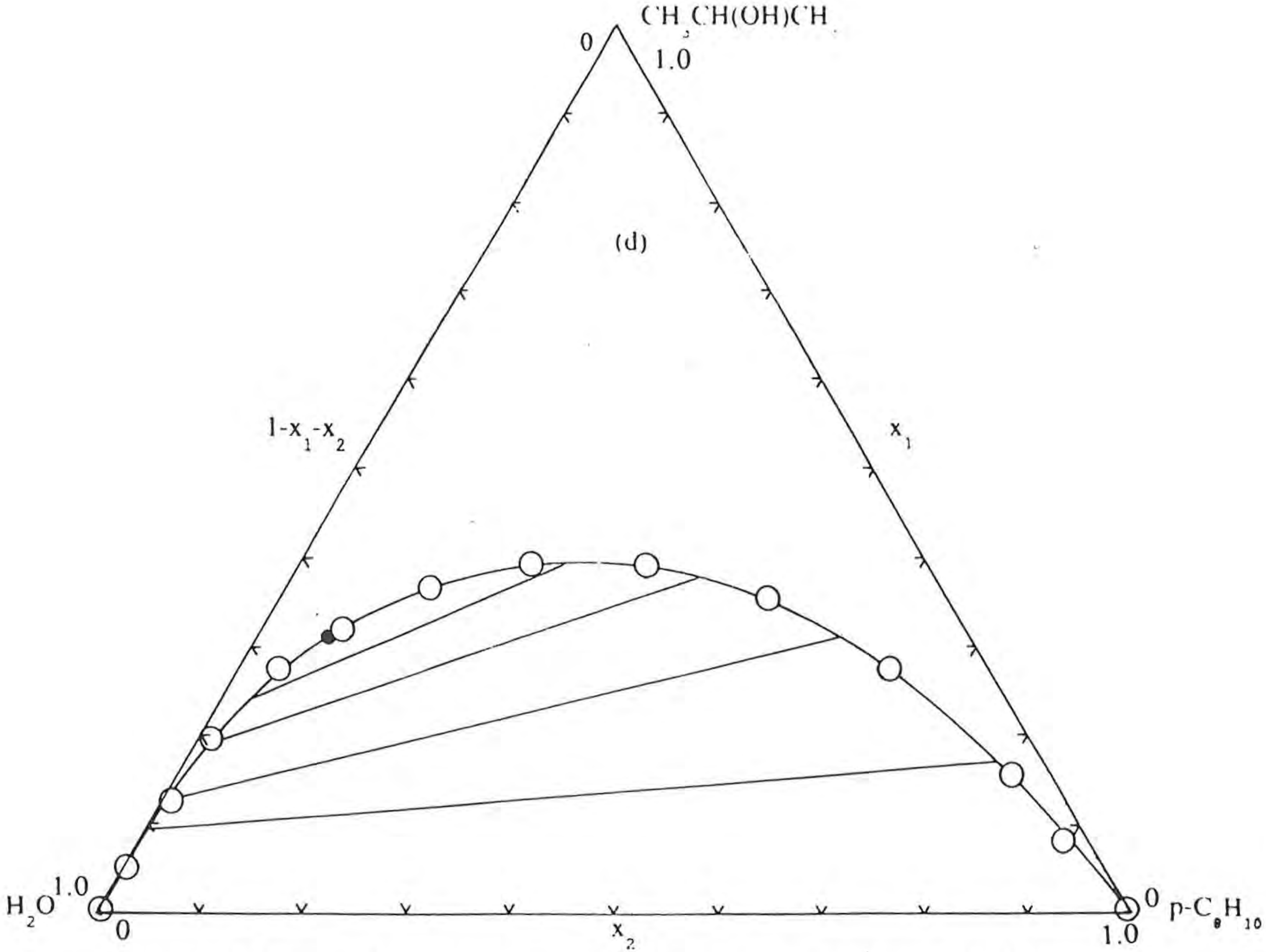


FIGURE 6.2(d) : The 2–propanol–p–xylene–water ternary system in mole fractions at 298.2 K

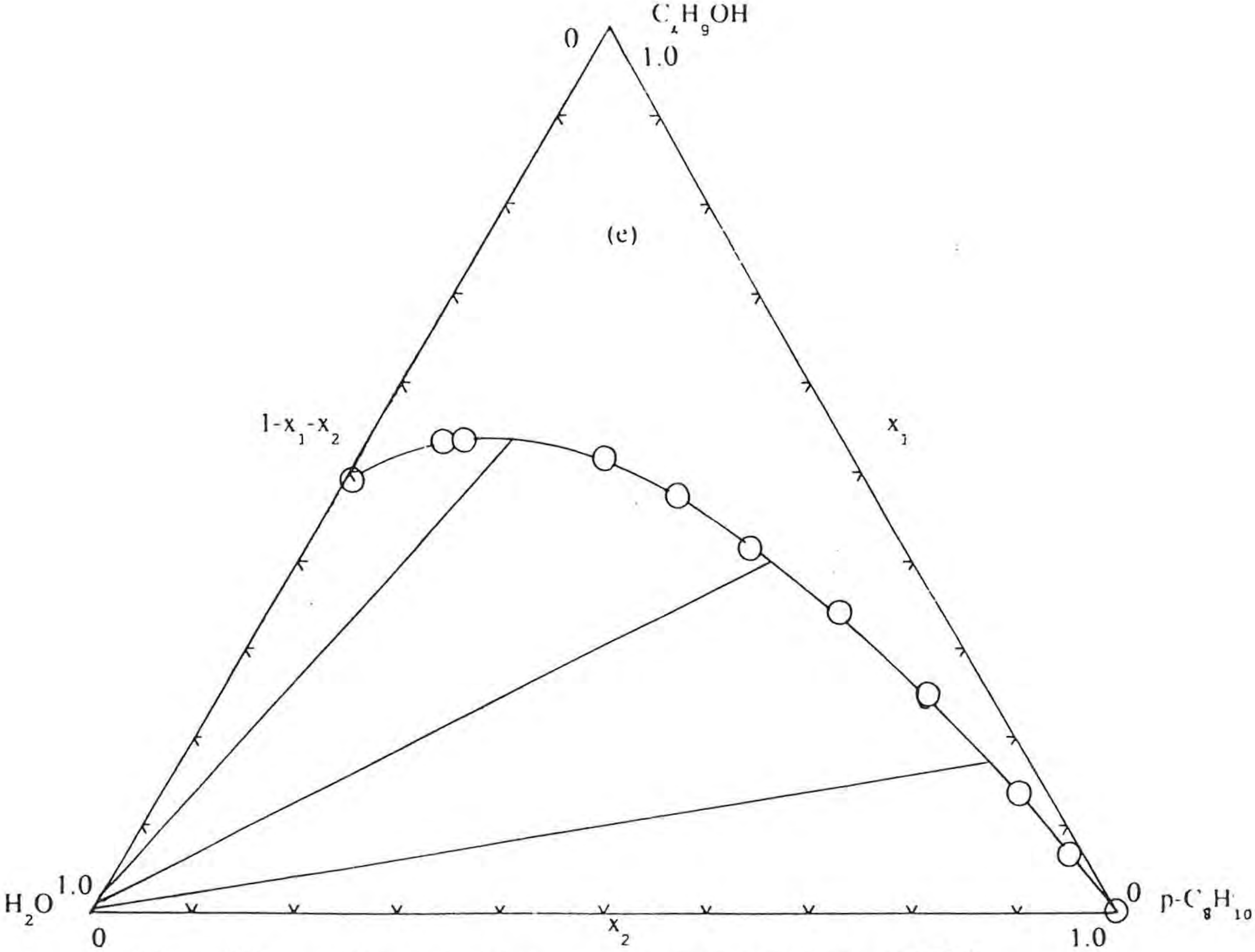


FIGURE 6.2(e) : The 1—butanol—p—xylene—water ternary system in mole fractions at 298.2 K

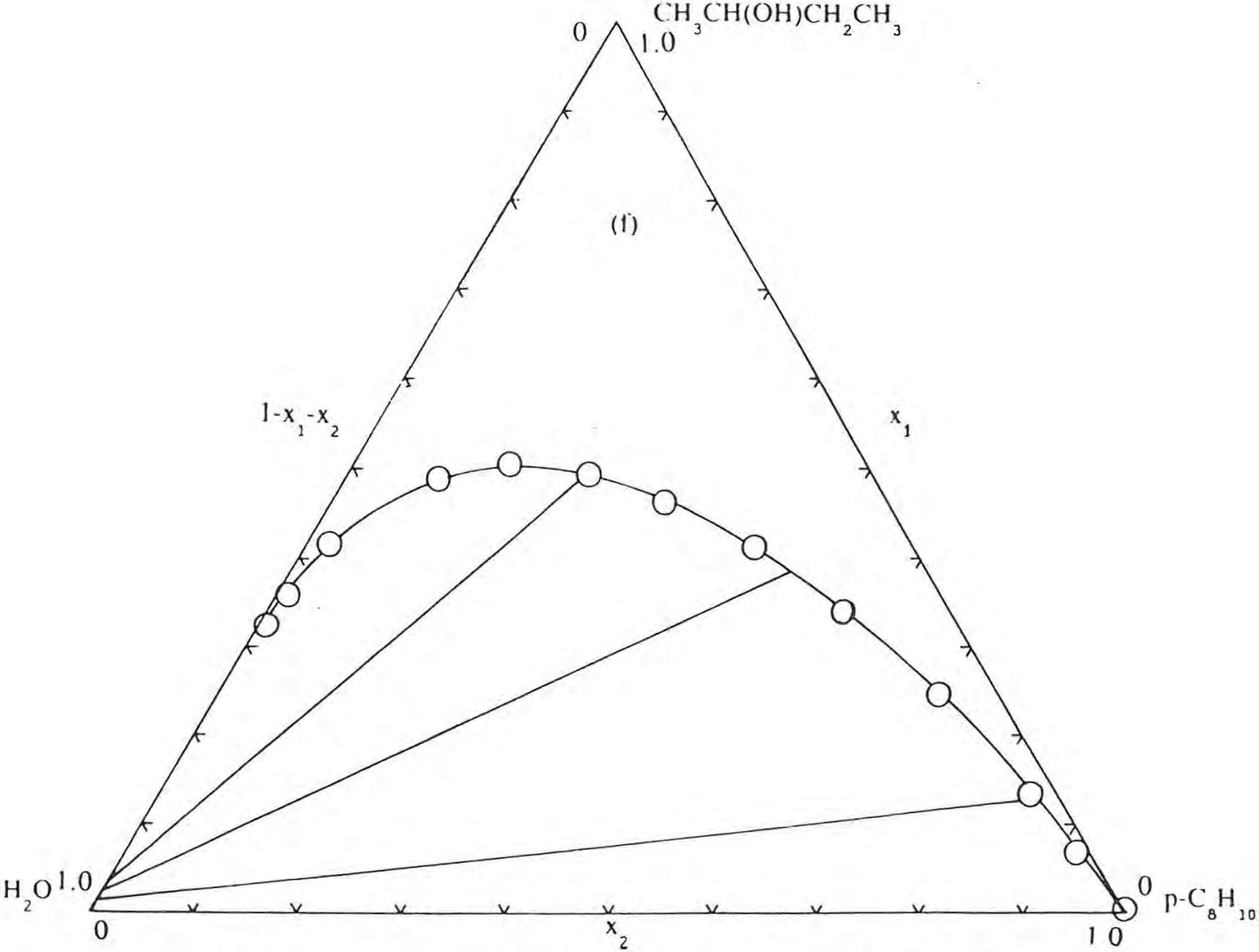


FIGURE 6.2(f) : The 2–butanol–p–xylene–water ternary system in mole fractions at 298.2 K

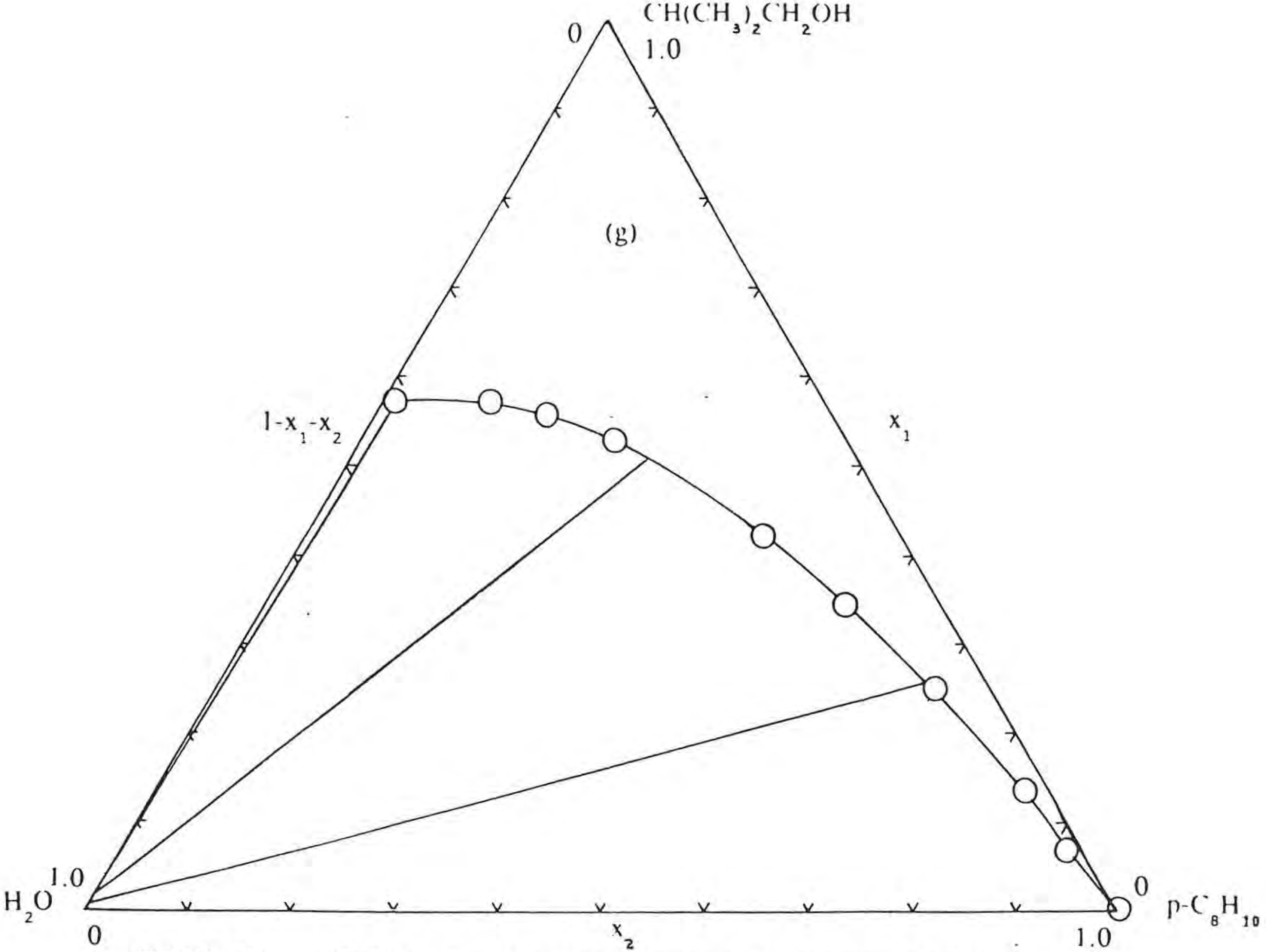


FIGURE 6.2(g) : The i–butanol–p–xylene–water ternary system in mole fractions at 298.2 K

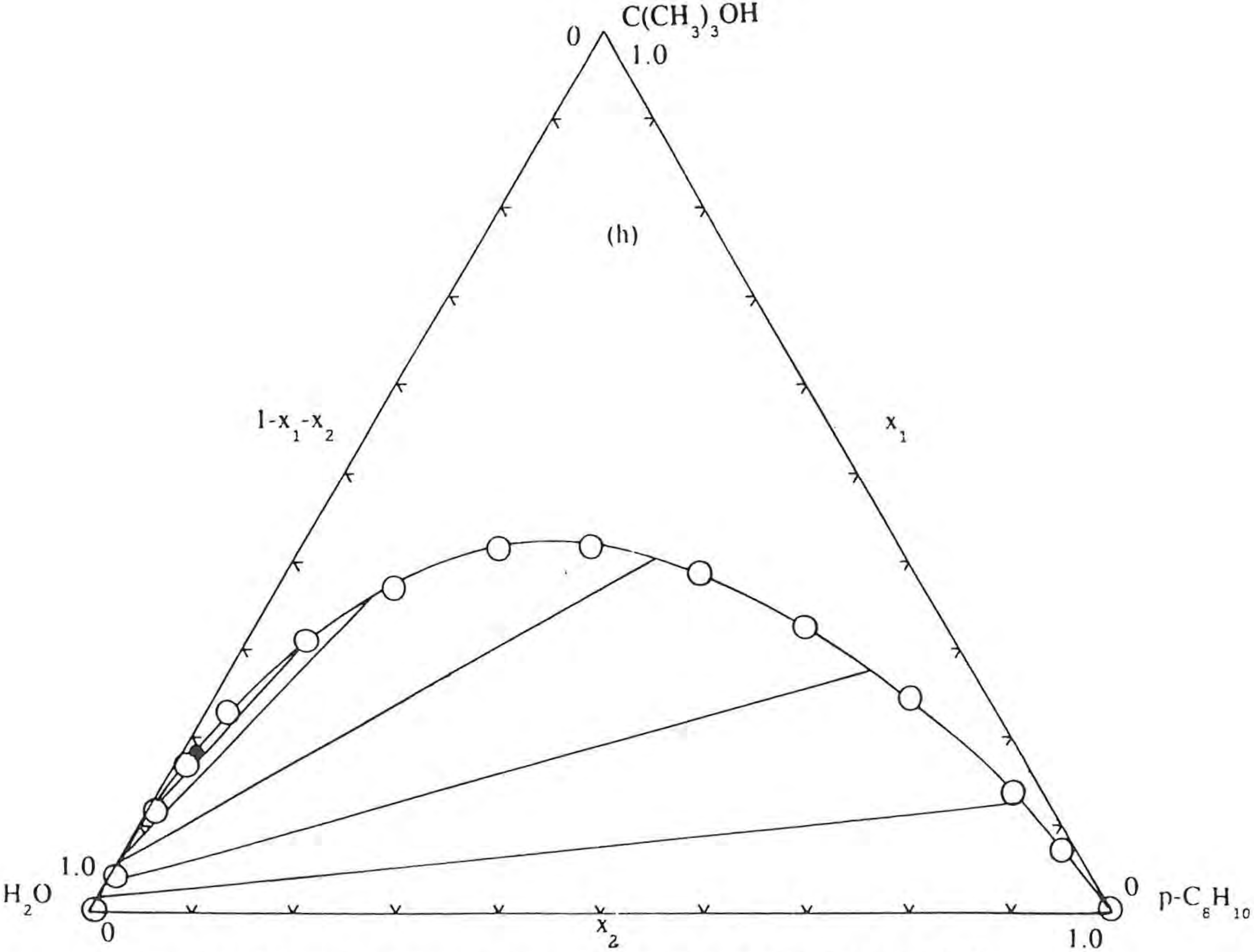


FIGURE 6.2(h) : The t–butanol–p–xylene–water ternary system in mole fractions at 298.2 K

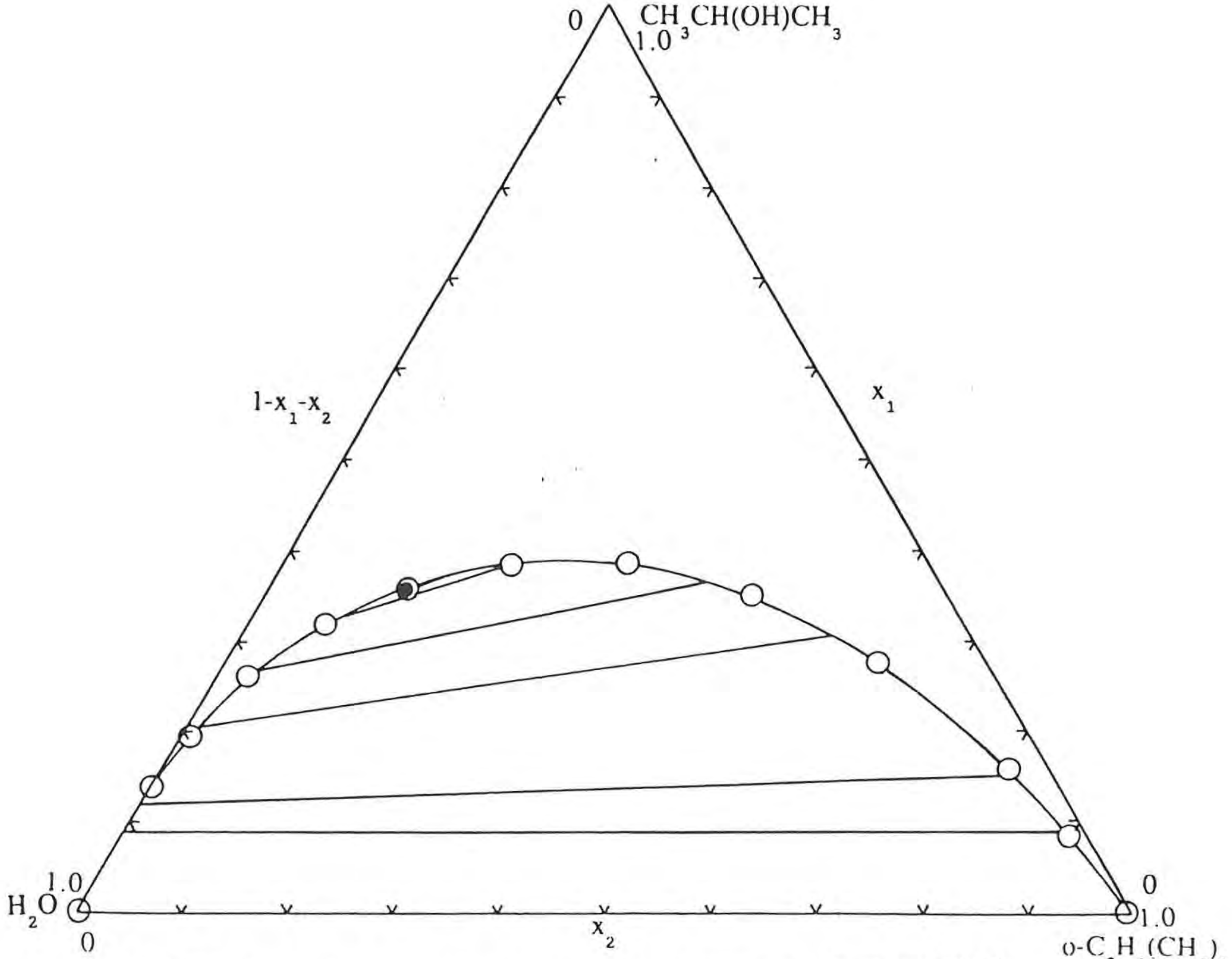


FIGURE 6.2(i) : The 2–propanol–o–xylene–water ternary system in mole fractions at 298.2 K

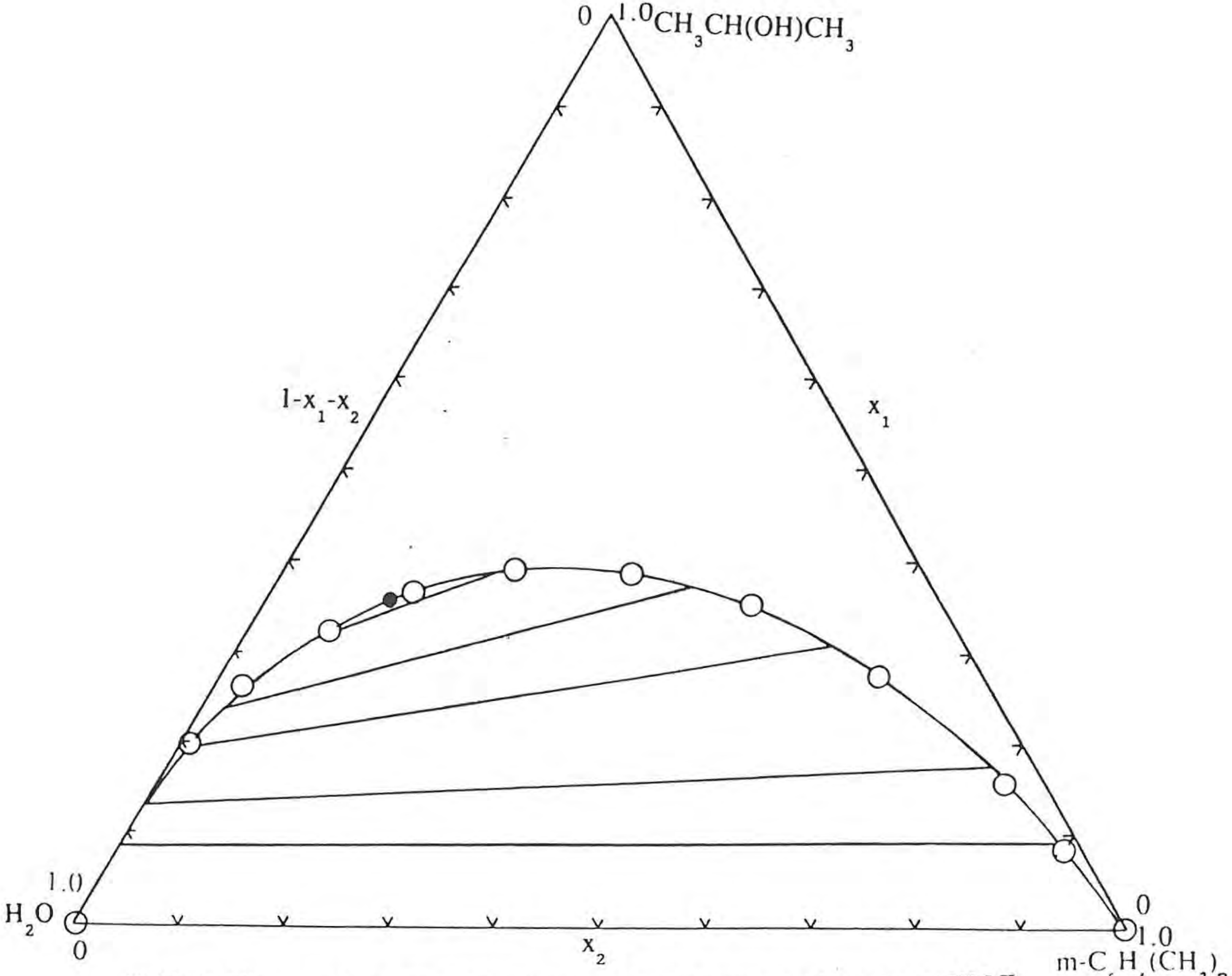
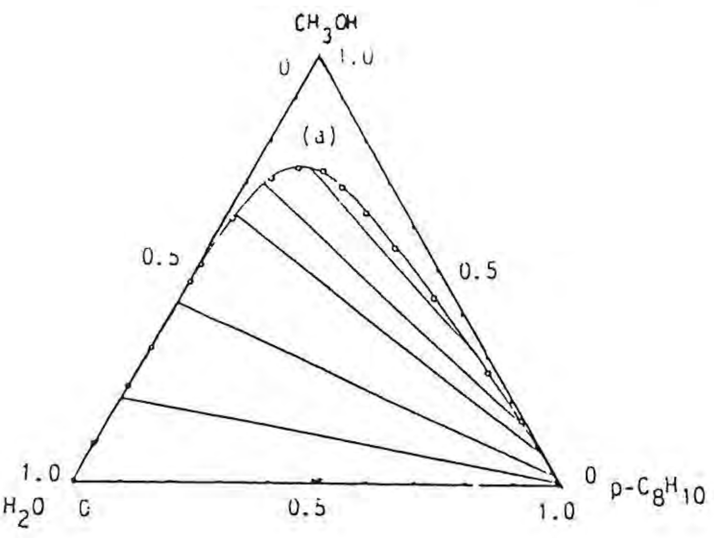
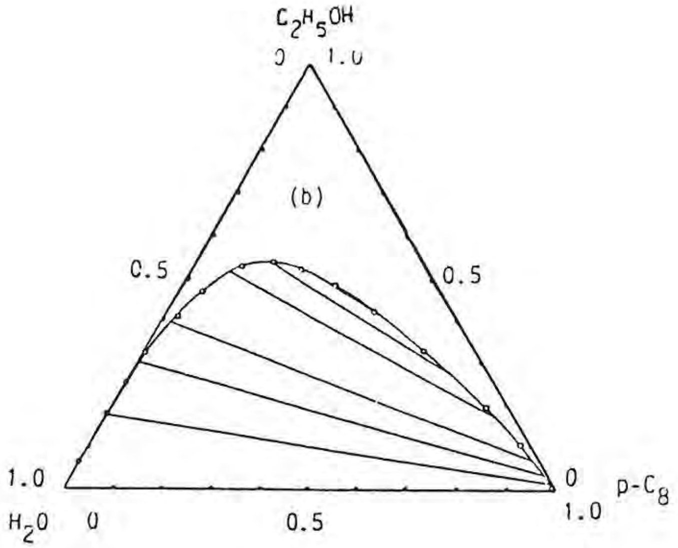
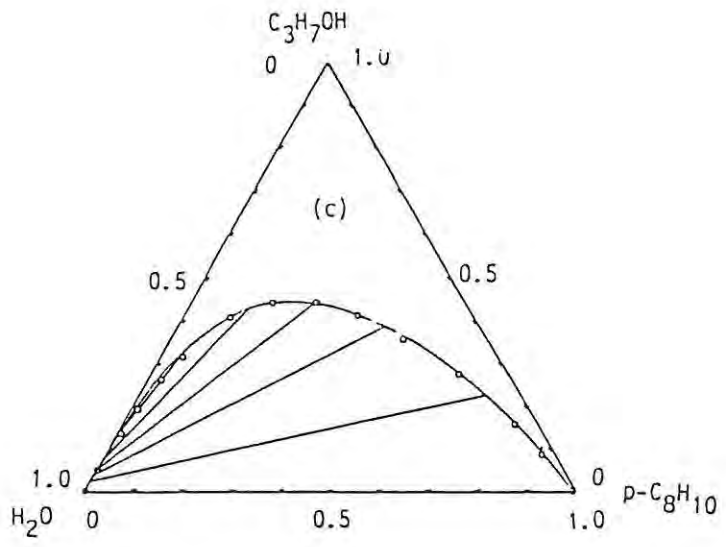
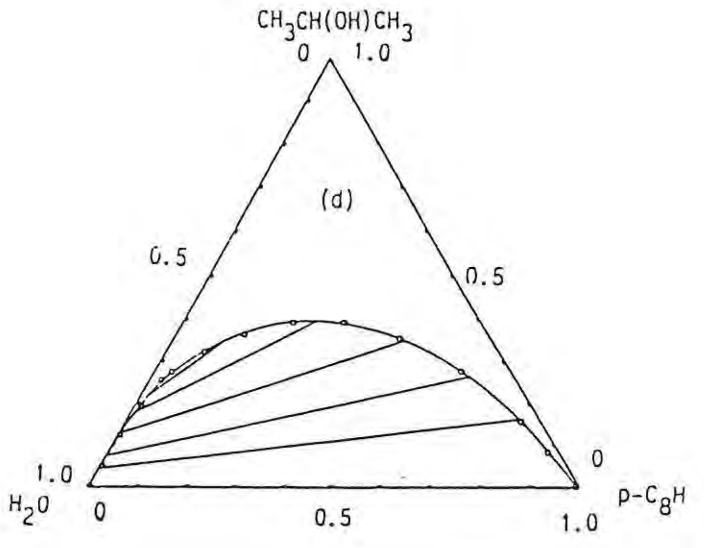


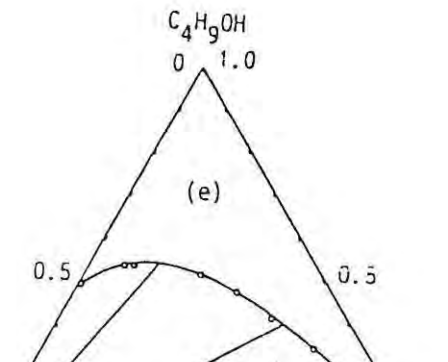
FIGURE 6.2(j) : The 2–propanol–m–xylene–water ternary system in mole fractions at 298.2 K

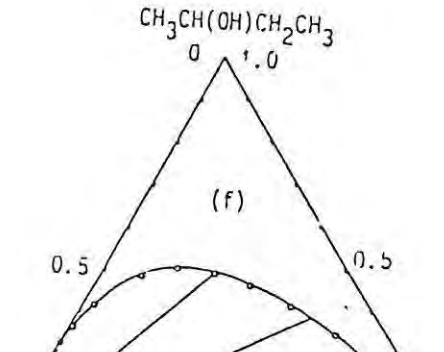

CH3OH
0
1.0
(a)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8H10


C2H5OH
0
1.0
(b)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8


C3H7OH
0
1.0
(c)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8H10


CH3CH(OH)CH3
0
1.0
(d)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8H


C4H9OH
0
1.0
(e)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8H10


CH3CH(OH)CH2CH3
0
1.0
(f)
0.5
0.5
1.0
H2O
0
0.5
1.0
0
p-C8H

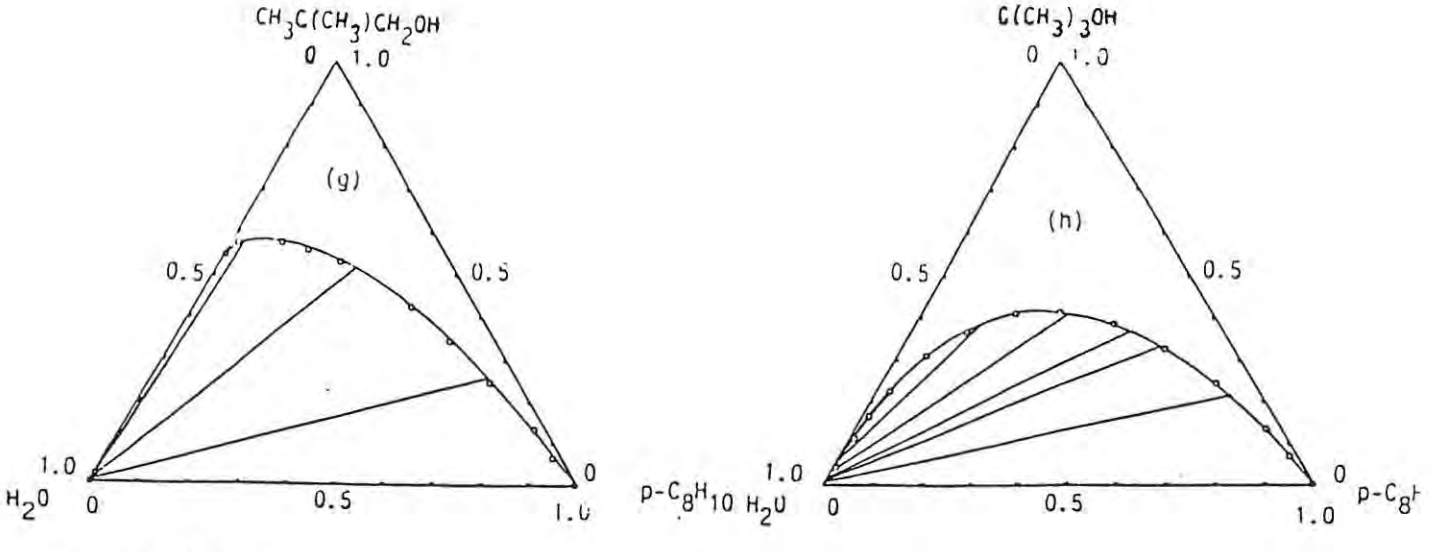


FIGURE 6.2(a–h) : Summary of liquid–liquid equilibrium curves and tielines for $\{x_1C_mH_{2m+1}OH + x_2C_8H_{10} + (1-x_1-x_2)H_2O\}$ at 298.2 K.

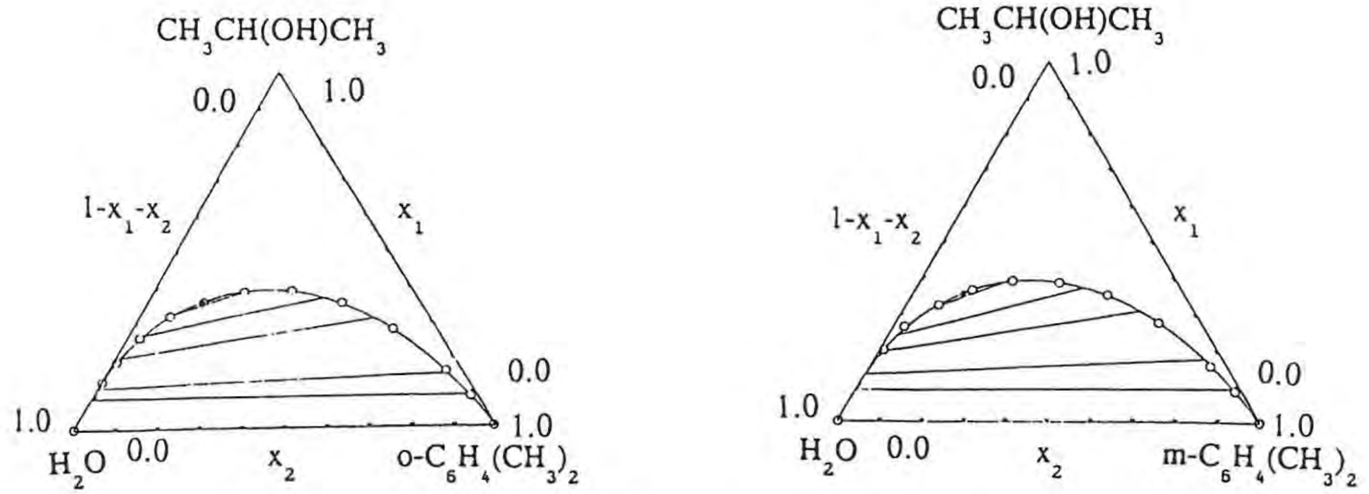


FIGURE 6.2(i–j) : Summary of liquid–liquid equilibrium curves and tielines for {$x_1CH_3CH(OH)CH_3 + x_2$ o–$C_6H_4(CH_3)_2$ or x_2 m–$C_6H_4(CH_3)_2$ + $(1-x_1-x_2)H_2O$} at 298.2 K.

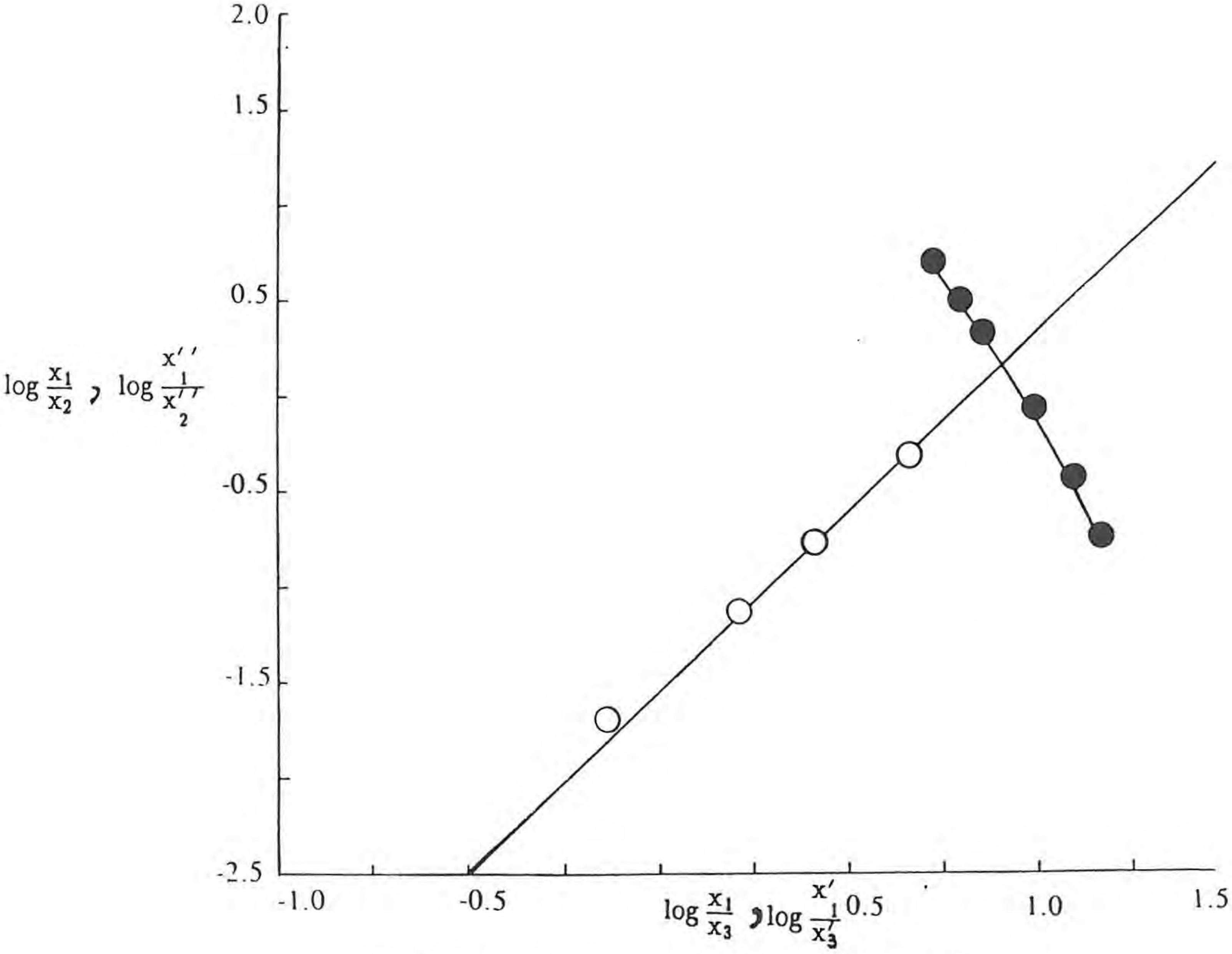


FIGURE 6.2(k) : Determination of plait point {Treybal method} : The methanol–p–xylene–water ternary system.

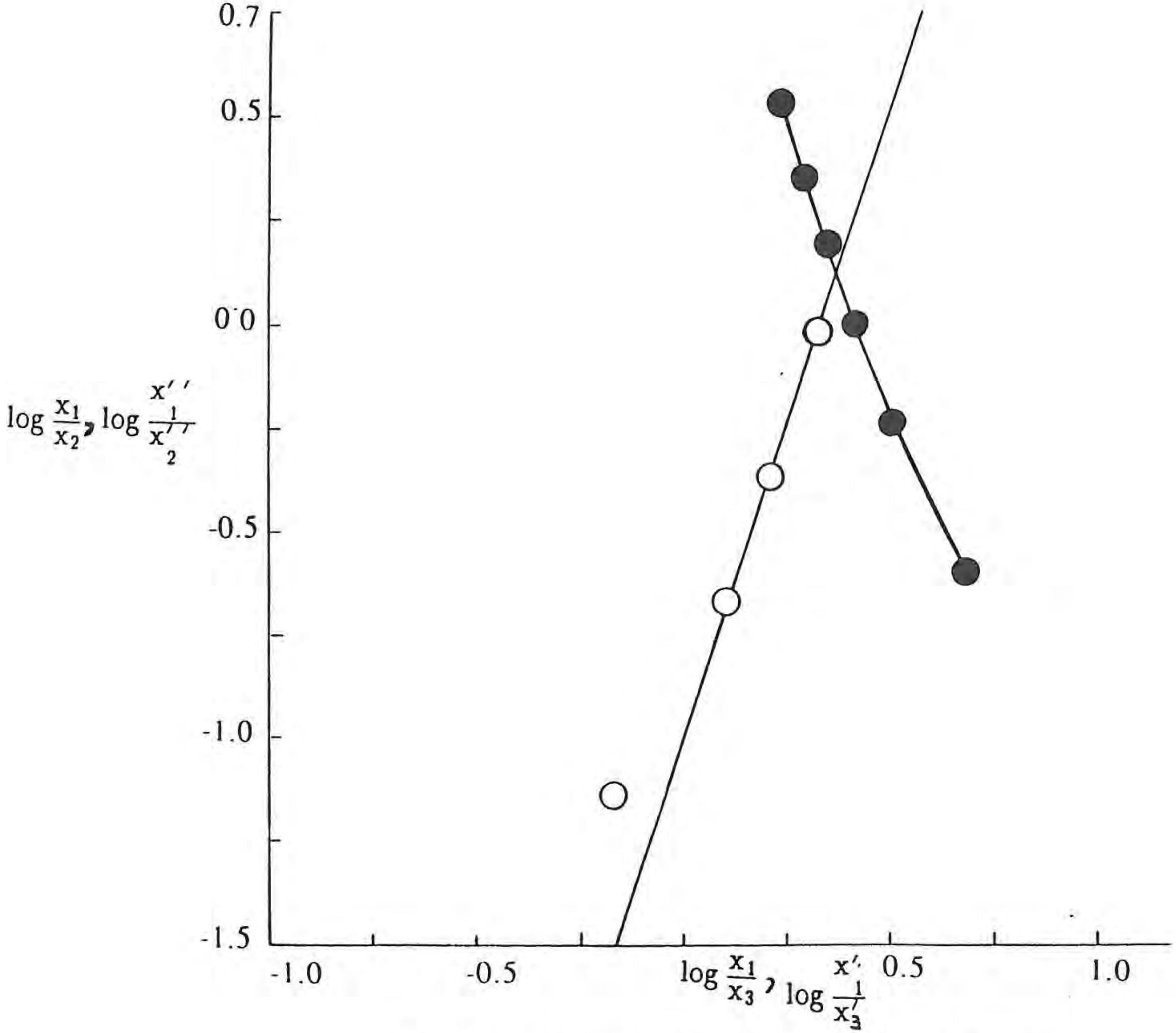


FIGURE 6.2(1) : Determination of plait point {Treybal method} : The ethanol—p—xylene—water ternary system.

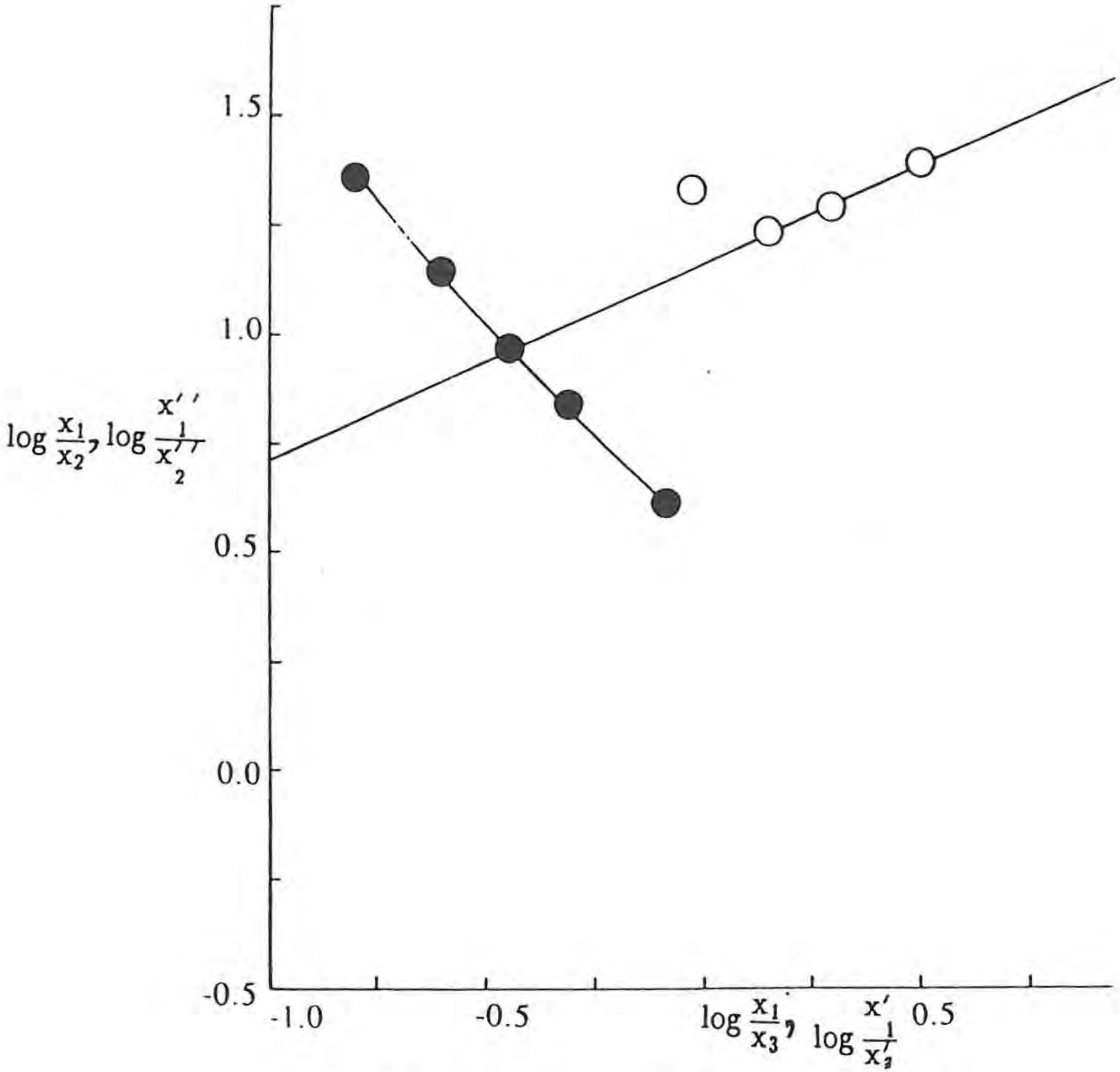


FIGURE 6.2(m) : **Determination of plait point {Treybal method} :**
The 1–propanol–p–xylene–water ternary system.

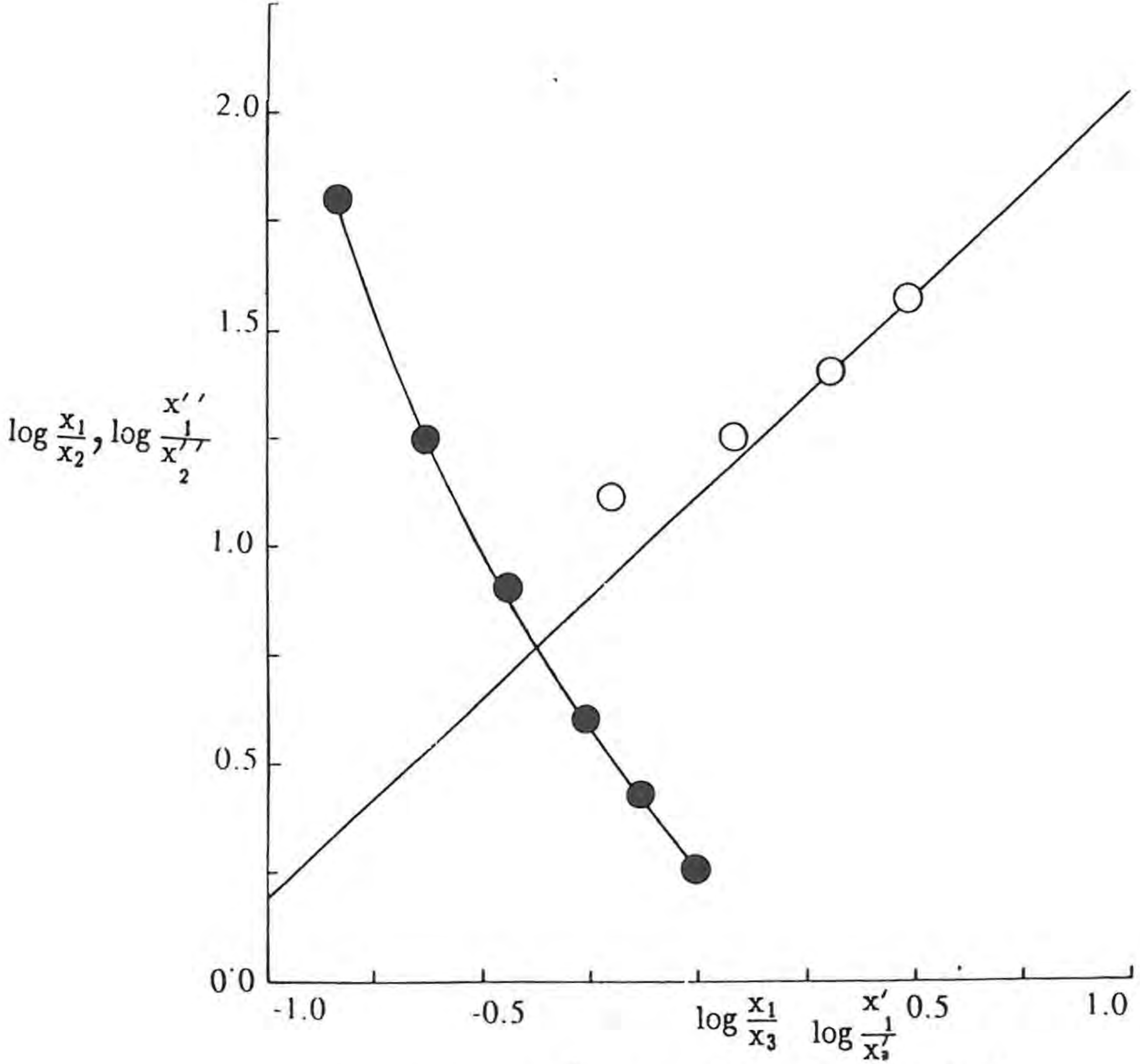


FIGURE 6.2(n) : Determination of plait point {Treybal method} : The 2–propanol–p–xylene–water ternary system.

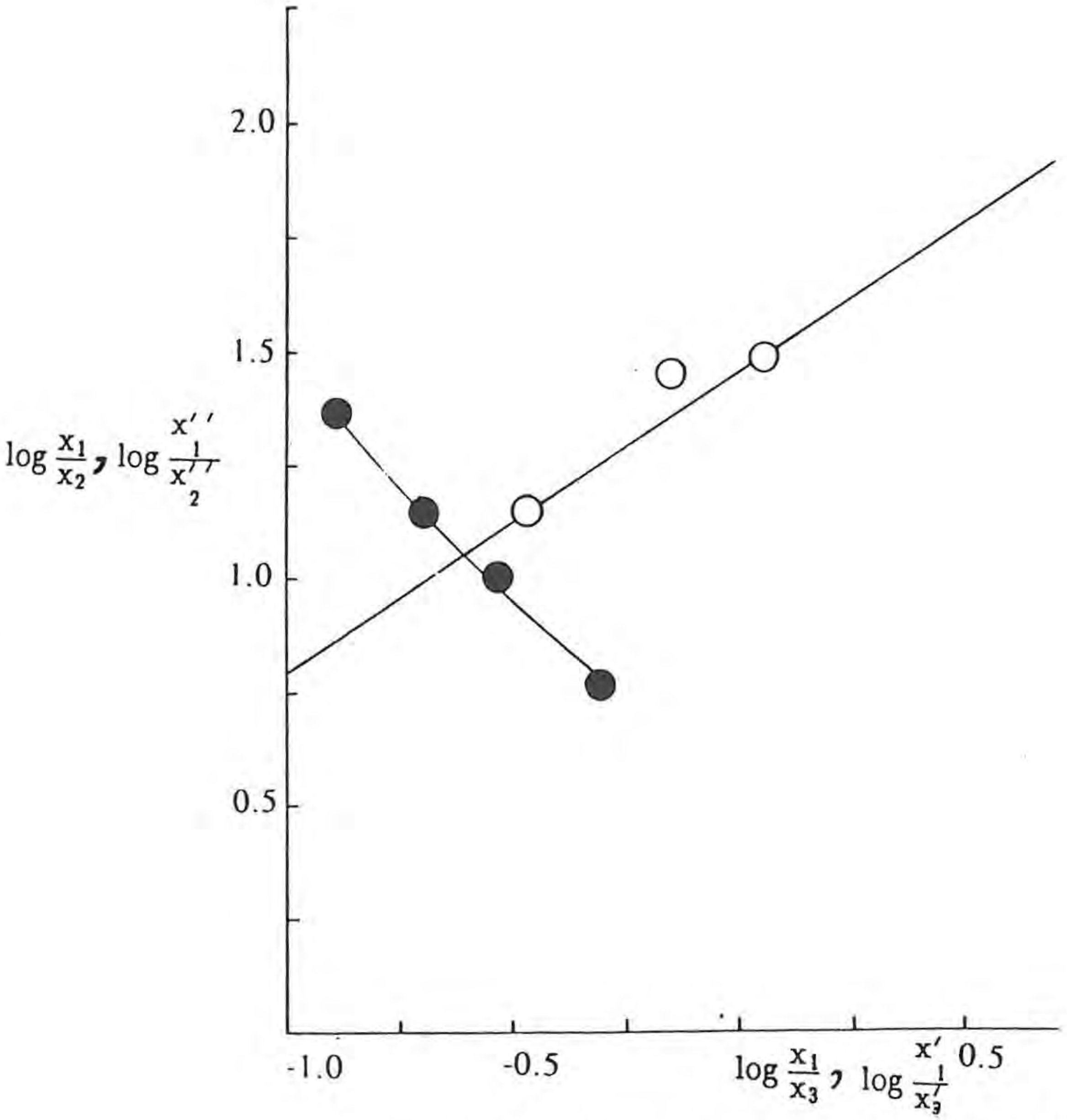


FIGURE 6.2(o) : Determination of plait point {Treybal method} : The t–butanol–p–xylene–water ternary system.

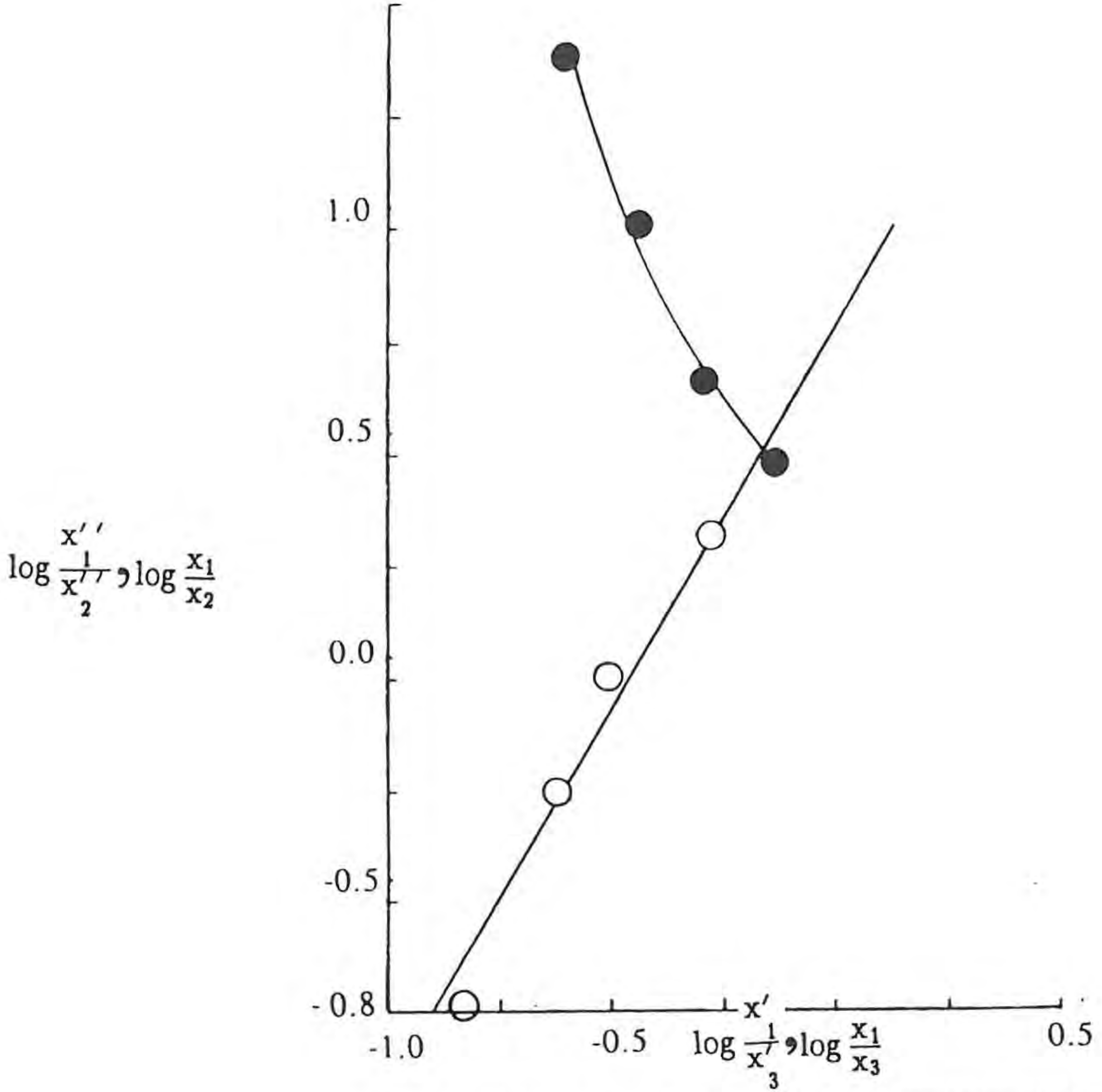


FIGURE 6.2(p) : **Determination of plait point {Treybal method} : The 2–propanol–m–xylene–water ternary system.**

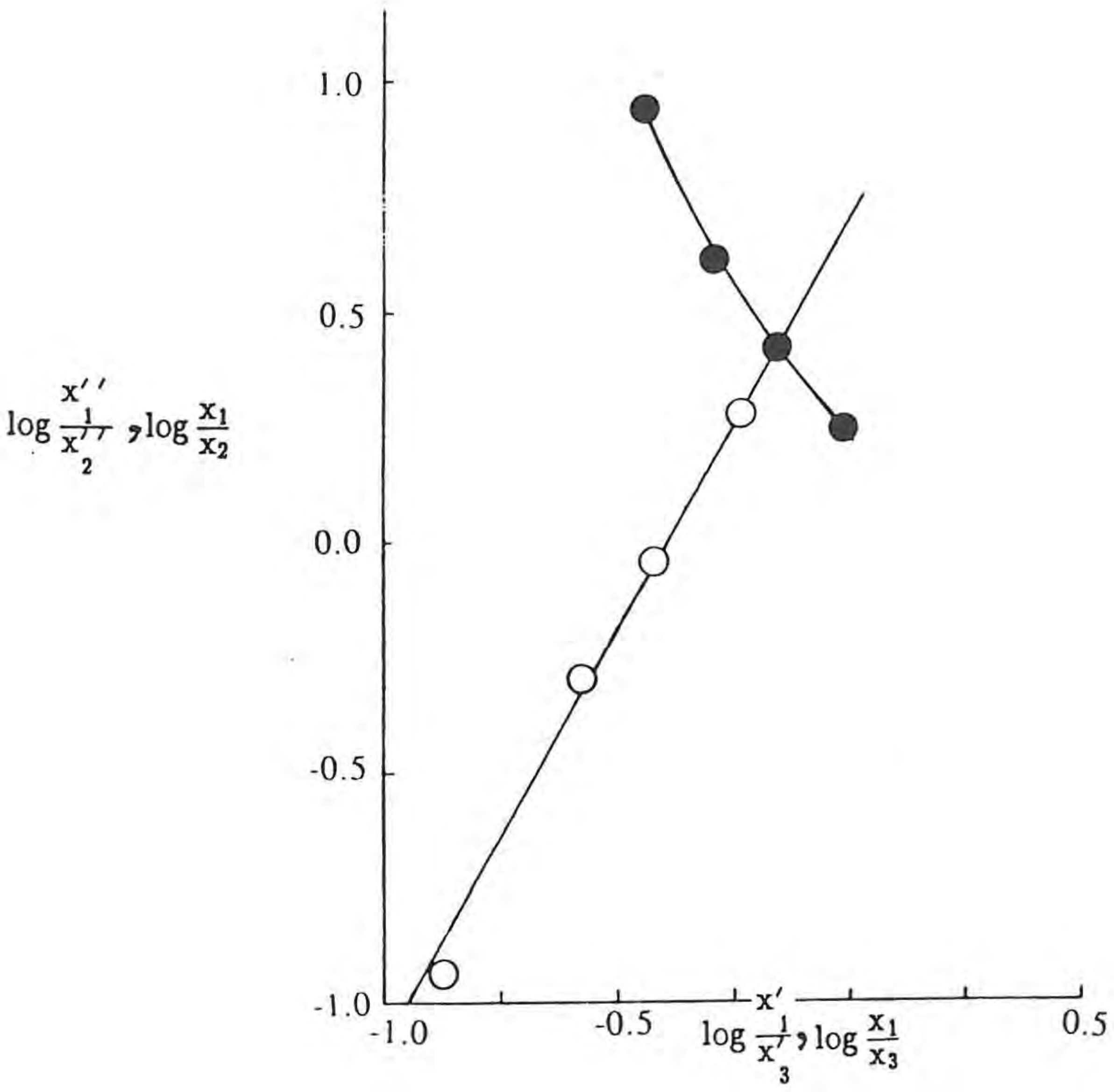


FIGURE 6.2(q) : Determination of plait point {Treybal method} : The 2–propanol–o–xylene–water ternary system.

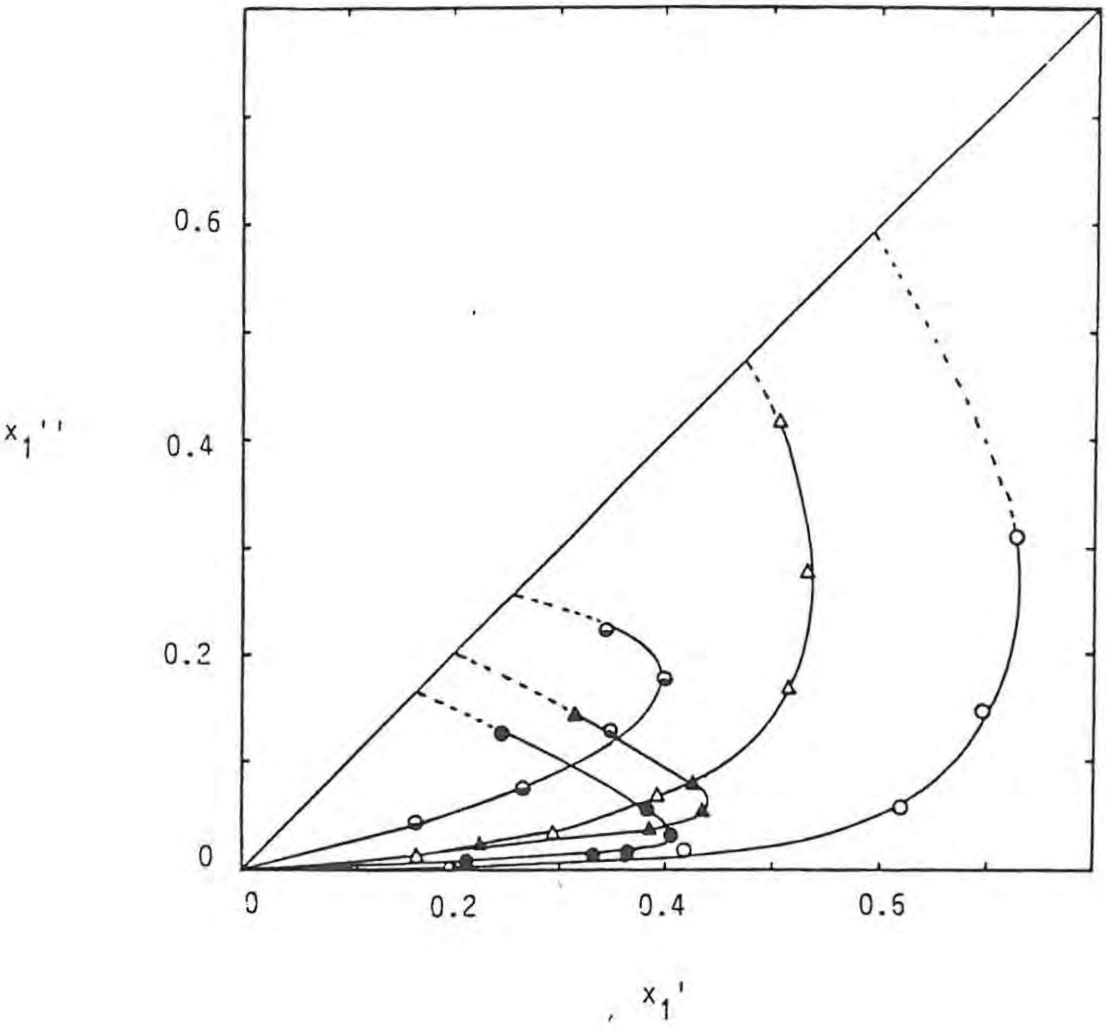


FIGURE 6.2(r) : A plot of x_1'' against x_1', showing the relative solubilities of the alkanol in the p–xylene–rich and water–rich layers. ○, CH_3OH; △, C_2H_5OH; ●, C_3H_7OH; ⊖, $CH_3CH(OH)CH_3$; ▲, $C(CH_3)_3OH$.

6.3 : THE ALCOHOL–TOLUENE–WATER TERNARY SYSTEM, AT 298.2K.

TABLE 6.3(a) : The composition of points on the coexistence curve for mixtures $\{x_1C_mH_{2m+1}OH + x_2C_6H_5(CH_3) + (1 - x_1 - x_2)H_2O\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH		C_2H_5OH		C_3H_7OH		$CH_3CH(OH)CH_3$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.405	0.006	0.174	0.001	0.091	0.001	0.091	0.001
0.504	0.014	0.242	0.003	0.138	0.005	0.138	0.005
0.604	0.038	0.319	0.014	0.194	0.014	0.193	0.019
0.648	0.057	0.404	0.041	0.259	0.031	0.255	0.049
0.675	0.100	0.424	0.053	0.320	0.055	0.298	0.083
0.662	0.153	0.460	0.099	0.403	0.118	0.353	0.154
0.632	0.219	0.472	0,159	0.429	0.185	0.378	0.247
0.577	0.301	0.456	0.228	0.438	0.286	0.371	0.362
0.502	0.406	0.430	0.323	0.397	0.416	0.329	0.500
0.393	0.546	0.378	0.441	0.346	0.544	0.252	0.656
0.234	0.736	0.296	0.591	0.252	0.698	0.142	0.834
0.130	0.857	0.174	0.785	0.143	0.836	0.073	0.918
0.000	0.999	0.094	0.889	0.074	0.920	0.000	0.999
		0.000	0.999	0.000	0.999		

C_4H_9OH		$CH_3CH(OH)CH_2CH_3$		$CH(CH_3)_2CH_2OH$		$C(CH_3)_3OH$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.019	0.000	0.051	0.000	0.021	0.000	0.057	0.002
0.488	0.000	0.312	0.000	0.546	0.000	0.138	0.010
0.524	0.034	0.410	0.027	0.568	0.031	0.191	0.021
0.527	0.047	0.432	0.039	0.572	0.054	0.257	0.038
0.548	0.110	0.460	0.070	0.568	0.111	0.307	0.062
0.534	0.190	0.478	0.100	0.546	0.186	0.375	0.129
0.506	0.271	0.489	0,157	0.511	0.277	0.411	0.205
0.462	0.372	0.476	0.256	0.462	0.372	0.391	0.319
0.398	0.481	0.446	0.375	0.397	0.479	0.363	0.438
0.322	0.603	0.400	0.483	0.315	0.593	0.305	0.573
0.225	0.725	0.331	0.598	0.214	0.722	0.220	0.707
0.118	0.858	0.227	0.734	0.117	0.849	0.116	0.855
0.060	0.928	0.120	0.885	0.060	0.924	0.060	0.928
0.000	0.999	0.061	0.933				

TABLE 6.3(b): The composition of the conjugate solutions x_1', x_2', x_1'', x_2'' for $\{x_1C_mH_{2m+1}OH + x_2C_6H_5(CH_3) + (1 - x_1 - x_2)H_2O\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH				C_2H_5OH			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		**toluene–rich**		**water–rich**		**toluene–rich**	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.290	0.002	0.051	0.946	0.470	0.170	0.341	0.510
0.372	0.004	0.068	0.926	0.466	0.112	0.285	0.610
0.469	0.010	0.092	0.902	0.445	0.072	0.230	0.697
0.547	0.022	0.133	0.856	0.410	0.042	0.178	0.778
0.653	0.057	0.222	0.765	0.315	0.012	0.090	0.890

C_3H_7OH				$CH_3CH(OH)CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		**toluene–rich**		**water–rich**		**toluene–rich**	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.049	0.000	0.315	0.600	0.125	0.008	0.330	0.488
0.057	0.000	0.368	0.490	0.150	0.010	0.360	0.405
0.064	0.000	0.410	0.365	0.170	0.012	0.380	0.305
0.072	0.000	0.430	0.270	0.192	0.016	0.377	0.238
0.080	0.000	0.428	0.182	0.230	0.030	0.351	0.154
0.095	0.001	0.383	0.100				
0.135	0.002	0.290	0.044				

TABLE 6.3(b): (CONTD.)

C_4H_9OH				$CH_3CH(OH)CH_2CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		toluene–rich		water–rich		toluene–rich	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.007	0.000	0.341	0.570	0.018	0.000	0.322	0.595
0.012	0.000	0.455	0.382	0.033	0.000	0.480	0.240
0.016	0.000	0.542	0.090	0.051	0.000	0.312	0.000
0.019	0.000	0.488	0.000				

$CH(CH_3)_2CH_2OH$				$C(CH_3)_3OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
water–rich		toluene–rich		water–rich		toluene–rich	
0.000	0.000	0.000	0.999	0.000	0.000	0.000	0.999
0.005	0.000	0.171	0.783	0.025	0.001	0.140	0.835
0.011	0.000	0.426	0.432	0.040	0.002	0.256	0.653
0.017	0.000	0.550	0.181	0.058	0.003	0.361	0.416
0.021	0.000	0.546	0.000	0.077	0.004	0.398	0.203
				0.090	0.006	0.372	0.127
				0.114	0.009	0.298	0.060

TABLE 6.3(c): The coefficients A_i, B_i and C_i in equations (4.1), (4.4) and (4.5) respectively.for $x_1C_mH_{2m+1}OH + x_2C_6H_5(CH_3) + (1 - x_1 - x_2)H_2O$ together with the standard deviation σ. The standard errors are given in parenthesis.

CH_3OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = 0.3292$ (0.31) $A_2 = 0.9924$ (0.25) $A_3 = 4.3973$ (0.77) $\sigma = 0.038$	$B_1 = 3.1293$ (0.33) $B_2 = 1.2342$ (0.05) $B_3 = 1.0778$ (0.08) $\sigma = 0.044$	$C_1 = 2.9219$ (0.28) $C_2 = 1.2091$ (0.05) $C_3 = 1.5702$ (0.09) $\sigma = 0.042$
C_2H_5OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.4813$ (0.14) $A_2 = 0.2395$ (0.15) $A_3 = 1.4863$ (0.40) $\sigma = 0.034$	$B_1 = 1.7357$ (0.13) $B_2 = 1.0554$ (0.04) $B_3 = 0.8699$ (0.04) $\sigma = 0.036$	$C_1 = 1.5762$ (0.09) $C_2 = 1.0198$ (0.03) $C_3 = 1.2509$ (0.05) $\sigma = 0.032$
C_3H_7OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.2307$ (0.04) $A_2 = -0.0341$ (0.04) $A_3 = 1.3843$ (0.11) $\sigma = 0.005$	$B_1 = 1.6216$ (0.03) $B_2 = 0.9697$ (0.01) $B_3 = 0.9167$ (0.01) $\sigma = 0.009$	$C_1 = 1.4560$ (0.02) $C_2 = 0.9313$ (0.01) $C_3 = 1.2469$ (0.01) $\sigma = 0.005$
$CH_3CH(OH)CH_3$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.4020$ (0.02) $A_2 = -0.1818$ (0.03) $A_3 = 0.7001$ (0.07) $\sigma = 0.004$	$B_1 = 1.2638$ (0.03) $B_2 = 0.9033$ (0.01) $B_3 = 0.8307$ (0.01) $\sigma = 0.008$	$C_1 = 1.1402$ (0.02) $C_2 = 0.8667$ (0.01) $C_3 = 1.1366$ (0.01) $\sigma = 0.004$

TABLE 6.3(c): (CONTD.)

<table>
<tr><th colspan="3">C_4H_9OH</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -1.0512\ (0.13)$
$A_2 = 0.1526\ (0.10)$
$A_3 = 0.8478\ (0.33)$
$\sigma = 0.007$</td><td>$B_1 = 2.5582\ (0.16)$
$B_2 = 1.1955\ (0.04)$
$B_3 = 1.0379\ (0.03)$
$\sigma = 0.038$</td><td>$C_1 = 2.1077\ (0.08)$
$C_2 = 1.1257\ (0.02)$
$C_3 = 1.3758\ (0.02)$
$\sigma = 0.022$</td></tr>
<tr><th colspan="3">$CH_3CH(OH)CH_2CH_3$</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -0.6174\ (0.13)$
$A_2 = -0.0657\ (0.12)$
$A_3 = 1.0058\ (0.34)$
$\sigma = 0.015$</td><td>$B_1 = 2.0115\ (0.16)$
$B_2 = 1.0191\ (0.04)$
$B_3 = 0.9664\ (0.04)$
$\sigma = 0.037$</td><td>$C_1 = 1.7566\ (0.11)$
$C_2 = 0.9733\ (0.03)$
$C_3 = 1.2916\ (0.04)$
$\sigma = 0.025$</td></tr>
<tr><th colspan="3">$CH(CH_3)_2CH_2OH$</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -1.3006\ (0.20)$
$A_2 = 0.2966\ (0.14)$
$A_3 = 0.7505\ (0.47)$
$\sigma = 0.008$</td><td>$B_1 = 2.7618\ (0.21)$
$B_2 = 1.2700\ (0.04)$
$B_3 = 1.0542\ (0.03)$
$\sigma = 0.042$</td><td>$C_1 = 2.2630\ (0.11)$
$C_2 = 1.1974\ (0.03)$
$C_3 = 1.4166\ (0.03)$
$\sigma = 0.026$</td></tr>
<tr><th colspan="3">$C(CH_3)_3OH$</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -0.2454\ (0.05)$
$A_2 = 0.0853\ (0.05)$
$A_3 = 1.3949\ (0.14)$
$\sigma = 0.008$</td><td>$B_1 = 1.5771\ (0.05)$
$B_2 = 1.0250\ (0.02)$
$B_3 = 0.9292\ (0.01)$
$\sigma = 0.014$</td><td>$C_1 = 1.3838\ (0.02)$
$C_2 = 0.9780\ (0.01)$
$C_3 = 1.2640\ (0.01)$
$\sigma = 0.006$</td></tr>
</table>

TABLE 6.3(d): Plait points for the alcohol–toluene–water ternary systems, in mole fractions. The plait points have been given in the form (x_1,x_2) where x_1 = mole fraction alcohol and x_2 = mole fraction of toluene.

System	Plait point
Methanol	(0.43,0.50)
Ethanol	(0.41,0.36)
1–Propanol	(0.19,0.01)
2–Propanol	(0.27,0.07)
t–Butanol	(0.16,0.02

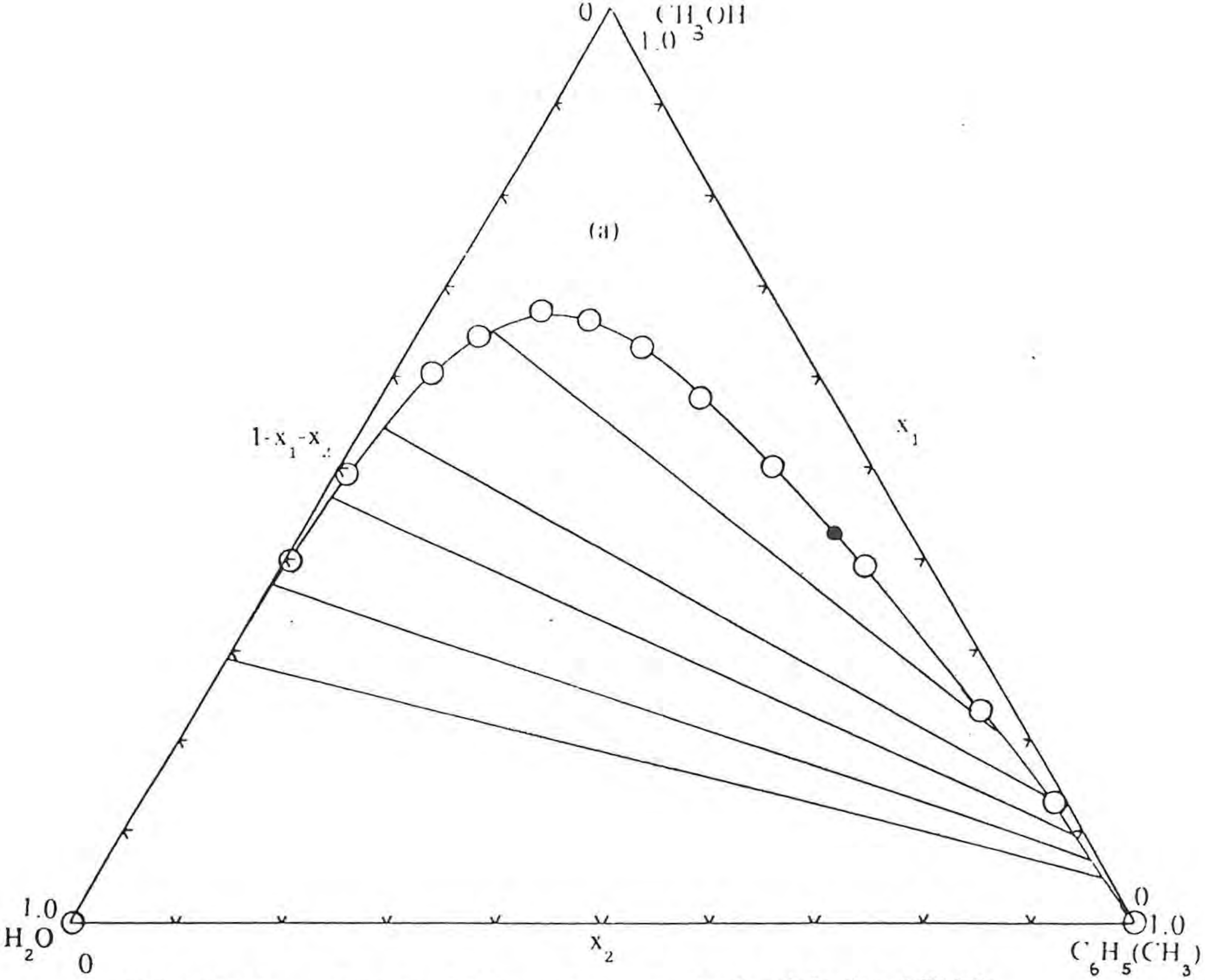


FIGURE 6.3(a) : The methanol—toluene—water ternary system in mole fractions at 298.2 K

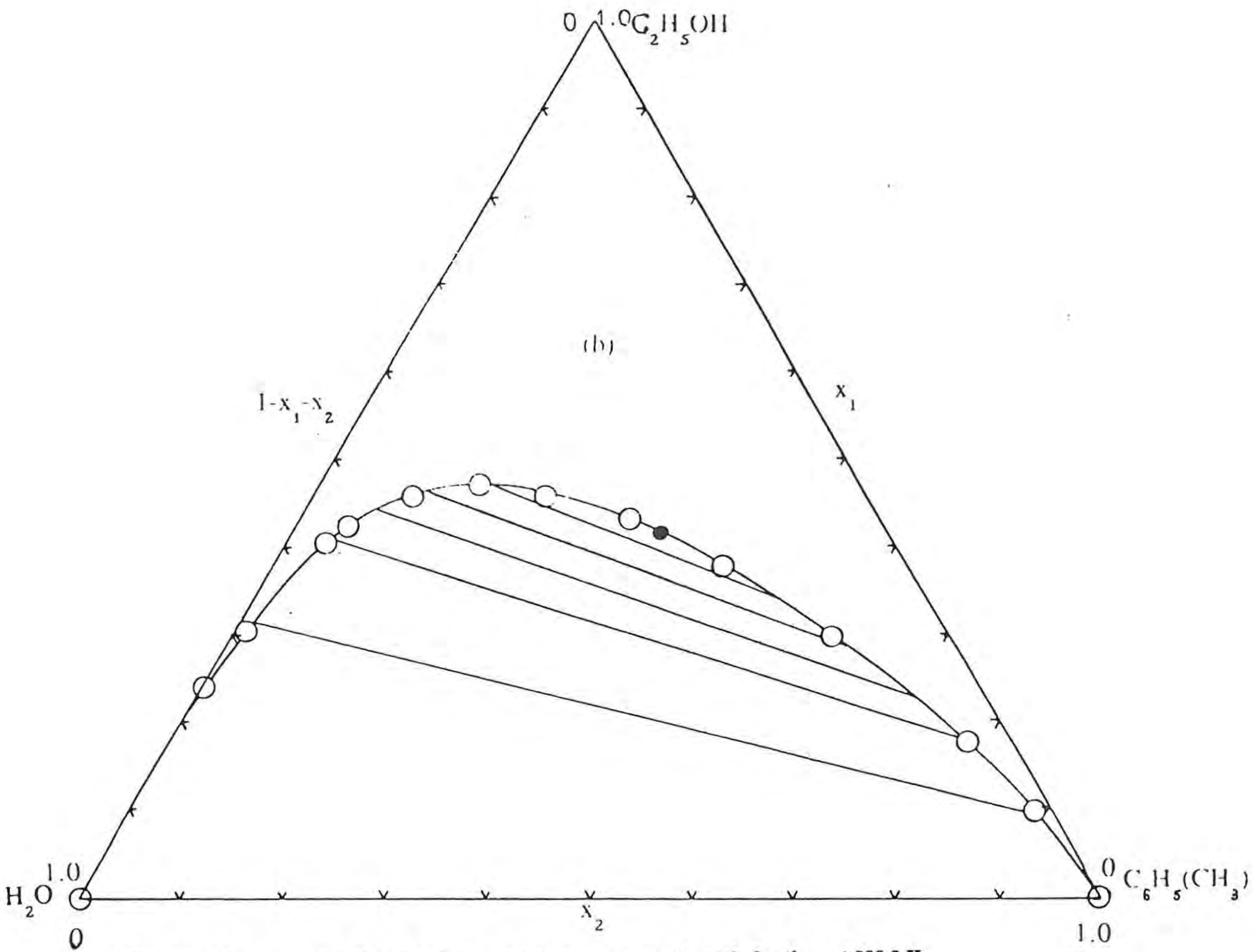


FIGURE 6.3(b) : The ethanol—toluene—water ternary system in mole fractions at 298.2 K

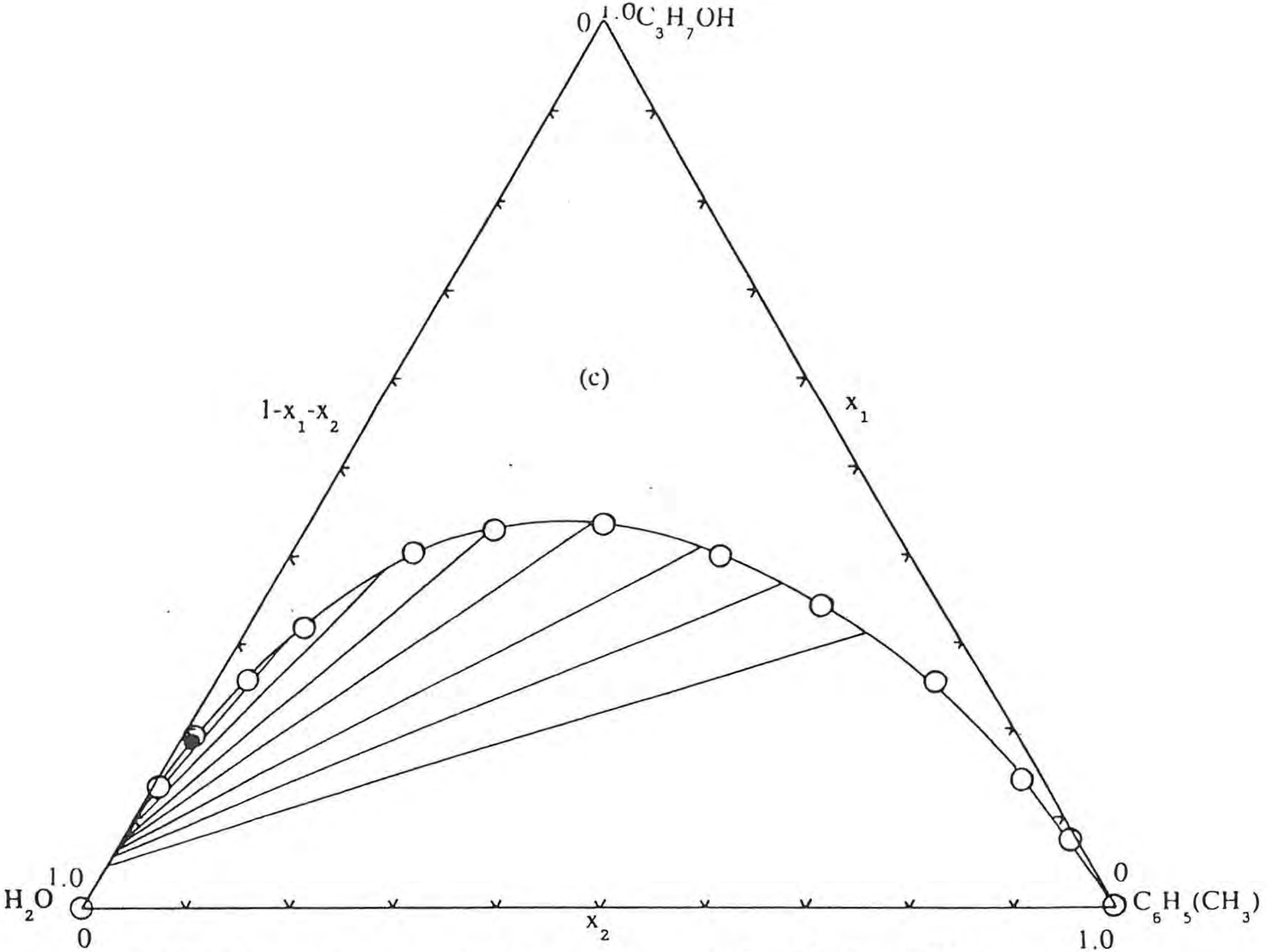


FIGURE 6.3(c) : The 1–propanol–toluene–water ternary system in mole fractions at 298.2 K

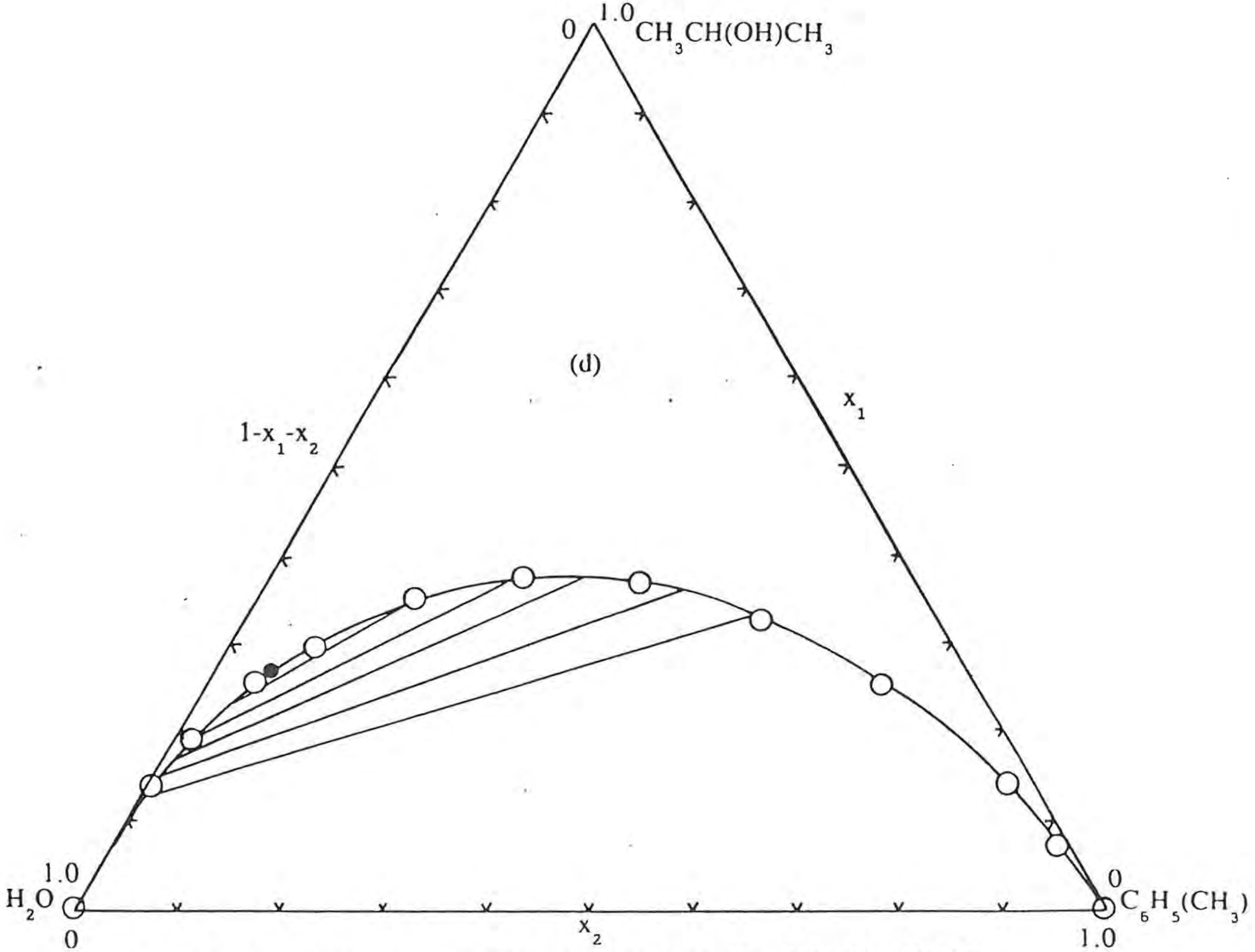


FIGURE 6.3(d) : The 2–propanol–toluene–water ternary system in mole fractions at 298.2 K

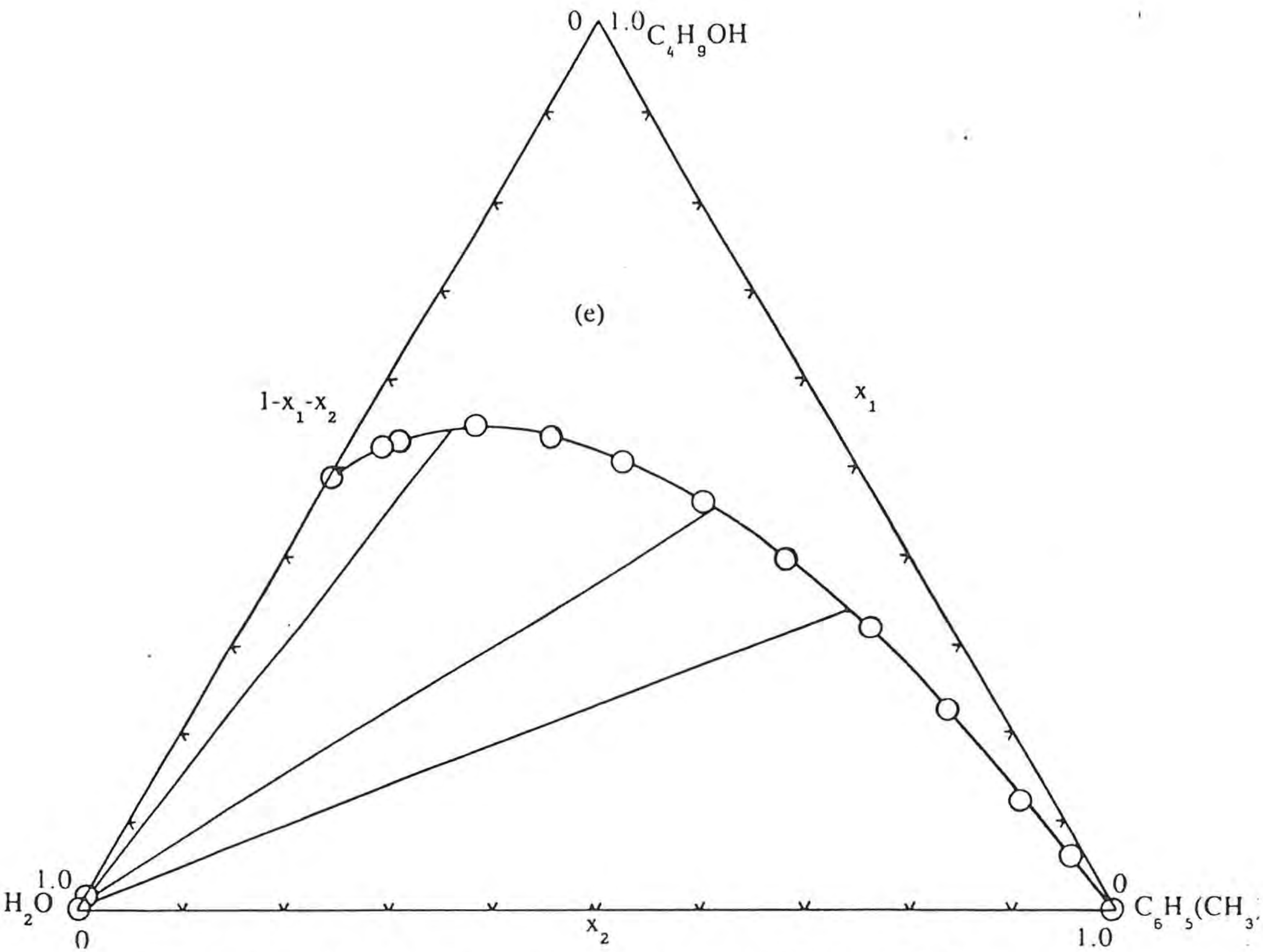


FIGURE 6.3(e) : The 1–butanol–toluene–water ternary system in mole fractions at 298.2 K

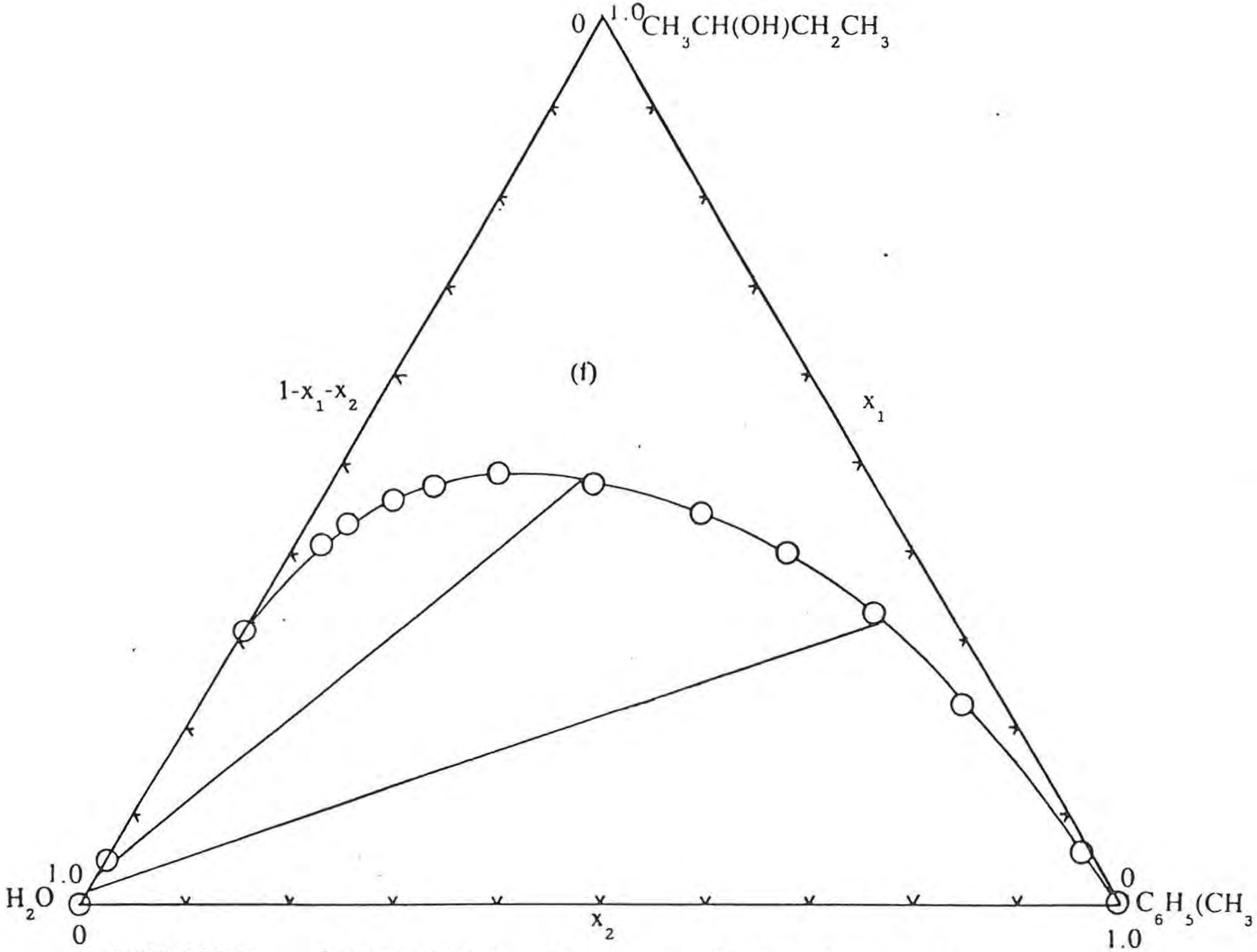


FIGURE 6.3(f) : he 2—butanol—toluene—water ternary system in mole fractions at 298.2 K

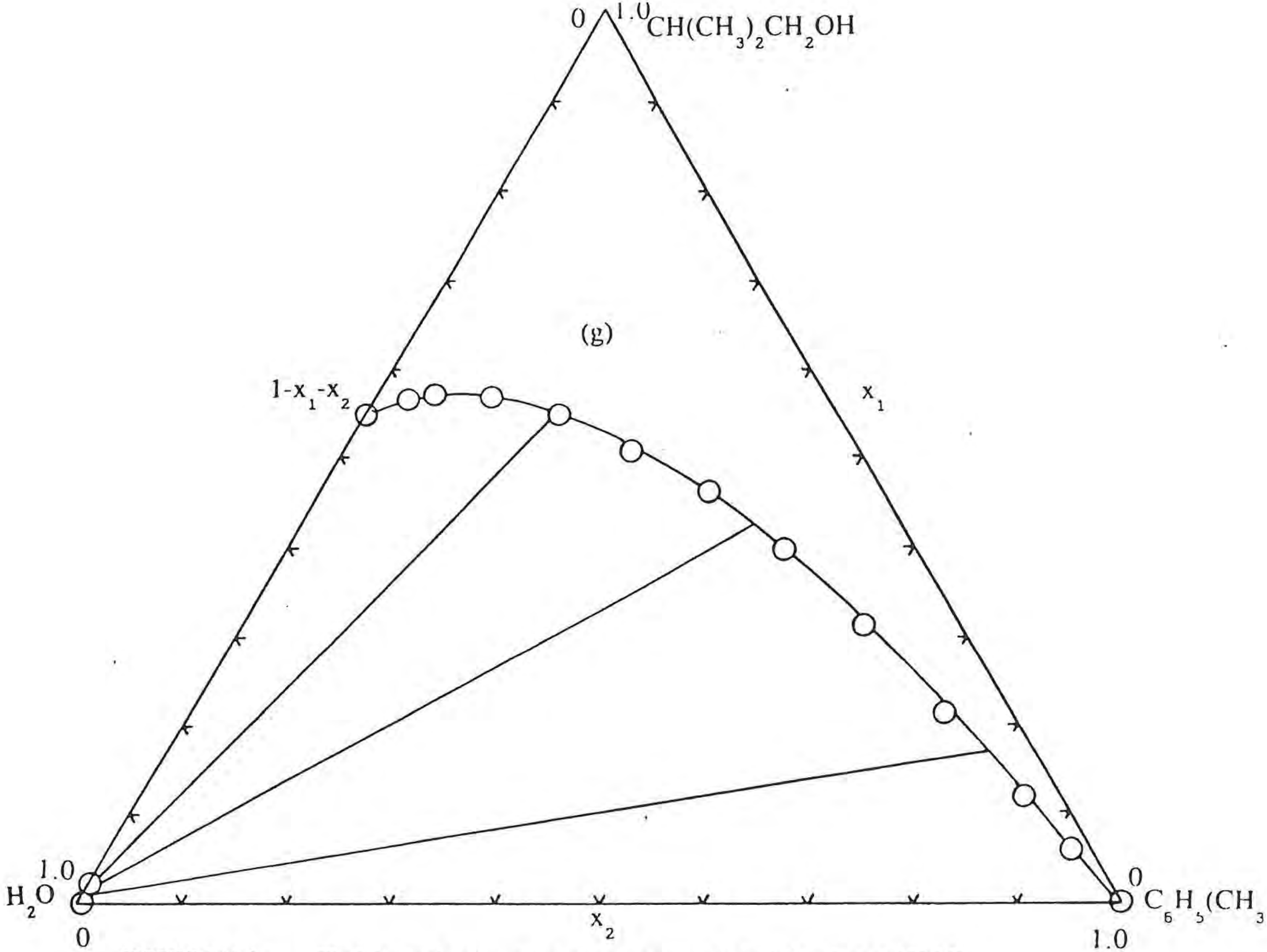


FIGURE 6.3(g) : **The i–butanol–toluene–water ternary system in mole fractions at 298.2 K**

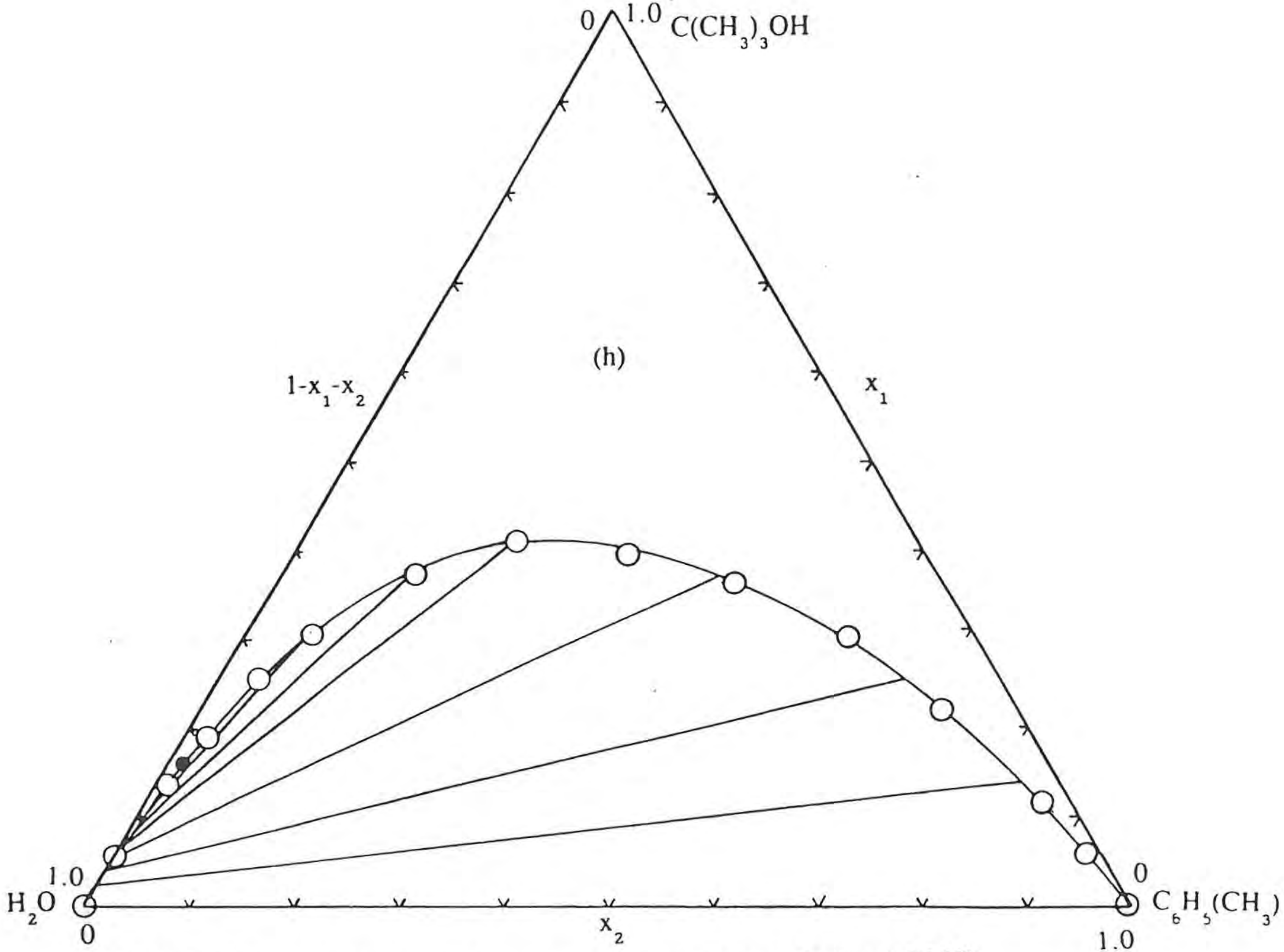
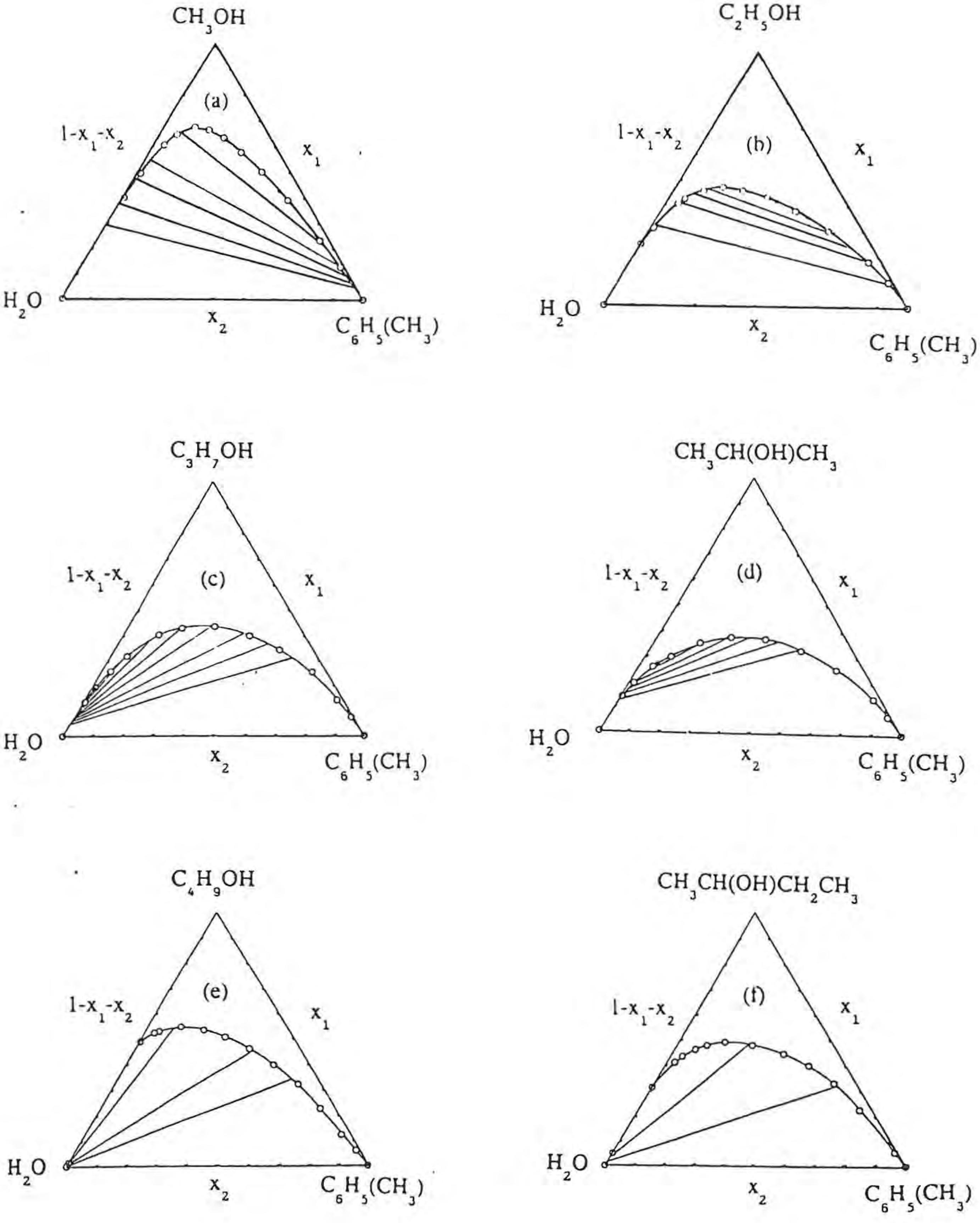


FIGURE 6.3(h) : The t–butanol–toluene–water ternary system in mole fractions at 298.2 K


CH$_3$OH
(a)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)
C$_2$H$_5$OH
(b)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)
C$_3$H$_7$OH
(c)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)
CH$_3$CH(OH)CH$_3$
(d)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)
C$_4$H$_9$OH
(e)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)
CH$_3$CH(OH)CH$_2$CH$_3$
(f)
1-x$_1$-x$_2$
x$_1$
H$_2$O
x$_2$
C$_6$H$_5$(CH$_3$)

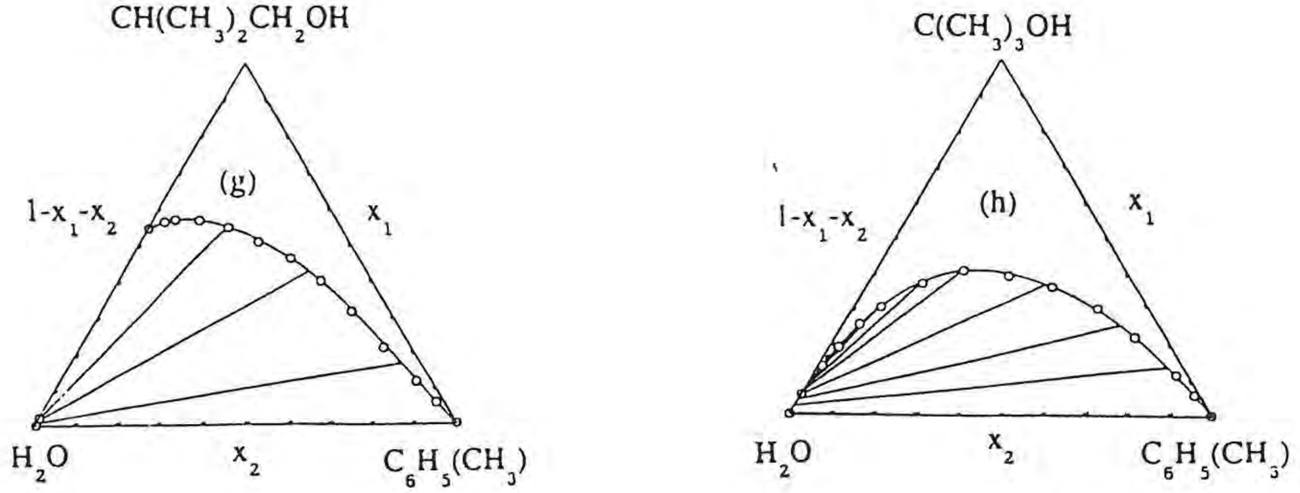


FIGURE 6.3(a–h) : Summary of liquid–liquid equilibrium curves and tielines for $\{x_1C_mH_{2m+1}OH + x_2C_6H_5(CH_3) + (1-x_1-x_2)H_2O\}$ at 298.2 K.

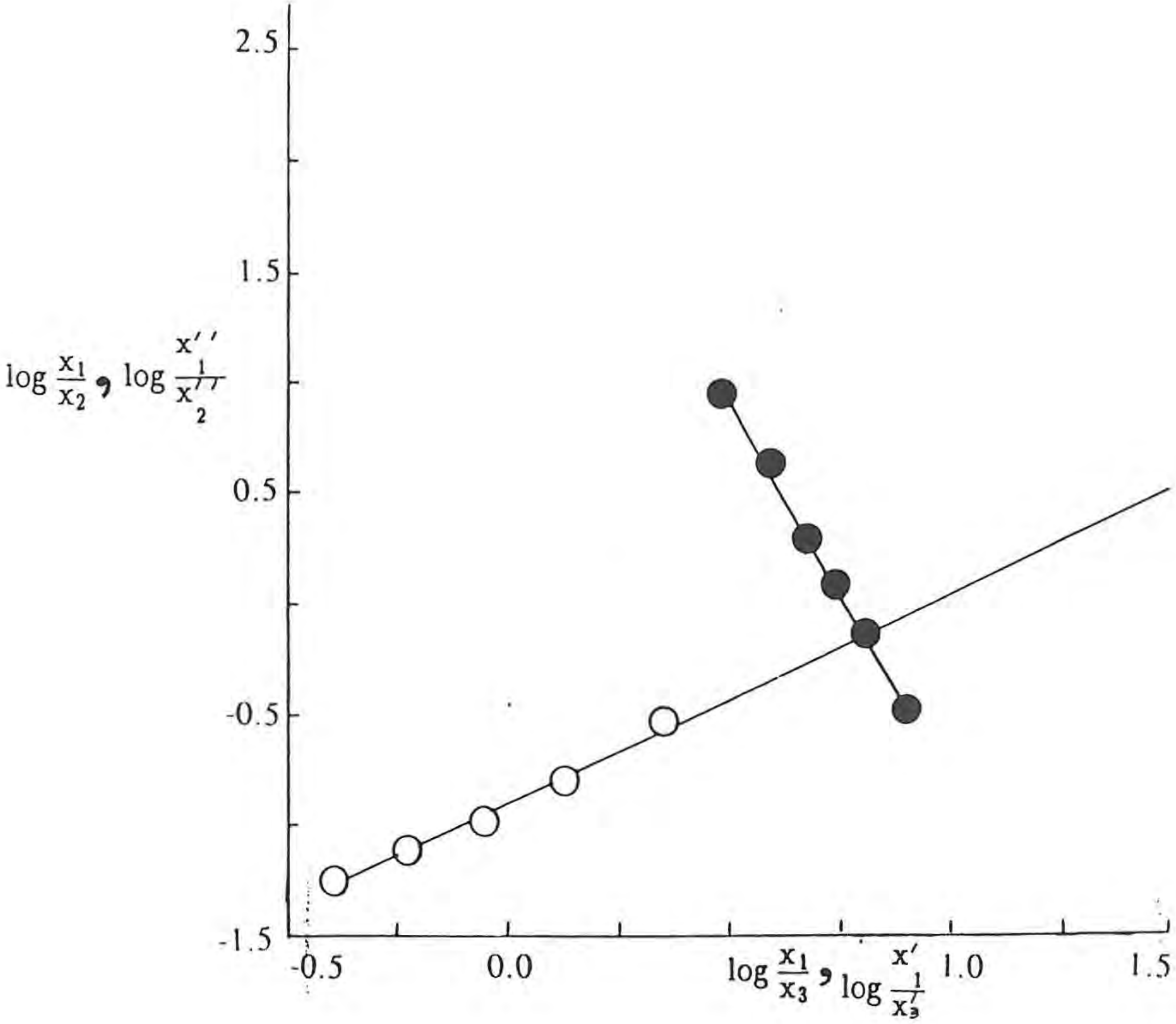


FIGURE 6.3(i) : **Determination of plait point {Treybal method} : The methanol–toluene–water ternary system.**

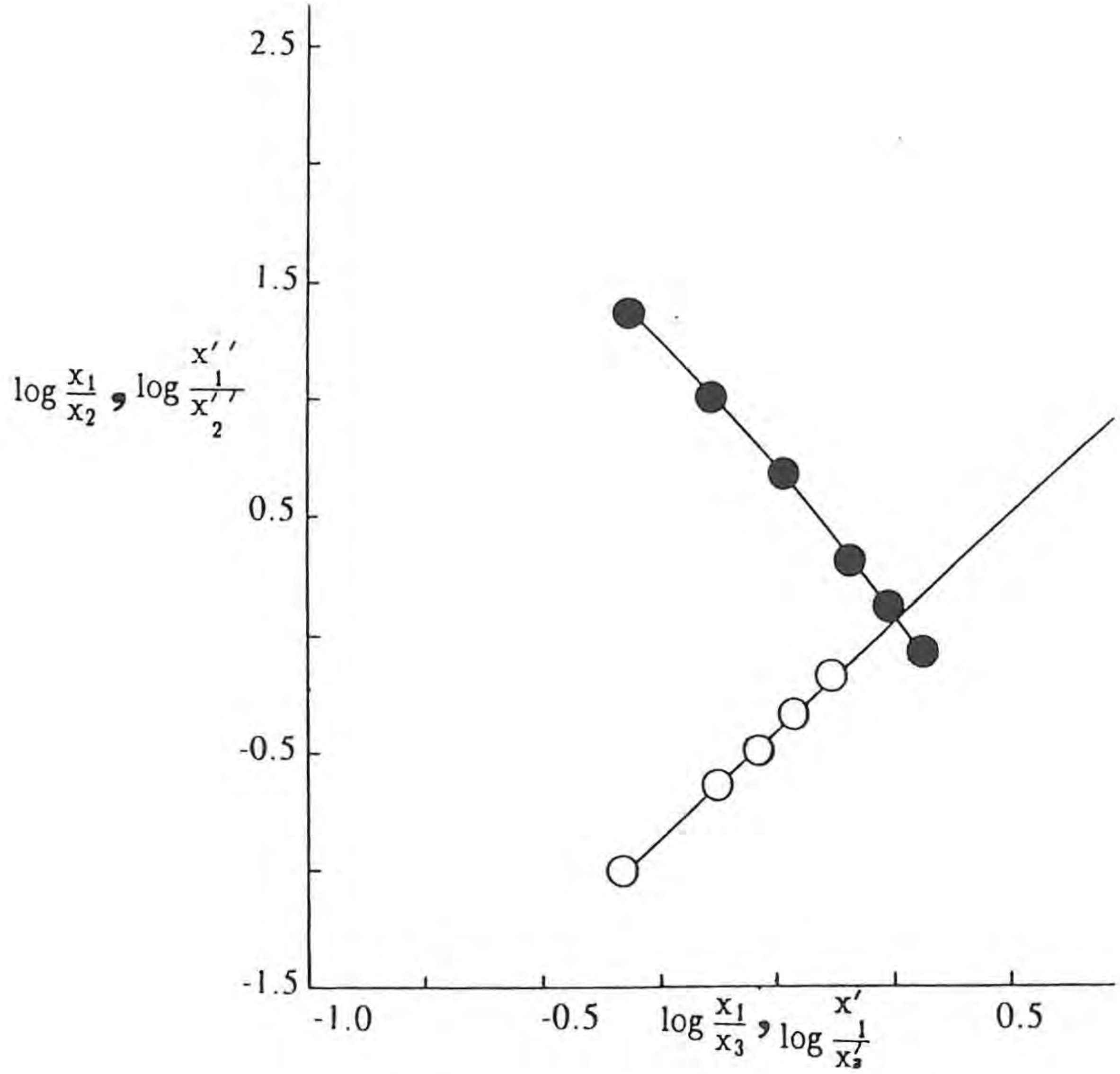


FIGURE 6.3(j) : **Determination of plait point {Treybal method} : The ethanol—toluene—water ternary system.**

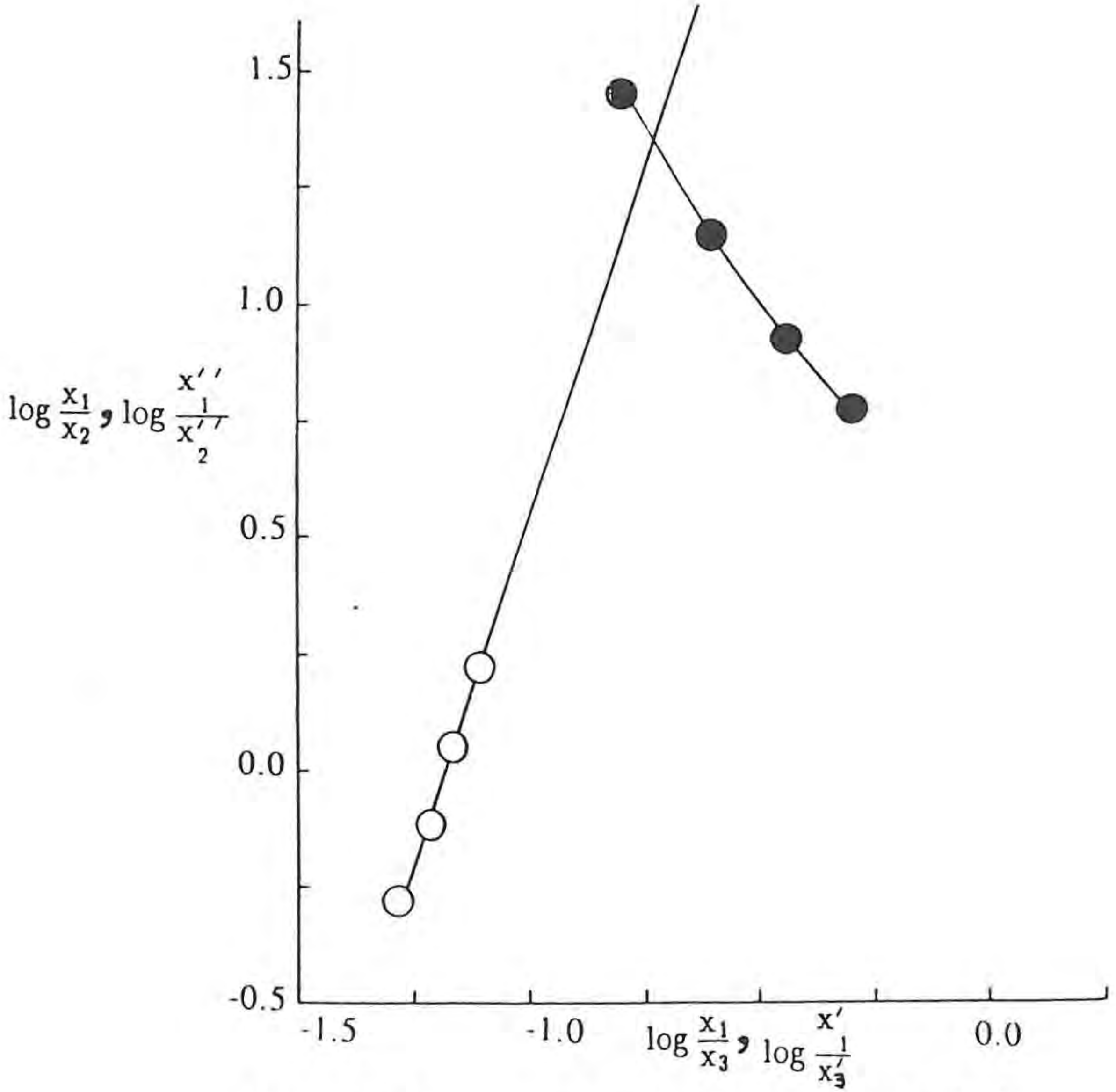


FIGURE 6.3(k) : Determination of plait point {Treybal method} : The 1–propanol–toluene–water ternary system.

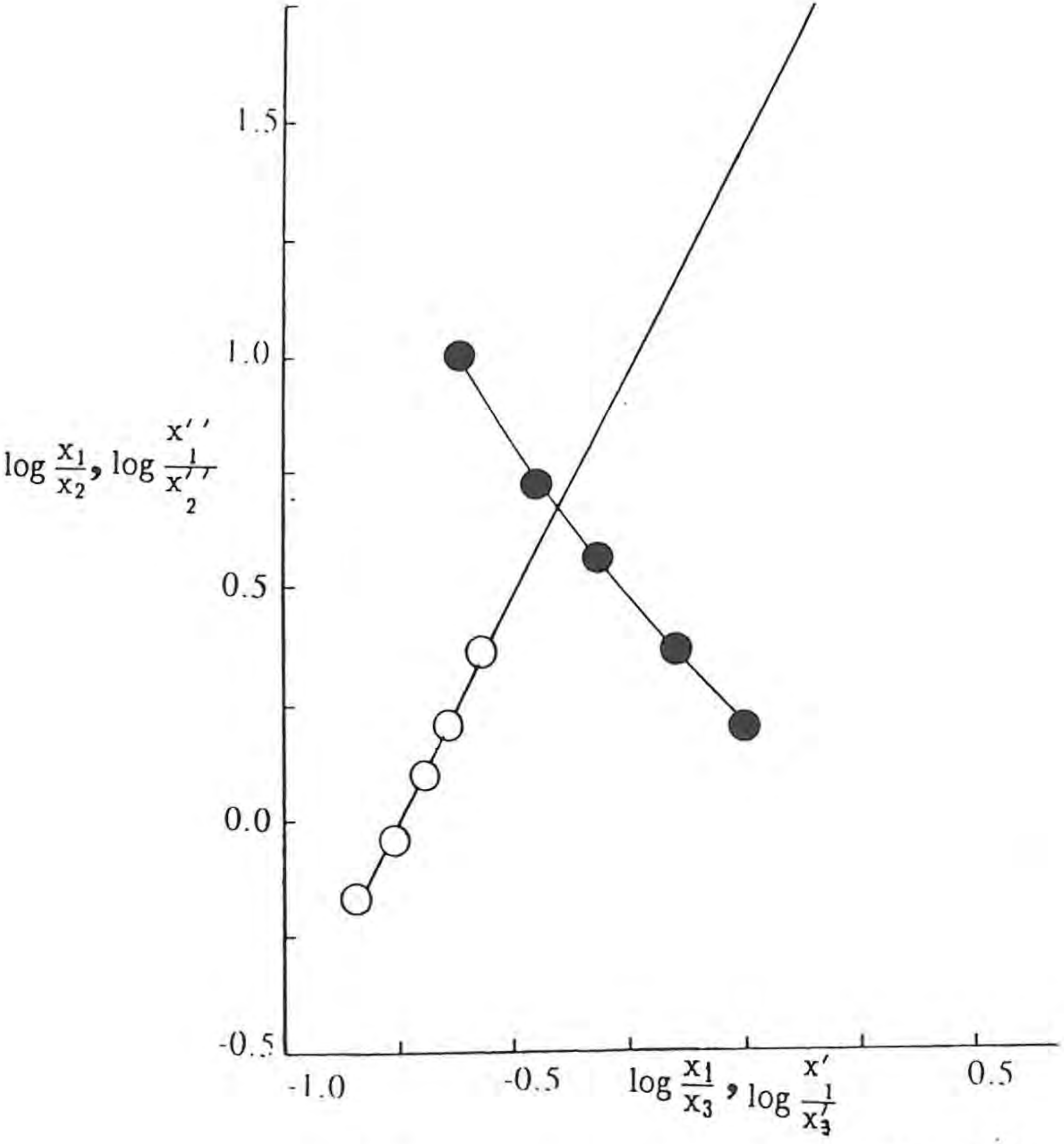


FIGURE 6.3(l) : Determination of plait point {Treybal method} : The 2–propanol–toluene–water ternary system.

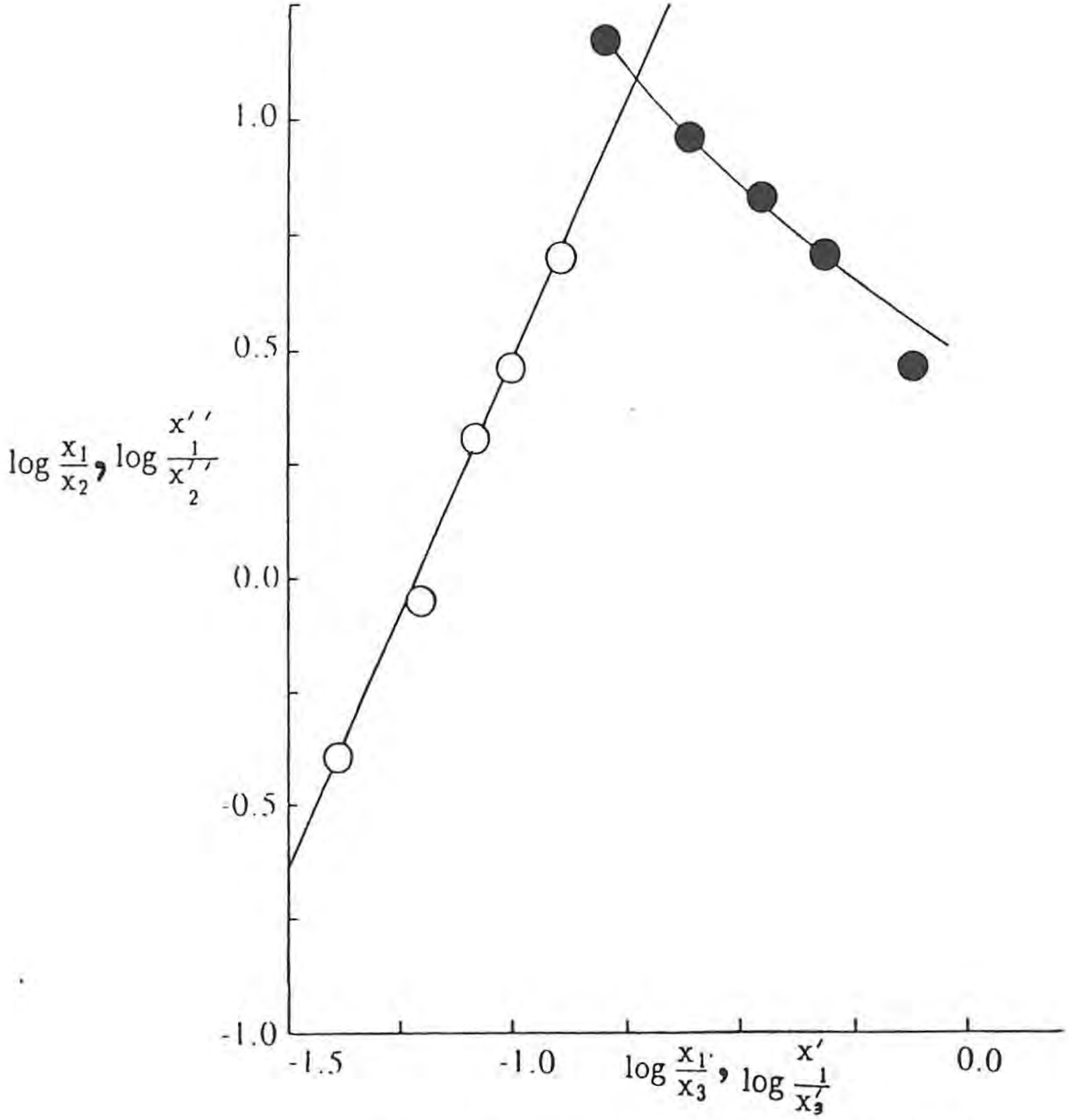


FIGURE 6.3(m) : Determination of plait point {Treybal method} : The t–butanol–toluene–water ternary system.

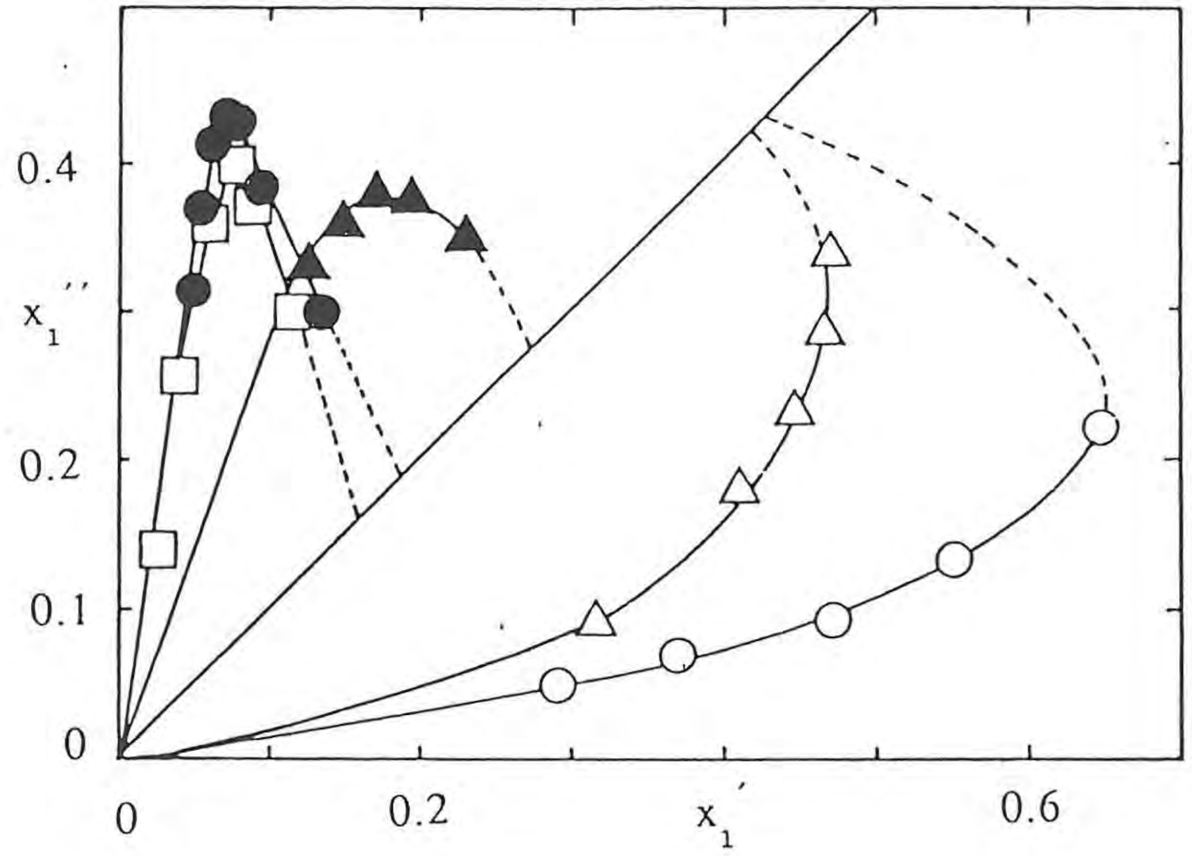


FIGURE 6.3(n) : A plot of x_1'' against x_1', showing the relative solubilities of the alkanol in the toluene–rich and water–rich layers.
○,CH_3OH; △,C_2H_5OH; ●,C_3H_7OH; ▲,$CH_3CH(OH)CH_3$; □,$C(CH_3)_3OH$.

6.4 : THE ALCOHOL–BENZENE–WATER TERNARY SYSTEM, AT 298.2K.

TABLE 6.4(a): The composition of points on the coexistence curve for mixtures $\{x_1C_mH_{2m+1}OH + x_2(C_6H_6) + (1 - x_1 - x_2)H_2O\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH			CH_3CH_2OH			$CH_3CH_2CH_2OH$		
x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
0.000	0.999	0.000	0.000	0.999	0.000	0.000	0.999	0.000
0.112	0.872	0.016	0.080	0.904	0.016	0.063	0.923	0.014
0.207	0.759	0.034	0.151	0.806	0.043	0.122	0.852	0.026
0.350	0.576	0.074	0.264	0.624	0.112	0.228	0.704	0.068
0.451	0.433	0.116	0.339	0.468	0.193	0.314	0.564	0.122
0.569	0.233	0.197	0.382	0.339	0.279	0.378	0.436	0.186
0.590	0.104	0.306	0.401	0.237	0.362	0.417	0.320	0.263
0.558	0.057	0.385	0.402	0.158	0.440	0.431	0.221	0.348
0.497	0.028	0.475	0.382	0.096	0.522	0.412	0.136	0.452
0.403	0.011	0.586	0.386	0.082	0.532	0.352	0.068	0.580
0.232	0.002	0.766	0.315	0.026	0.659	0.259	0.036	0.705
0.000	0.000	0.999	0.240	0.012	0.748	0.193	0.021	0.786
			0.173	0.003	0.824	0.138	0.011	0.851
			0.000	0.000	0.999	0.091	0.002	0.904
						0.000	0.000	0.999

$CH_3CH(OH)CH_3$			C_4C_9OH			$CH_3CH_2CH(OH)CH_3$		
x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
0.000	0.999	0.000	0.000	0.999	0.000	0.000	0.999	0.000
0.063	0.925	0.012	0.052	0.938	0.010	0.052	0.939	0.009
0.124	0.856	0.020	0.103	0.876	0.021	0.102	0.877	0.021
0.225	0.691	0.084	0.197	0.749	0.054	0.199	0.753	0.048
0.302	0.541	0.157	0.284	0.629	0.087	0.284	0.628	0.088
0.350	0.404	0.246	0.361	0.513	0.126	0.356	0.506	0.138
0.369	0.284	0.347	0.423	0.400	0.177	0.410	0.389	0.201
0.354	0.182	0.464	0.474	0.300	0.226	0.449	0.283	0.268
0.301	0.099	0.600	0.508	0.207	0.285	0.472	0.192	0.336
0.221	0.044	0.735	0.526	0.056	0.418	0.467	0.111	0.422
0.164	0.017	0.819	0.506	0.035	0.459	0.427	0.045	0.528
0.070	0.001	0.929	0.488	0.000	0.512	0.377	0.018	0.605
0.000	0.000	0.999				0.339	0.006	0.655
						0.312	0.000	0.688

TABLE 6.4(a): (CONTD.)

$CH(CH_3)_2CH_2OH$			$C(CH_3)_3OH$		
x_1	x_2	x_3	x_1	x_2	x_3
0.000	0.999	0.000	0.000	0.999	0.000
0.052	0.937	0.001	0.052	0.939	0.009
0.103	0.881	0.015	0.102	0.874	0.024
0.198	0.753	0.049	0.196	0.744	0.060
0.287	0.635	0.078	0.275	0.610	0.115
0.364	0.519	0.117	0.336	0.479	0.185
0.432	0.410	0.158	0.372	0.352	0.276
0.487	0.308	0.205	0.384	0.243	0.373
0.528	0.214	0.258	0.364	0.148	0.488
0.556	0.132	0.312	0.299	0.071	0.630
0.567	0.060	0.373	0.255	0.046	0.699
0.554	0.012	0.434	0.191	0.026	0.783
0.546	0.000	0.454	0.137	0.014	0.849
			0.094	0.006	0.900
			0.000	0.000	0.999

TABLE 6.4(b): The composition of conjugate phases x_1', x_2', x_1'' and x_2'' for $\{x_1C_mH_{2m+1}OH + x_2C_6H_6 + (1 - x_1 - x_2)H_2O\}$ at 298.15 K.

CH_3OH				C_2H_5OH			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.130	0.001	0.047	0.948	0.069	0.001	0.035	0.961
0.267	0.003	0.070	0.923	0.146	0.002	0.067	0.925
0.427	0.015	0.112	0.871	0.255	0.015	0.100	0.874
0.598	0.120	0.180	0.788	0.304	0.025	0.166	0.776
0.554	0.292	0.229	0.727	0.378	0.079	0.244	0.654
C_3H_7OH				$CH_3CH(OH)CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.043	0.001	0.095	0.879	0.053	0.001	0.057	0.930
0.054	0.001	0.287	0.603	0.096	0.002	0.188	0.739
0.061	0.001	0.391	0.385	0.114	0.006	0.327	0.470
0.072	0.002	0.424	0.179	0.151	0.012	0.348	0.179
0.081	0.002	0.389	0.111	0.179	0.023	0.306	0.106
C_4H_9OH				$CH_3CH(OH)CH_2CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.001	0.001	0.157	0.808	0.001	0.001	0.138	0.831
0.002	0.001	0.309	0.595	0.001	0.001	0.277	0.641
0.002	0.002	0.430	0.386	0.002	0.002	0.391	0.433
0.003	0.002	0.495	0.243	0.006	0.004	0.464	0.247
0.010	0.003	0.389	0.533	0.011	0.003	0.460	0.096
$CH_3C(CH_3)CH_2OH$				$C(CH)_3OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.000	0.000	0.164	0.798	0.001	0.000	0.085	0.808
0.001	0.001	0.293	0.622	0.004	0.001	0.306	0.543
0.001	0.001	0.418	0.431	0.007	0.002	0.380	0.310
0.002	0.001	0.520	0.239	0.017	0.182	0.380	0.201
0.003	0.001	0.561	0.100	0.021	0.218	0.358	0.133

TABLE 6.4(c): The coefficients A_i, B_i and C_i in equations (4.1). (4.4) and (4.5) respectively for $x_1C_mH_{2m+1}OH + x_2C_6H_6 + (1 - x_1 - x_2)H_2O$ together with the standard deviation σ. The standard errors are given in parenthesis.

CH_3OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = 0.0586$ (0.22) $A_2 = 0.7163$ (0.20) $A_3 = 3.3764$ (0.58) $\sigma = 0.023$	$B_1 = 2.7045$ (0.25) $B_2 = 1.1989$ (0.05) $B_3 = 1.0497$ (0.06) $\sigma = 0.052$	$C_1 = 2.4567$ (0.18) $C_2 = 1.1628$ (0.04) $C_3 = 1.4958$ (0.06) $\sigma = 0.049$
CH_3CH_2OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.6273$ (0.10) $A_2 = -0.0024$ (0.10) $A_3 = 0.7232$ (0.27) $\sigma = 0.021$	$B_1 = 1.3597$ (0.08) $B_2 = 0.9754$ (0.03) $B_3 = 0.7847$ (0.04) $\sigma = 0.024$	$C_1 = 1.2468$ (0.06) $C_2 = 0.9444$ (0.02) $C_3 = 1.1388$ (0.04) $\sigma = 0.021$
$CH_3CH_2CH_2OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.1673$ (0.06) $A_2 = 0.1768$ (0.07) $A_3 = 1.7221$ (0.17) $\sigma = 0.022$	$B_1 = 1.6952$ (0.05) $B_2 = 1.0480$ (0.02) $B_3 = 0.9451$ (0.02) $\sigma = 0.015$	$C_1 = 1.5126$ (0.04) $C_2 = 1.0072$ (0.01) $C_3 = 1.3035$ (0.02) $\sigma = 0.019$
$C(CH_3)_3OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.3532$ (0.04) $A_2 = -0.1368$ (0.04) $A_3 = 0.7841$ (0.11) $\sigma = 0.005$	$B_1 = 1.2686$ (0.05) $B_2 = 0.9279$ (0.02) $B_3 = 0.8545$ (0.02) $\sigma = 0.006$	$C_1 = 1.3377$ (0.04) $C_2 = 0.8881$ (0.02) $C_3 = 1.1613$ (0.02) $\sigma = 0.004$

TABLE 6.4(c) (CONTD.) :

C_4H_9OH		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -1.4910$ (0.06) $A_2 = -0.0435$ (0.04) $A_3 = -0.1606$ (0.13) $\sigma = 0.004$	$B_1 = 1.3760$ (0.03) $B_2 = 0.9724$ (0.01) $B_3 = 0.5238$ (0.02) $\sigma = 0.005$	$C_1 = 1.3322$ (0.03) $C_2 = 0.9626$ (0.01) $C_3 = 0.9351$ (0.02) $\sigma = 0.004$
$CH_3CH_2CH(OH)CH_3$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.8423$ (0.07) $A_2 = -0.0040$ (0.06) $A_3 = 0.6417$ (0.19) $\sigma = 0.009$	$B_1 = 1.4684$ (0.04) $B_2 = 0.9845$ (0.01) $B_3 = 0.7151$ (0.02) $\sigma = 0.011$	$C_1 = 1.3963$ (0.03) $C_2 = 0.9687$ (0.01) $C_3 = 1.1087$ (0.02) $\sigma = 0.009$
$CH(CH_3)_2CH_2OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -1.8247$ (0.05) $A_2 = -0.0945$ (0.03) $A_3 = -0.5865$ (0.10) $\sigma = 0.003$	$B_1 = 1.4335$ (0.06) $B_2 = 0.9821$ (0.02) $B_3 = 0.4891$ (0.04) $\sigma = 0.003$	$C_1 = 1.3876$ (0.06) $C_2 = 0.9722$ (0.02) $C_3 = 0.9057$ (0.05) $\sigma = 0.002$
$CH(CH_3)_2CH_2OH$		
Hlavaty	**Beta**	**Log–Gamma**
$A_1 = -0.2839$ (0.04) $A_2 = -0.0057$ (0.05) $A_3 = 1.1348$ (0.12) $\sigma = 0.006$	$B_1 = 1.4040$ (0.04) $B_2 = 0.9755$ (0.01) $B_3 = 0.8910$ (0.15) $\sigma = 0.012$	$C_1 = 1.2743$ (0.02) $C_2 = 0.9429$ (0.01) $C_3 = 1.2322$ (0.01) $\sigma = 0.006$

TABLE 6.4(d): Plait points for the alcohol–benzene–water ternary systems, in mole fractions. The plait points have been given in the form (x_1,x_2) where x_1 = mole fractions of alcohol and x_2 = mole fraction of benzene.

System	Plait point
Methanol	(0.49,0.44)
Ethanol	(0.37,0.39)
1–Propanol	(0.11,0.01)
2–Propanol	(0.22,0.05)
t–Butanol	(0.11,0.02

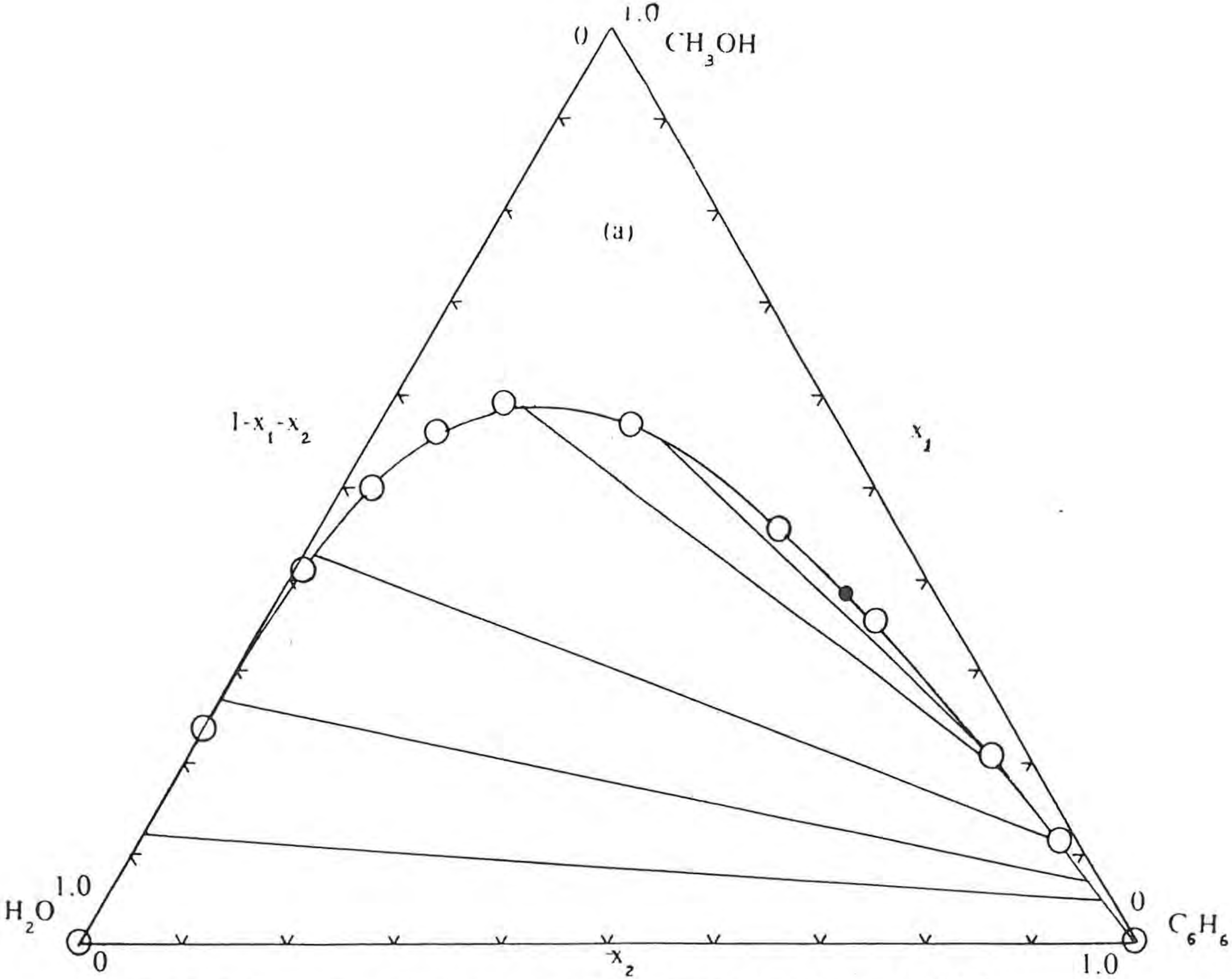


FIGURE 6.4(a) : The methanol—benzene—water ternary system in mole fractions at 298.2 K

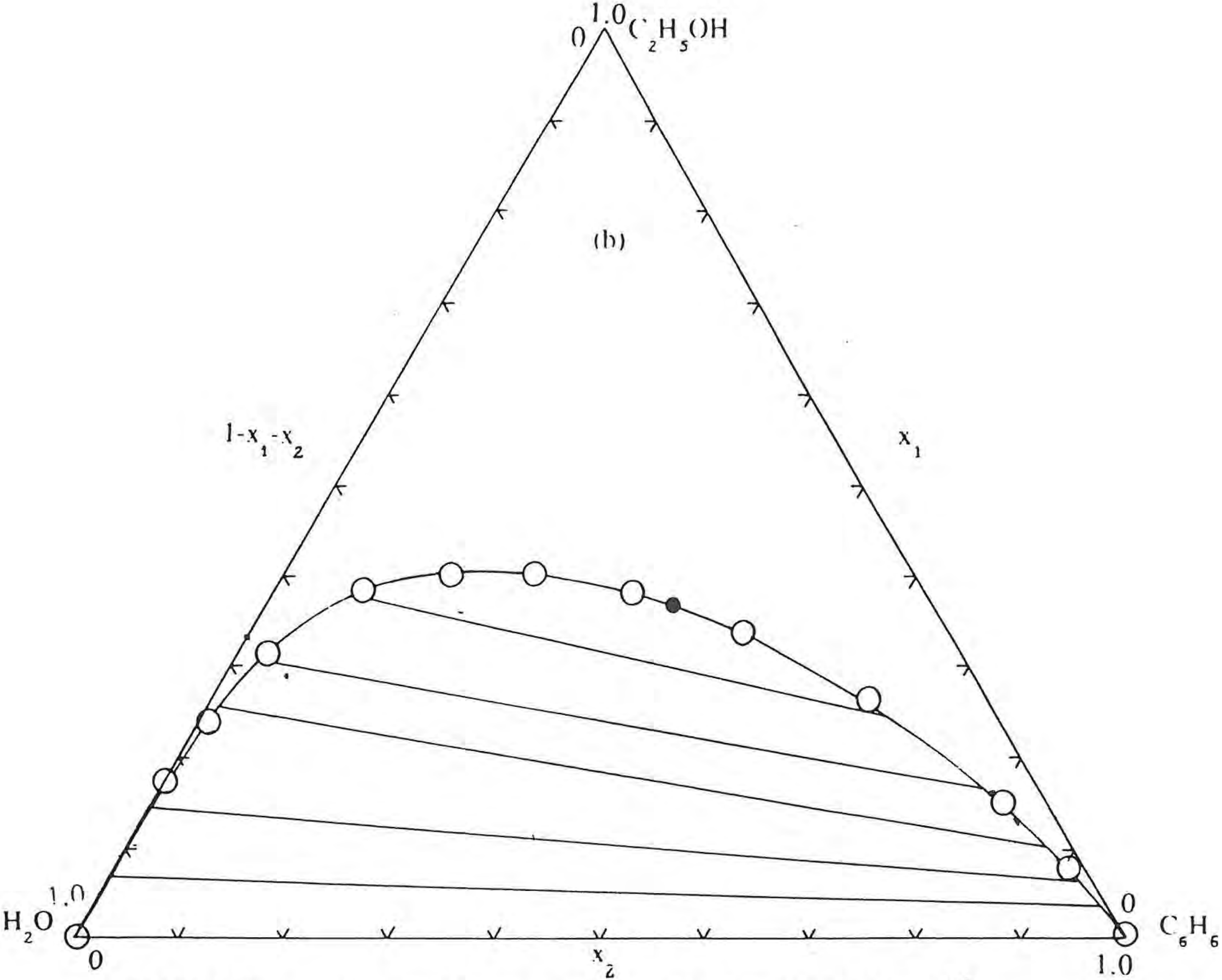


FIGURE 6.4(b) : The ethanol—benzene—water ternary system in mole fractions at 298.2 K

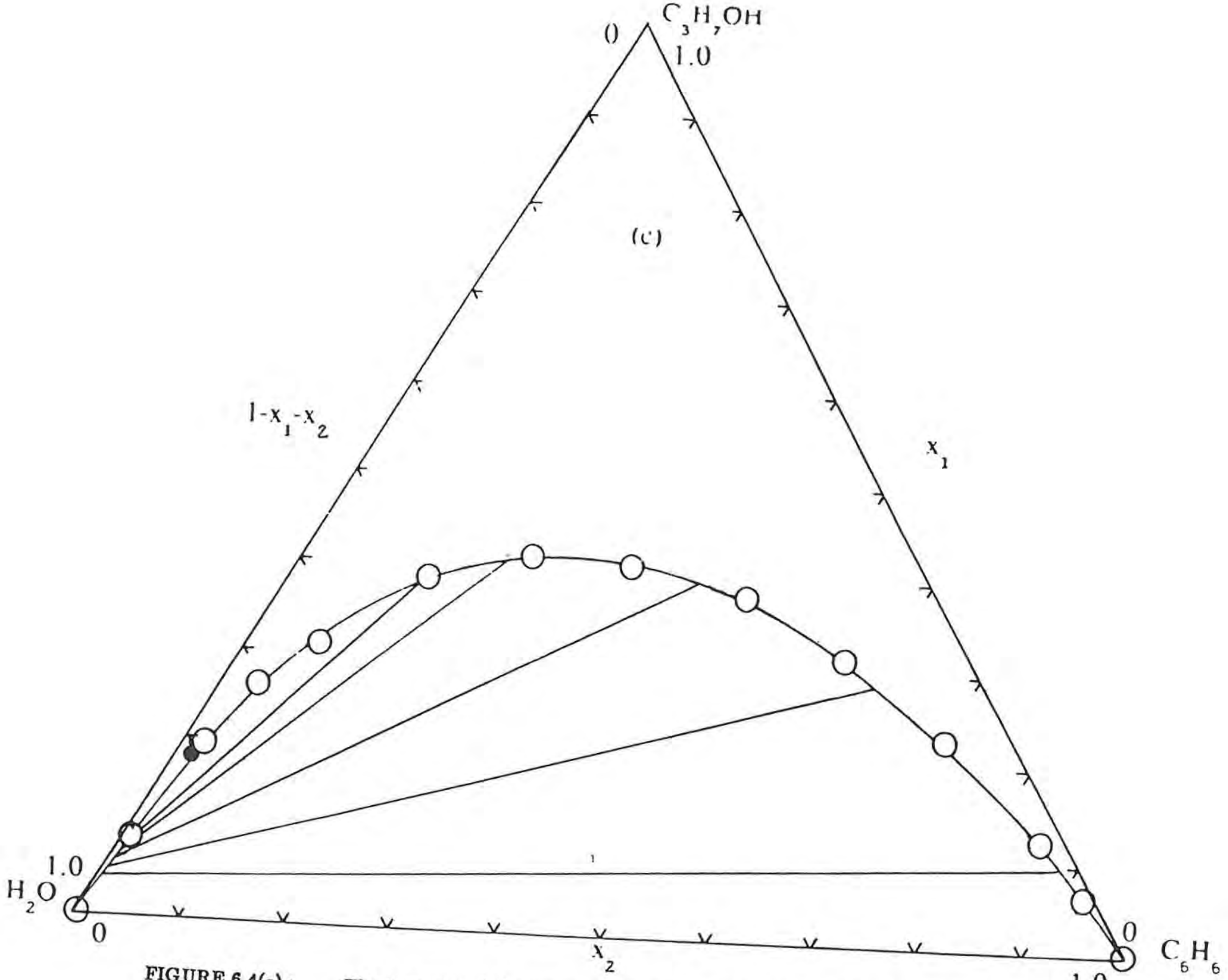


FIGURE 6.4(c) : The 1—propanol—benzene—water ternary system in mole fractions at 298.2 K

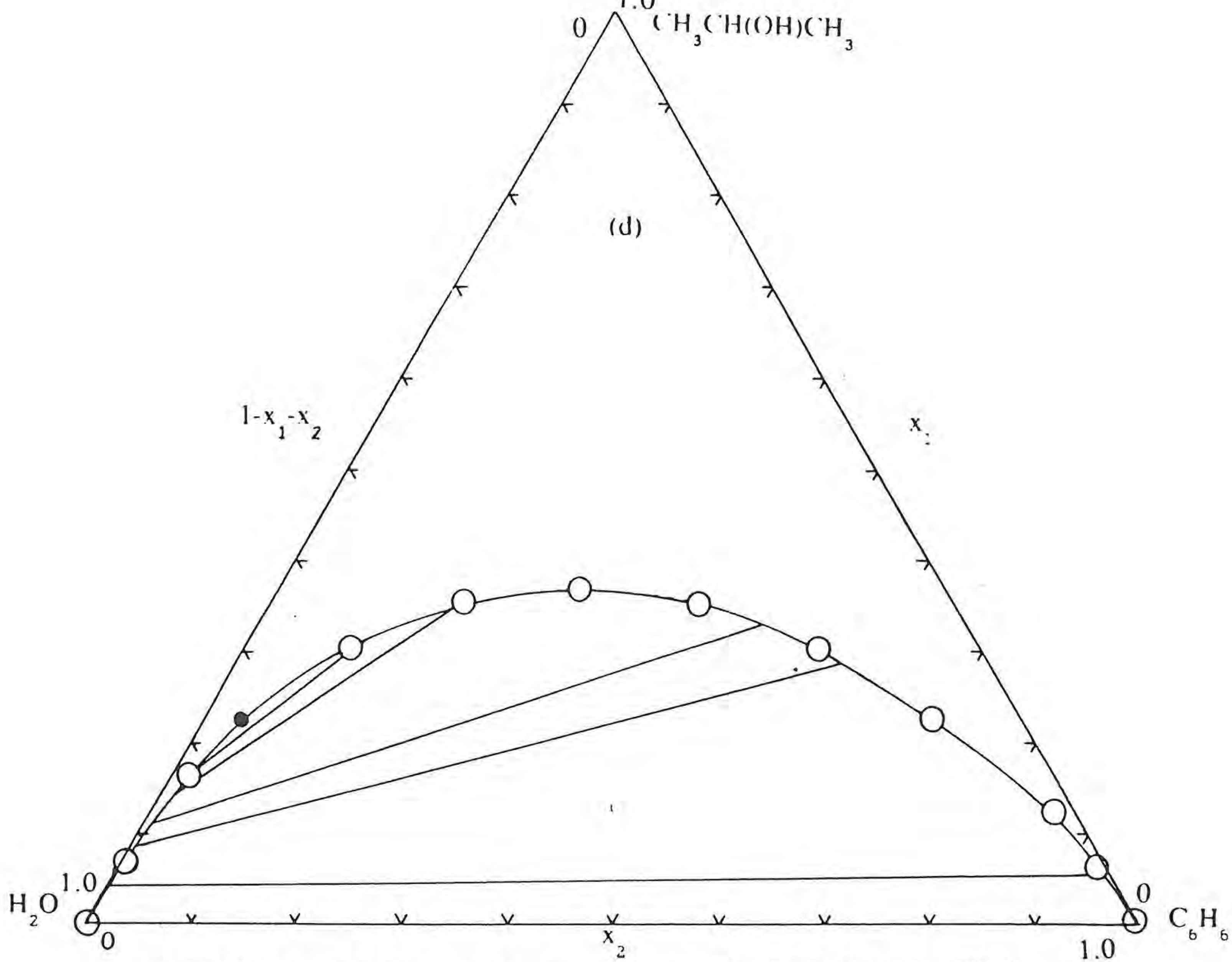


FIGURE 6.4(d) : The 2–propanol–benzene–water ternary system in mole fractions at 298.2 K

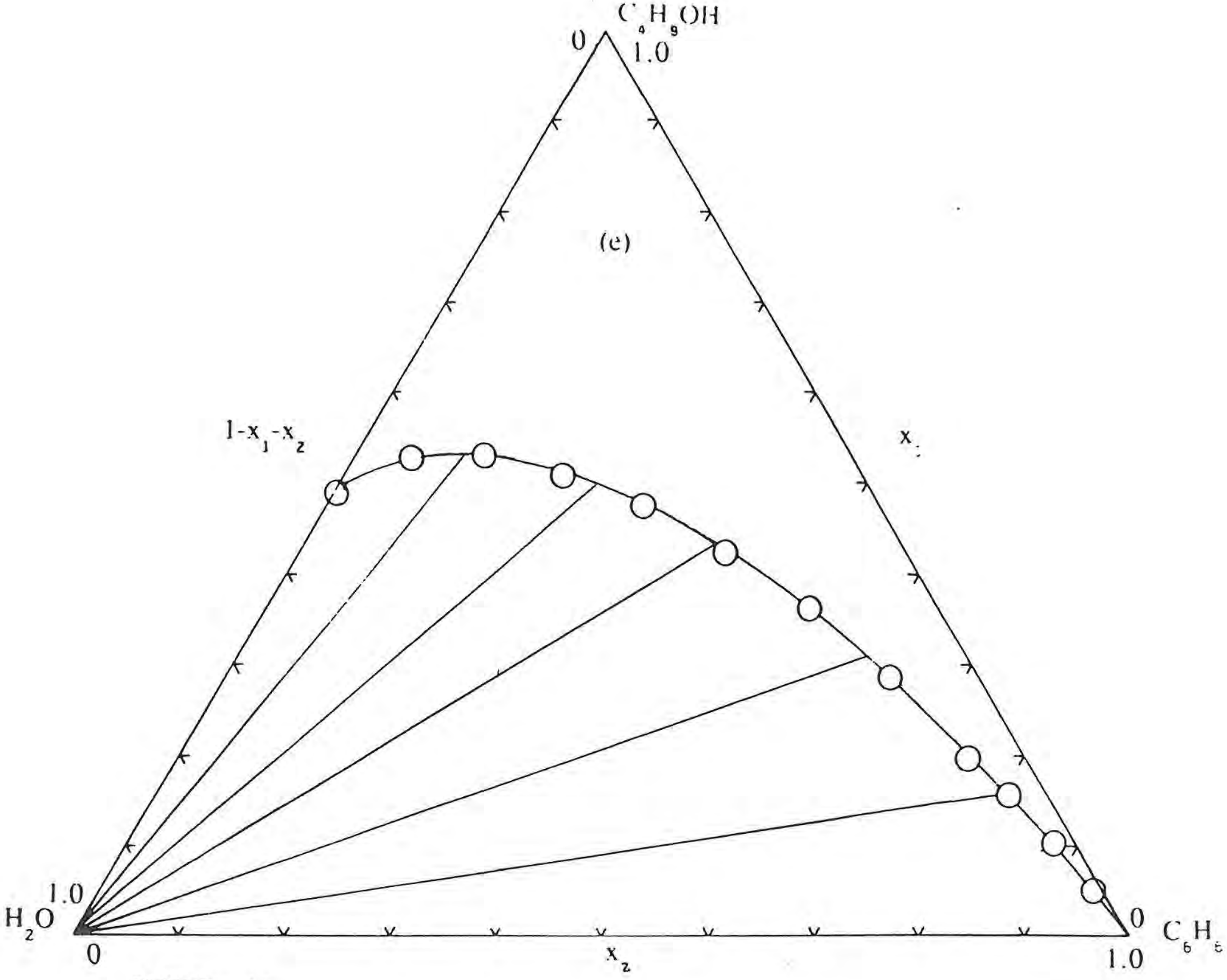


FIGURE 6.4(e) : The 1–butanol–benzene–water ternary system in mole fractions at 298.2 K

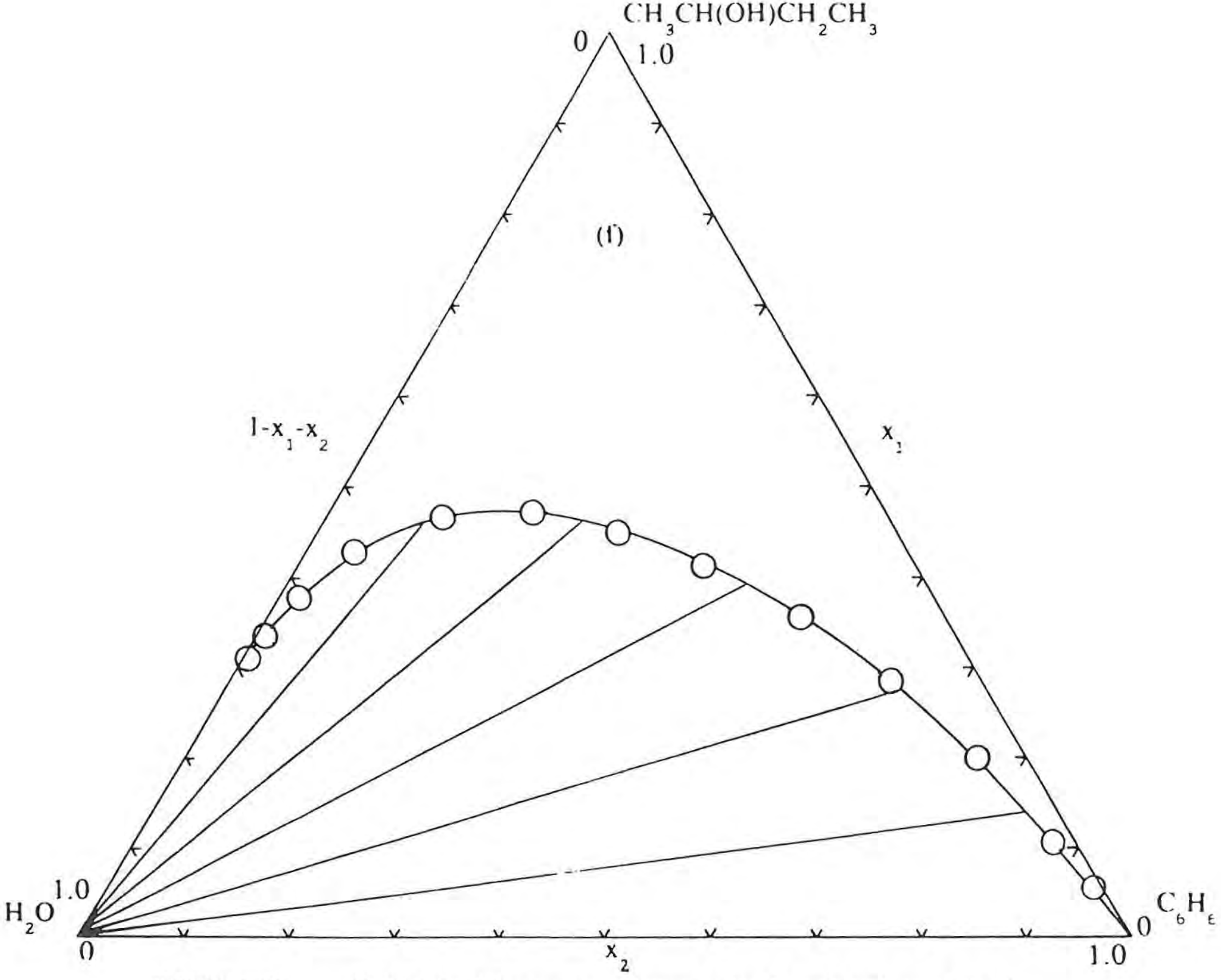


FIGURE 6.4(f) : The 2—butanol—benzene—water ternary system in mole fractions at 298.2 K

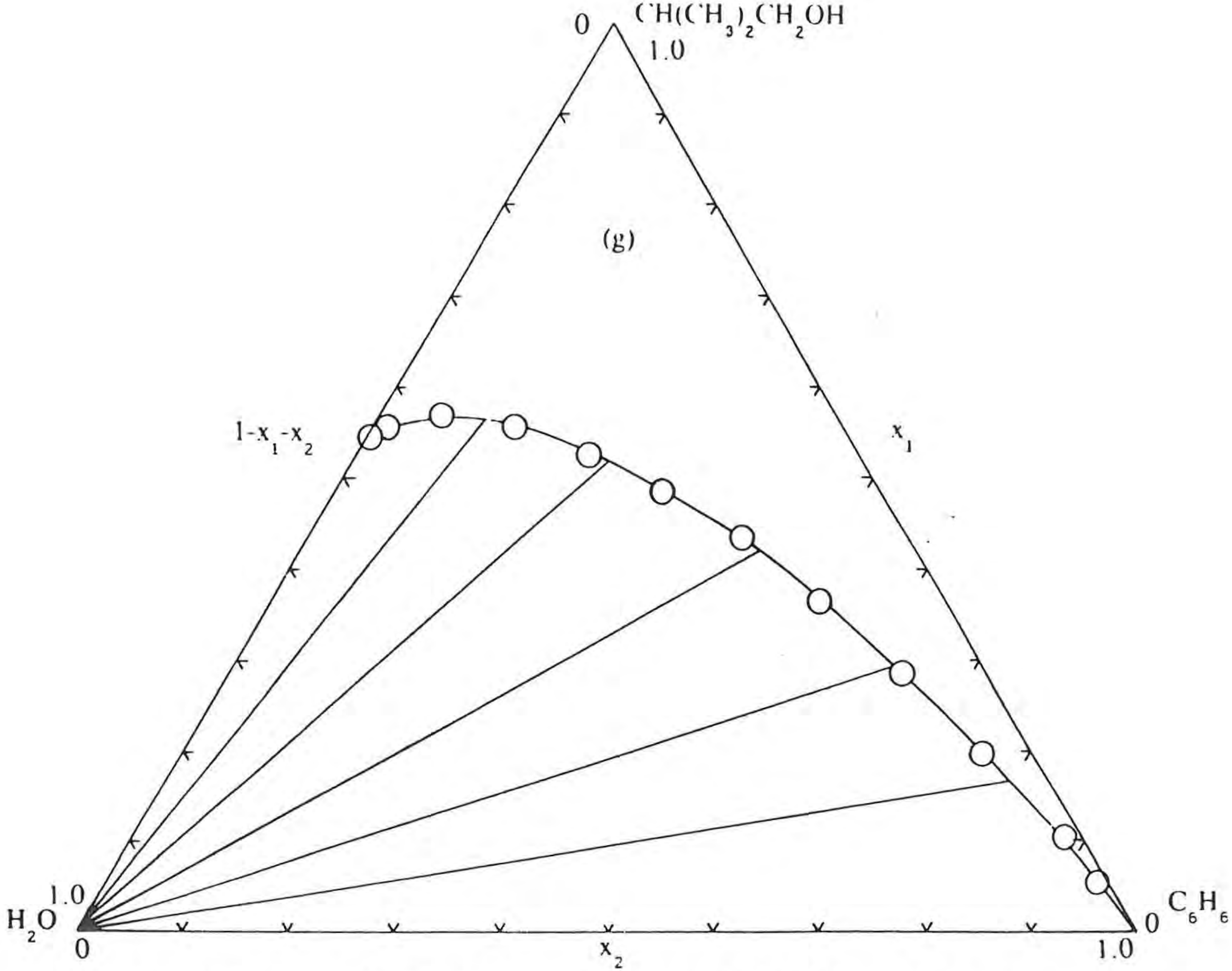


FIGURE 6.4(g) : **The i–butanol–bensene–water ternary system in mole fractions at 298.2 K**

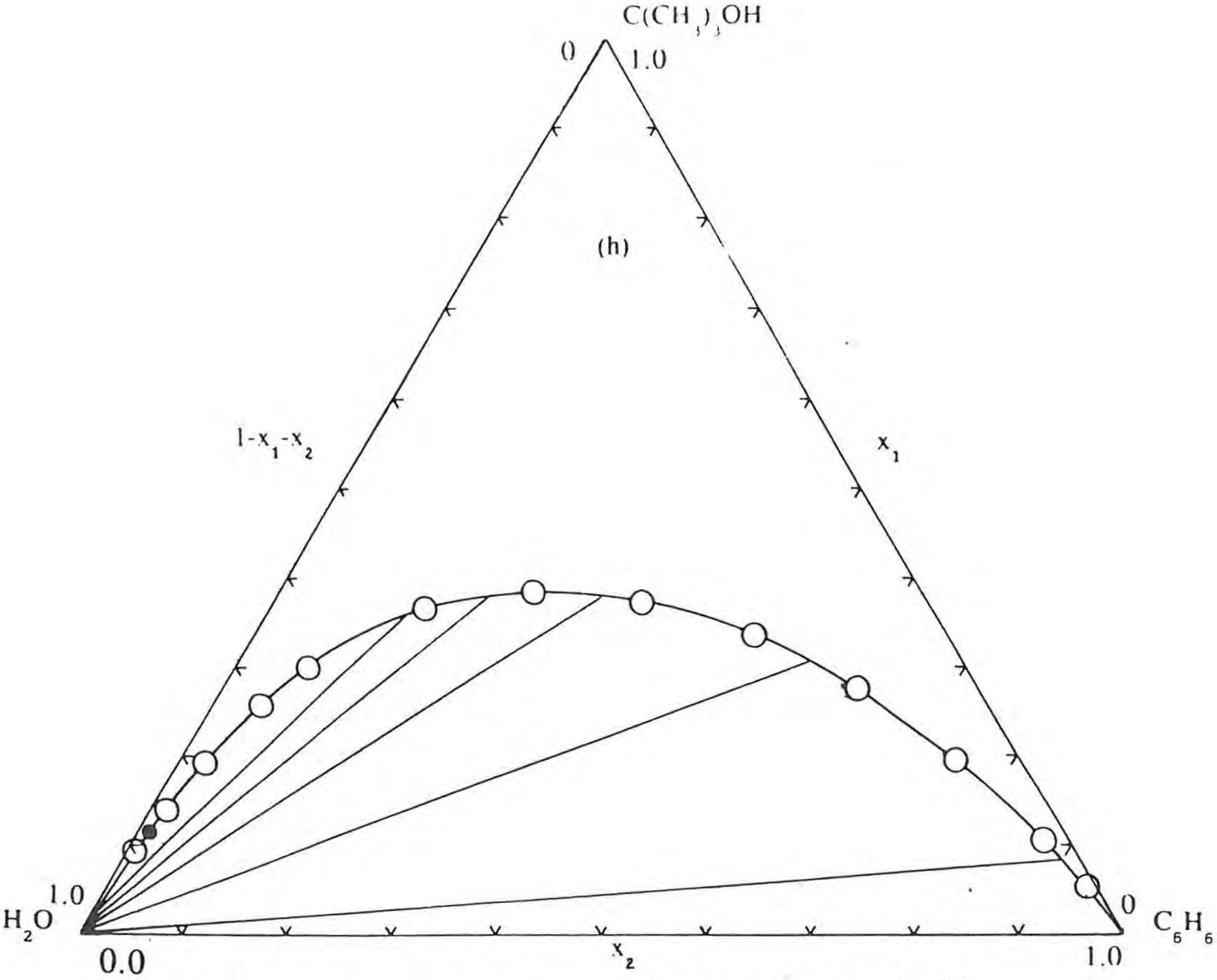
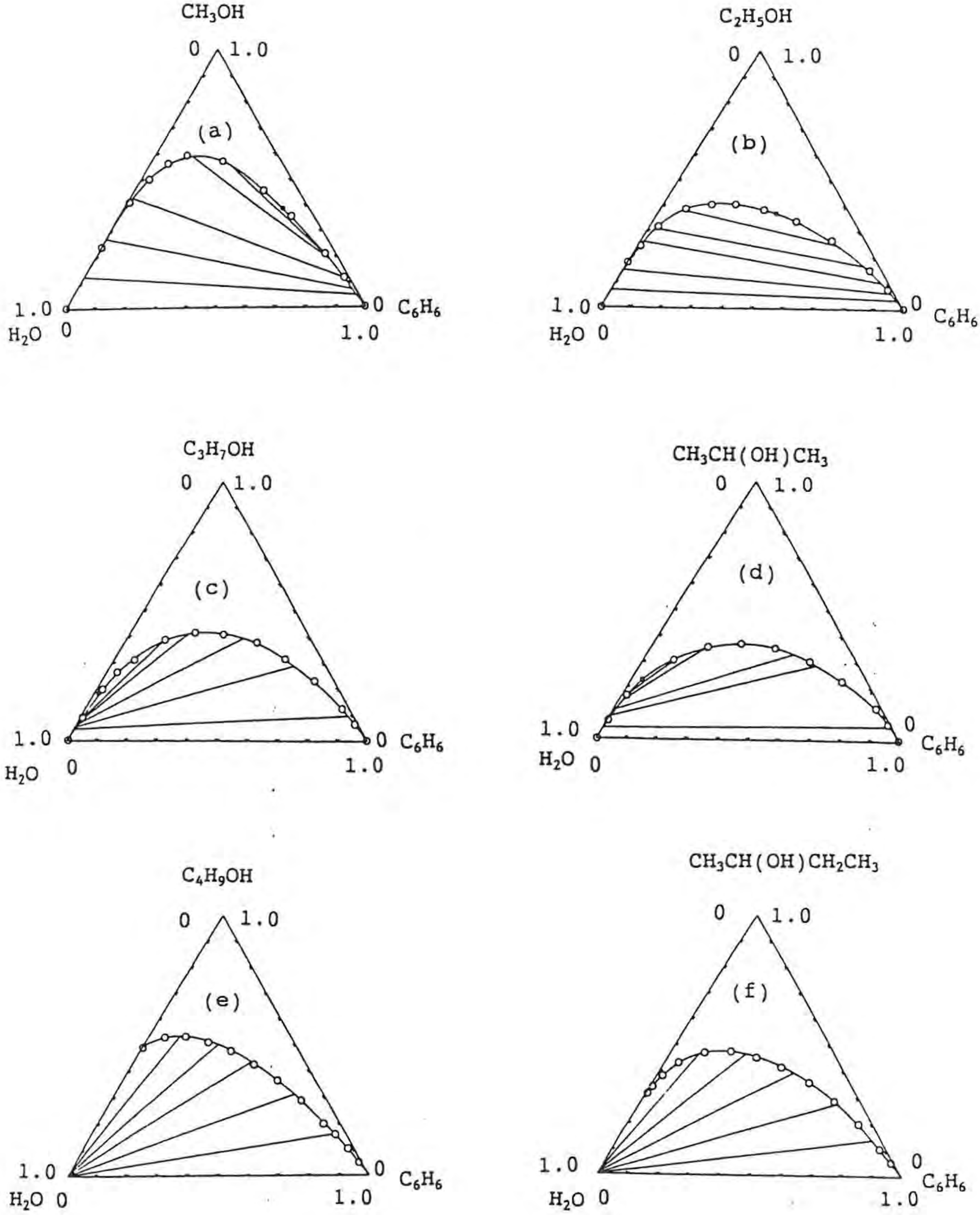


FIGURE 6.4(h) : The t–butanol–benzene–water ternary system in mole fractions at 298.2 K


CH_3OH
0
1.0
(a)
1.0
H_2O
0
0
C_6H_6
1.0
C_2H_5OH
0
1.0
(b)
1.0
H_2O
0
0
C_6H_6
1.0
C_3H_7OH
0
1.0
(c)
1.0
H_2O
0
0
C_6H_6
1.0
$CH_3CH(OH)CH_3$
0
1.0
(d)
1.0
H_2O
0
0
C_6H_6
1.0
C_4H_9OH
0
1.0
(e)
1.0
H_2O
0
0
C_6H_6
1.0
$CH_3CH(OH)CH_2CH_3$
0
1.0
(f)
1.0
H_2O
0
0
C_6H_6
1.0

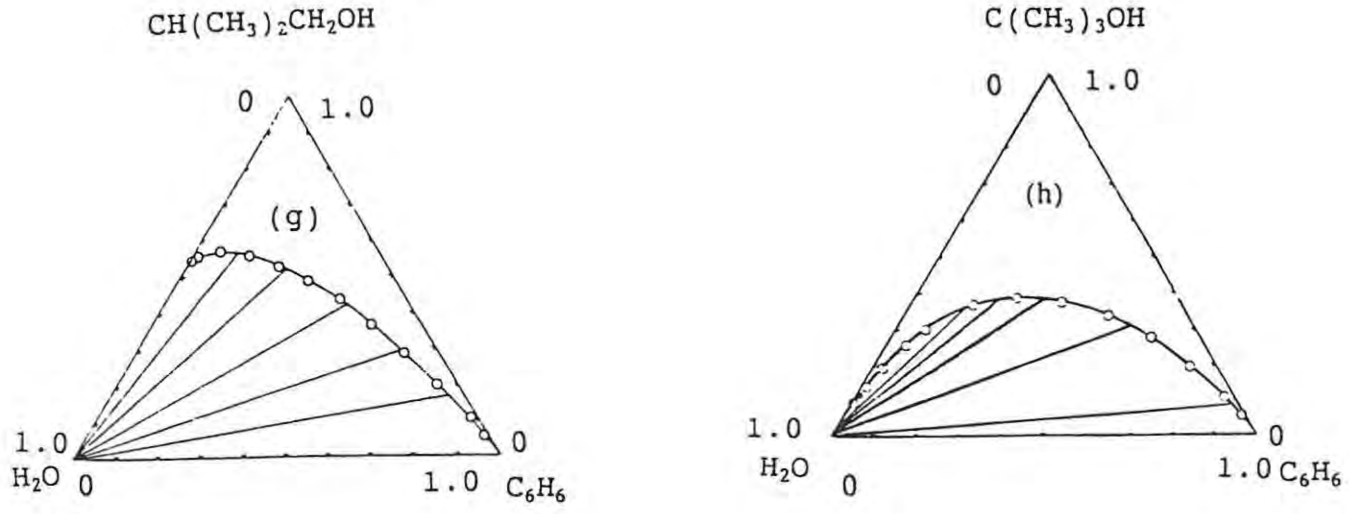


FIGURE 6.4(a–h) : Summary of liquid–liquid equilibrium curves and tielines for $\{x_1C_mH_{2m+1}OH + x_2C_6H_6 + (1-x_1-x_2)H_2O\}$ at 298.2 K.

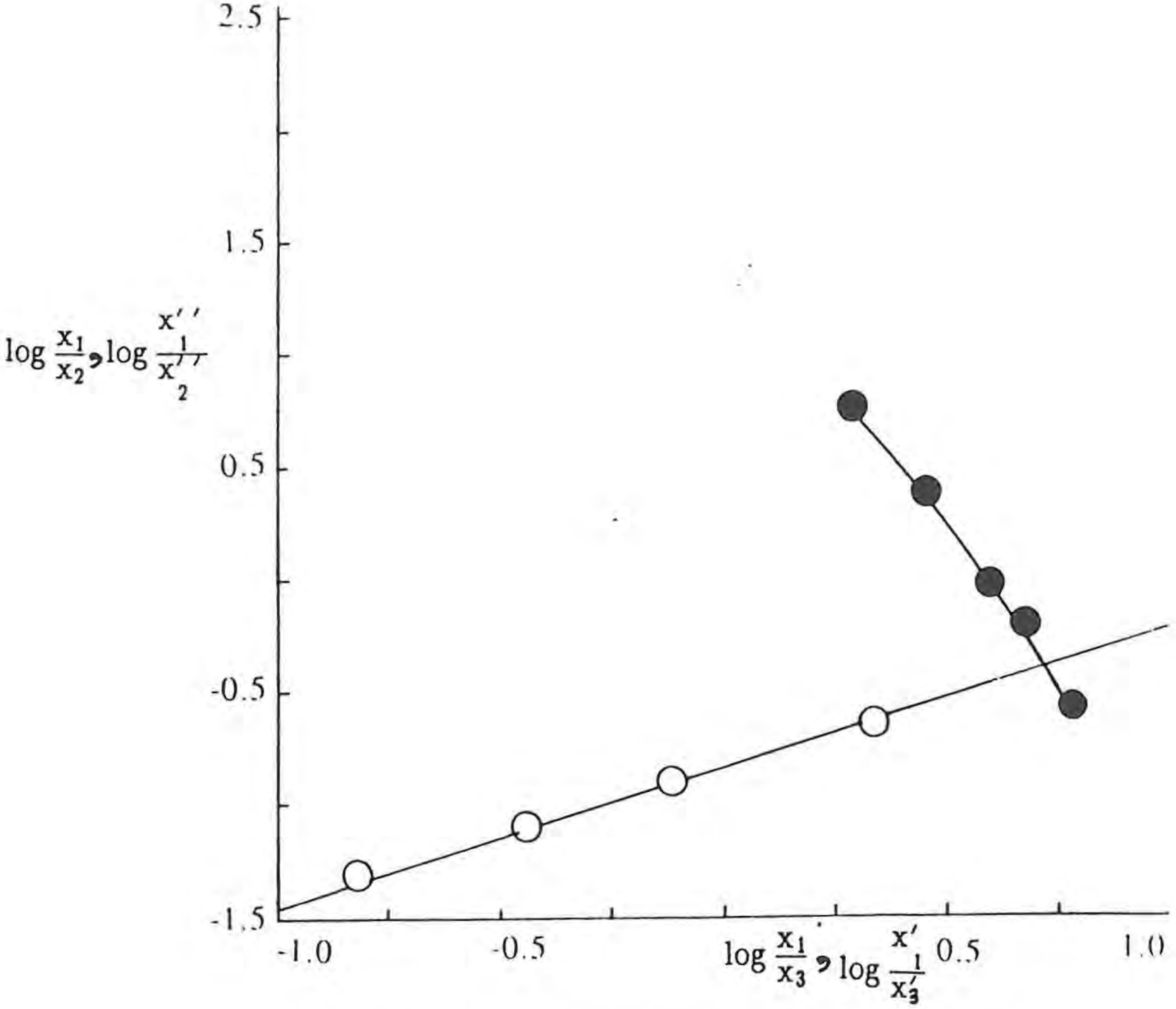


FIGURE 6.4(i) : Determination of plait point {Treybal method} : The methanol—benzene—water ternary system.

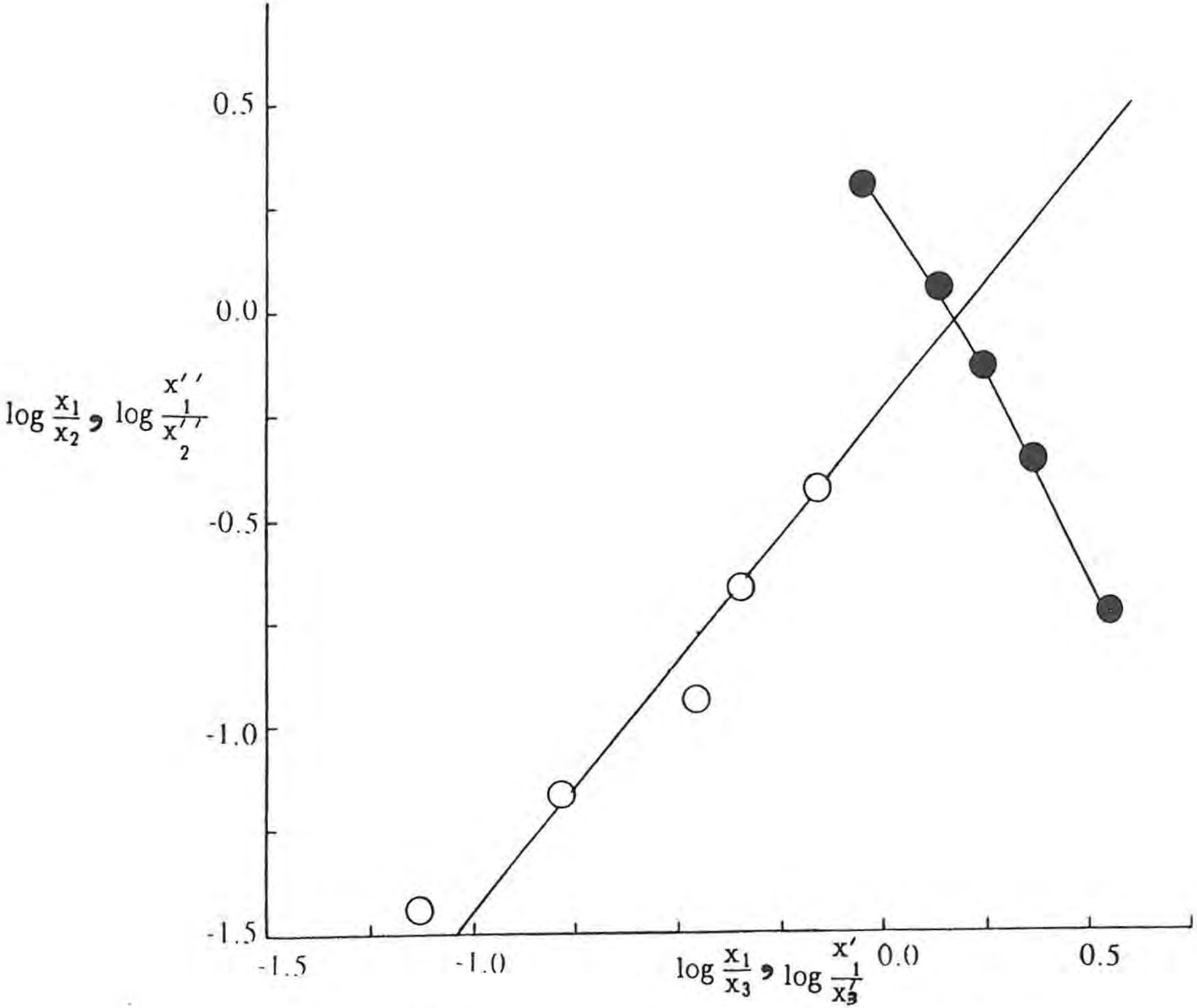


FIGURE 6.4(j) : Determination of plait point {Treybal method} : The ethanol—benzene—water ternary system.

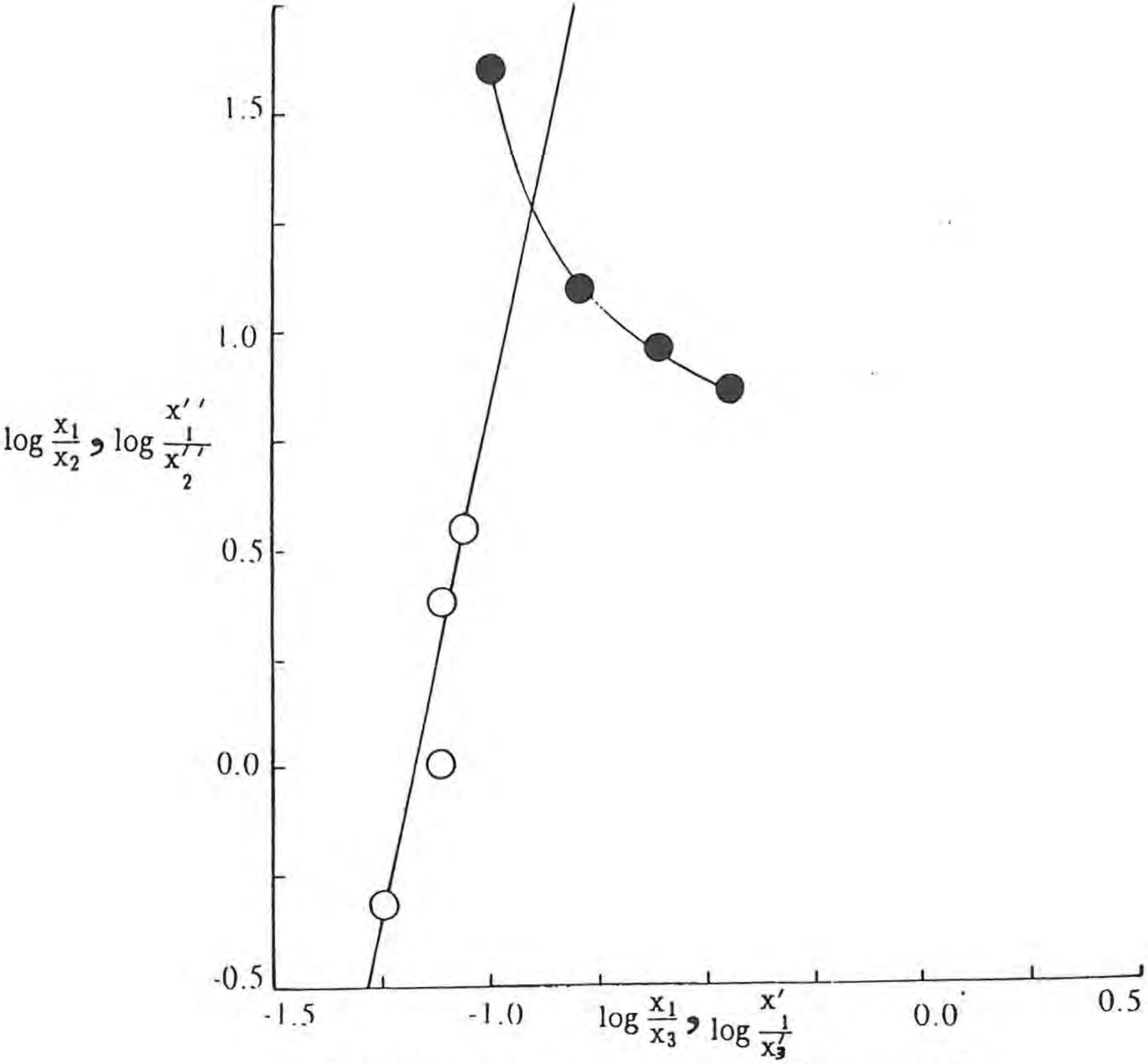


FIGURE 6.4(k) : **Determination of plait point {Treybal method} : The 1–propanol–benzene–water ternary system.**

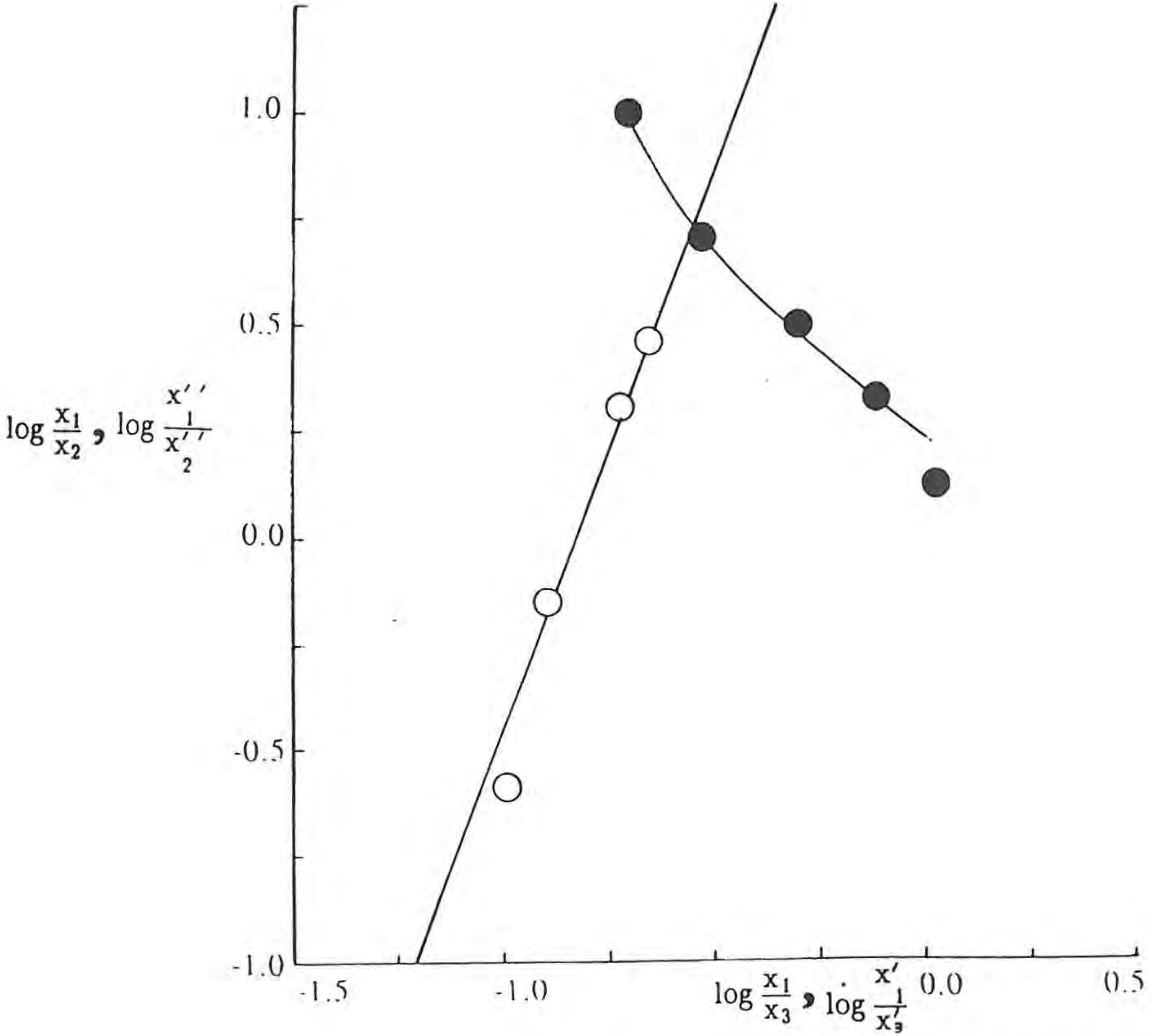


FIGURE 6.4(l) : **Determination of plait point {Treybal method} : The 2–propanol–benzene–water ternary system.**

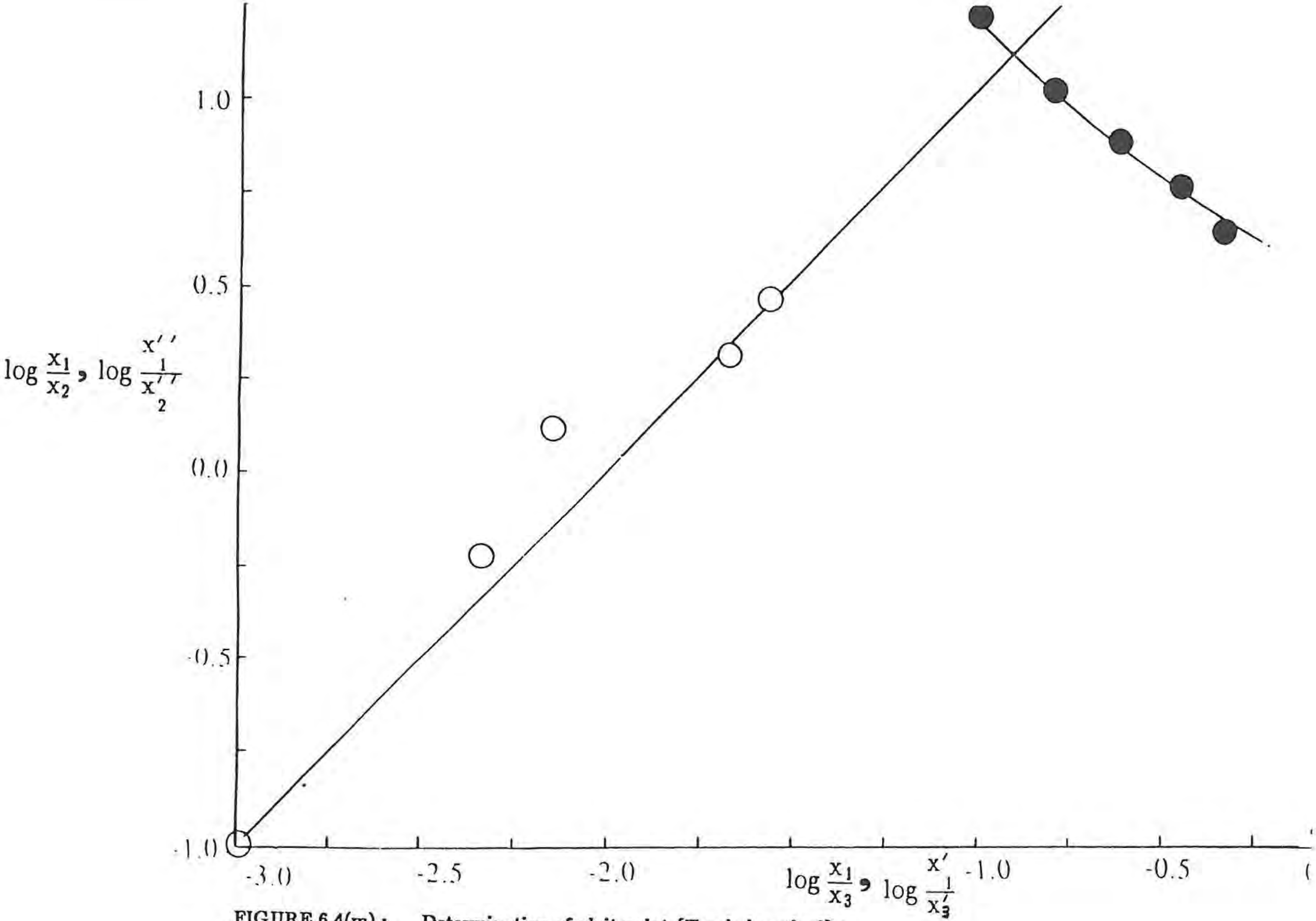


FIGURE 6.4(m) : **Determination of plait point {Treybal method} : The t–butanol–benzene–water ternary system.**

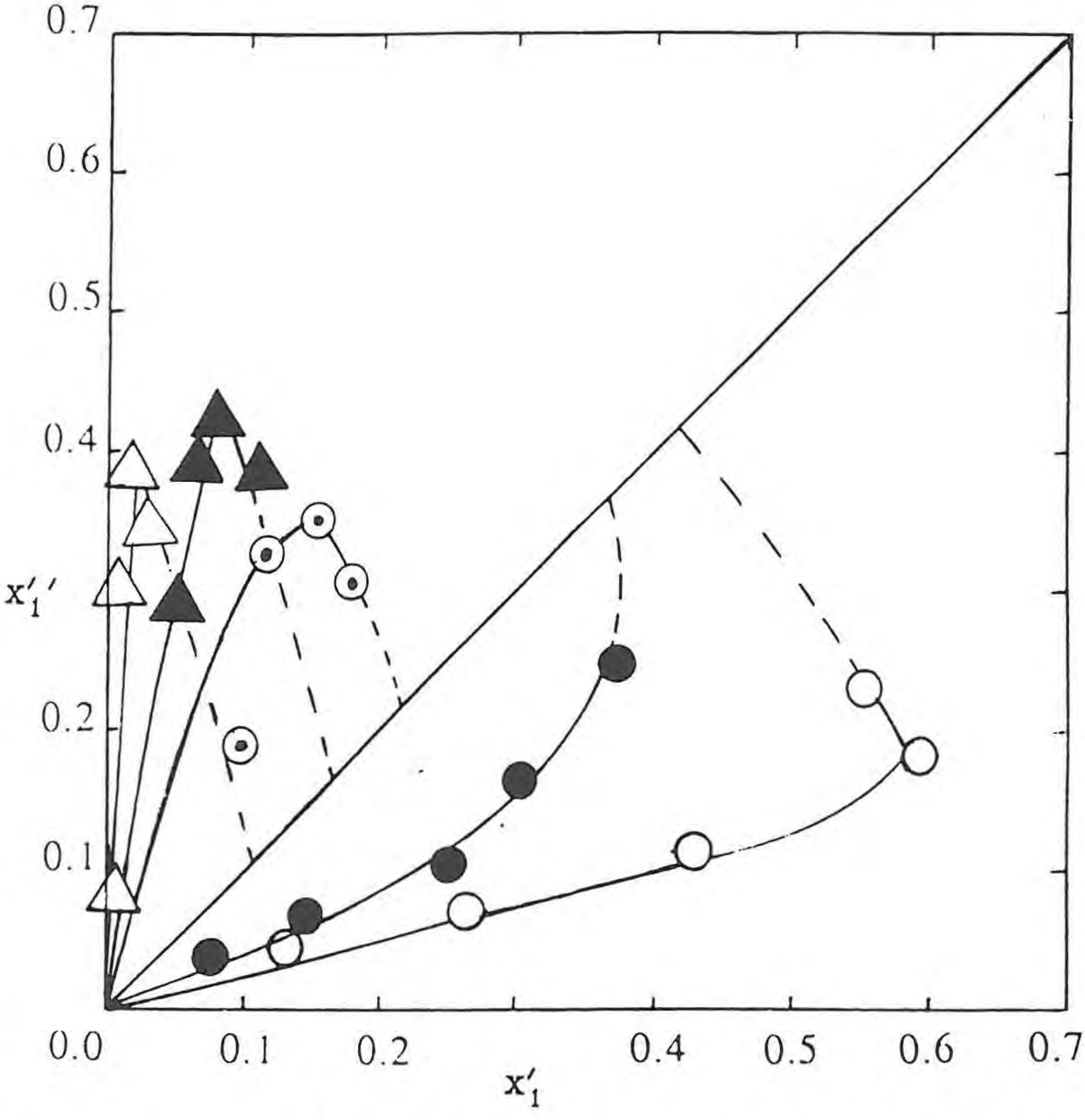


FIGURE 6.4(n) : A plot of x_1'' against x_1', showing the relative solubilities of the alkanol in the benzene–rich and water–rich layers.

○, CH_3OH; ●, C_2H_5OH; ▲, C_3H_7OH; ⊙, $CH_3CH(OH)CH_3$; △, $C(CH_3)_3OH$.

6.5 : THE ALCOHOL–CYCLOHEXANE–WATER TERNARY SYSTEM, AT 298.2K.

TABLE 6.5(a): The composition of points on the coexistence curve for mixtures $\{x_1C_mH_{2m+1}OH + x_2C_6H_{12} + (1 - x_1 - x_2)H_20\}$ where x_1 and x_2 refer to mole fractions.

CH_3OH		C_2H_5OH		C_3H_7OH		$CH_3CH(OH)CH_3$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.212	0.001	0.144	0.001	0.070	0.001	0.140	0.004
0.360	0.002	0.207	0.001	0.113	0.004	0.198	0.011
0.457	0.003	0.280	0.004	0.165	0.011	0.275	0.026
0.565	0.006	0.366	0.010	0.229	0.020	0.315	0.049
0.682	0.016	0.466	0.024	0.347	0.060	0.365	0.096
0.780	0.029	0.495	0.030	0.412	0.116	0.392	0.183
0.845	0.080	0.597	0.083	0.440	0.205	0.394	0.280
0.842	0.136	0.621	0.146	0.430	0.300	0.370	0.396
0.825	0.175	0.607	0.215	0.393	0.413	0.320	0.534
0.093	0.907	0.560	0.307	0.330	0.542	0.240	0.688
0.000	0.999	0.492	0.404	0.246	0.688	0.131	0.846
		0.406	0.518	0.132	0.847	0.068	0.923
		0.298	0.655	0.068	0.922	0.000	0.999
		0.165	0.815	0.000	0.999		
		0.088	0.903				
		0.000	0.999				

C_4H_9OH		$CH_3CH(OH)CH_2CH_3$		$CH(CH_3)_2CH_2OH$		$C(CH_3)_3OH$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.019	0.000	0.051	0.000	0.021	0.000	0.115	0.006
0.488	0.000	0.312	0.000	0.546	0.000	0.138	0.009
0.502	0.014	0.360	0.006	0.555	0.009	0.192	0.017
0.546	0.120	0.391	0.013	0.574	0.042	0.259	0.031
0.530	0.201	0.445	0.038	0.579	0.127	0.361	0.080
0.493	0.289	0.500	0.110	0.558	0.211	0.416	0.157
0.444	0.392	0.504	0.191	0.517	0.304	0.429	0.252
0.375	0.501	0.482	0.284	0.460	0.405	0.411	0.362
0.300	0.620	0.438	0.386	0.389	0.513	0.364	0.481
0.212	0.746	0.377	0.498	0.306	0.629	0.297	0.612
0.110	0.871	0.302	0.621	0.213	0.752	0.212	0.744
0.056	0.934	0.212	0.746	0.110	0.874	0.110	0.873
0.000	0.999	0.111	0.875	0.055	0.937	0.056	0.938
		0.055	0.935	0.000	0.999	0.000	0.999
		0.000	0.999				

TABLE 6.5(b): The composition of conjugate phases x_1', x_2', x_1'' and x_2'' for $\{x_1C_mH_{2m+1}OH + x_2C_6H_{12} + (1-x_1-x_2)H_2O\}$.

CH_3OH				C_2H_5OH			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.323	0.001	0.025	0.974	0.282	0.004	0.008	0.990
0.533	0.005	0.051	0.949	0.374	0.012	0.015	0.982
0.737	0.023	0.074	0.926	0.469	0.025	0.028	0.970
				0.560	0.059	0.061	0.930
				0.621	0.145	0.137	0.845
				0.591	0.249	0.200	0.770

C_3H_7OH				$CH_3CH(OH)CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.061	0.001	0.371	0.460	0.141	0.004	0.141	0.830
0.092	0.003	0.429	0.300	0.202	0.012	0.203	0.746
0.100	0.004	0.440	0.218	0.245	0.021	0.247	0.680
0.121	0.006	0.426	0.140	0.290	0.032	0.292	0.592
0.160	0.010	0.360	0.062	0.354	0.089	0.359	0.435
				0.376	0.120	0.382	0.362

C_4H_9OH				$CH_3CH(OH)CH_2CH_3$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.019	0.000	0.488	0.000	0.051	0.000	0.312	0.000
0.016	0.000	0.530	0.050	0.042	0.000	0.445	0.040
0.014	0.000	0.542	0.110	0.030	0.000	0.495	0.241
0.009	0.000	0.431	0.409	0.025	0.000	0.416	0.428
0.005	0.000	0.300	0.615	0.018	0.000	0.280	0.650

$CH(CH_3)_2CH_2OH$				$C(CH)_3OH$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.021	0.000	0.546	0.000	0.060	0.003	0.342	0.528
0.018	0.000	0.580	0.086	0.072	0.003	0.405	0.373
0.014	0.000	0.467	0.395	0.080	0.004	0.429	0.240
0.007	0.000	0.330	0.592	0.090	0.005	0.396	0.121
				0.120	0.007	0.275	0.038

TABLE 6.5(c): The coefficients A_i, B_i and C_i in equations (4.1). (4.2) and (4.3) respectively.for $\{x_1C_mH_{2m+1}OH + x_2C_6H_{12} + (1 - x_1 - x_2)H_2O\}$ together with the standard deviation σ. The standard errors are given in parenthesis.

<table>
<tr><th colspan="3">CH_3OH</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = 1.5677$ (0.22)
$A_2 = 0.6750$ (0.31)
$A_3 = 6.4140$ (0.71)
$\sigma = 0.030$</td><td>$B_1 = 5.2462$ (0.31)
$B_2 = 1.2801$ (0.03)
$B_3 = 1.4031$ (0.04)
$\sigma = 0.055$</td><td>$C_1 = 4.7025$ (0.33)
$C_2 = 1.2452$ (0.03)
$C_3 = 1.8745$ (0.06)
$\sigma = 0.073$</td></tr>
<tr><th colspan="3">CH_2H_5OH</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = 0.3317$ (0.12)
$A_2 = 0.7951$ (0.13)
$A_3 = 3.9594$ (0.35)
$\sigma = 0.045$</td><td>$B_1 = 2.8685$ (0.16)
$B_2 = 1.1868$ (0.03)
$B_3 = 1.0982$ (0.03)
$\sigma = 0.031$</td><td>$C_1 = 2.5705$ (0.11)
$C_2 = 1.1466$ (0.02)
$C_3 = 1.5229$ (0.03)
$\sigma = 0.026$</td></tr>
<tr><th colspan="3">C_3H_7OH</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -0.2181$ (0.07)
$A_2 = 0.1107$ (0.07)
$A_3 = 1.5927$ (0.19)
$\sigma = 0.029$</td><td>$B_1 = 1.6878$ (0.06)
$B_2 = 1.0150$ (0.02)
$B_3 = 0.9373$ (0.02)
$\sigma = 0.016$</td><td>$C_1 = 1.4968$ (0.03)
$C_2 = 0.9722$ (0.01)
$C_3 = 1.2747$ (0.01)
$\sigma = 0.010$</td></tr>
<tr><th colspan="3">$CH_3CH(OH)CH_3$</th></tr>
<tr><th>Hlavaty</th><th>Beta</th><th>Log–Gamma</th></tr>
<tr><td>$A_1 = -0.5225$ (0.06)
$A_2 = -0.1319$ (0.07)
$A_3 = -0.6793$ (0.19)
$\sigma = 0.023$</td><td>$B_1 = 1.3547$ (0.06)
$B_2 = 0.9359$ (0.02)
$B_3 = 0.8194$ (0.02)
$\sigma = 0.018$</td><td>$C_1 = 1.2452$ (0.04)
$C_2 = 0.9070$ (0.02)
$C_3 = 1.1562$ (0.02)
$\sigma = 0.014$</td></tr>
</table>

TABLE 6.5(c) (CONTD.) :

<table>
<tr><td colspan="3">C_4H_9OH</td></tr>
<tr><td>Hlavaty</td><td>Beta</td><td>Log–Gamma</td></tr>
<tr><td>$A_1 = -1.1628$ (0.16)
$A_2 = 0.0885$ (0.12)
$A_3 = 0.5666$ (0.38)
$\sigma = 0.008$</td><td>$B_1 = 2.4075$ (0.19)
$B_2 = 1.1599$ (0.04)
$B_3 = 1.0227$ (0.03)
$\sigma = 0.058$</td><td>$C_1 = 2.0142$ (0.10)
$C_2 = 1.0979$ (0.03)
$C_3 = 1.3547$ (0.03)
$\sigma = 0.034$</td></tr>
<tr><td colspan="3">$CH_3CH(OH)CH_2CH_3$</td></tr>
<tr><td>Hlavaty</td><td>Beta</td><td>Log–Gamma</td></tr>
<tr><td>$A_1 = -0.5152$ (0.10)
$A_2 = 0.1928$ (0.10)
$A_3 = 1.5256$ (0.29)
$\sigma = 0.014$</td><td>$B_1 = 2.1885$ (0.09)
$B_2 = 1.1142$ (0.03)
$B_3 = 0.9871$ (0.03)
$\sigma = 0.047$</td><td>$C_1 = 1.8882$ (0.07)
$C_2 = 1.0624$ (0.02)
$C_3 = 1.3438$ (0.03)
$\sigma = 0.029$</td></tr>
<tr><td colspan="3">$CH(CH_3)_2CH_2OH$</td></tr>
<tr><td>Hlavaty</td><td>Beta</td><td>Log–Gamma</td></tr>
<tr><td>$A_1 = -1.2040$ (0.17)
$A_2 = 0.1512$ (0.12)
$A_3 = 0.7586$ (0.41)
$\sigma = 0.008$</td><td>$B_1 = 2.6645$ (0.19)
$B_2 = 1.1773$ (0.04)
$B_3 = 1.0452$ (0.03)
$\sigma = 0.062$</td><td>$C_1 = 2.2296$ (0.10)
$C_2 = 1.1159$ (0.03)
$C_3 = 1.3855$ (0.03)
$\sigma = 0.036$</td></tr>
<tr><td colspan="3">$C(CH_3)_3OH$</td></tr>
<tr><td>Hlavaty</td><td>Beta</td><td>Log–Gamma</td></tr>
<tr><td>$A_1 = -0.2159$ (0.05)
$A_2 = -0.0243$ (0.05)
$A_3 = 0.4499$ (0.14)
$\sigma = 0.007$</td><td>$B_1 = 1.6048$ (0.05)
$B_2 = 0.9833$ (0.01)
$B_3 = 0.9225$ (0.01)
$\sigma = 0.012$</td><td>$C_1 = 1.4674$ (0.02)
$C_2 = 0.9537$ (0.01)
$C_3 = 1.2722$ (0.01)
$\sigma = 0.006$</td></tr>
</table>

TABLE 6.5(d): Plait points for the alcohol–cyclohexane–water ternary systems, in mole fractions. The plait points have been given in the form (x_1,x_2). where x_1 = mole fractions of alcohol and x_2 = mole fraction of cyclohexane.

System	Plait point
Ethanol	(0.35,0.59)
1–Propanol	(0.20,0.02)
2–Propanol	(0.39,0.24)
t–Butanol	(0.18,0.02)

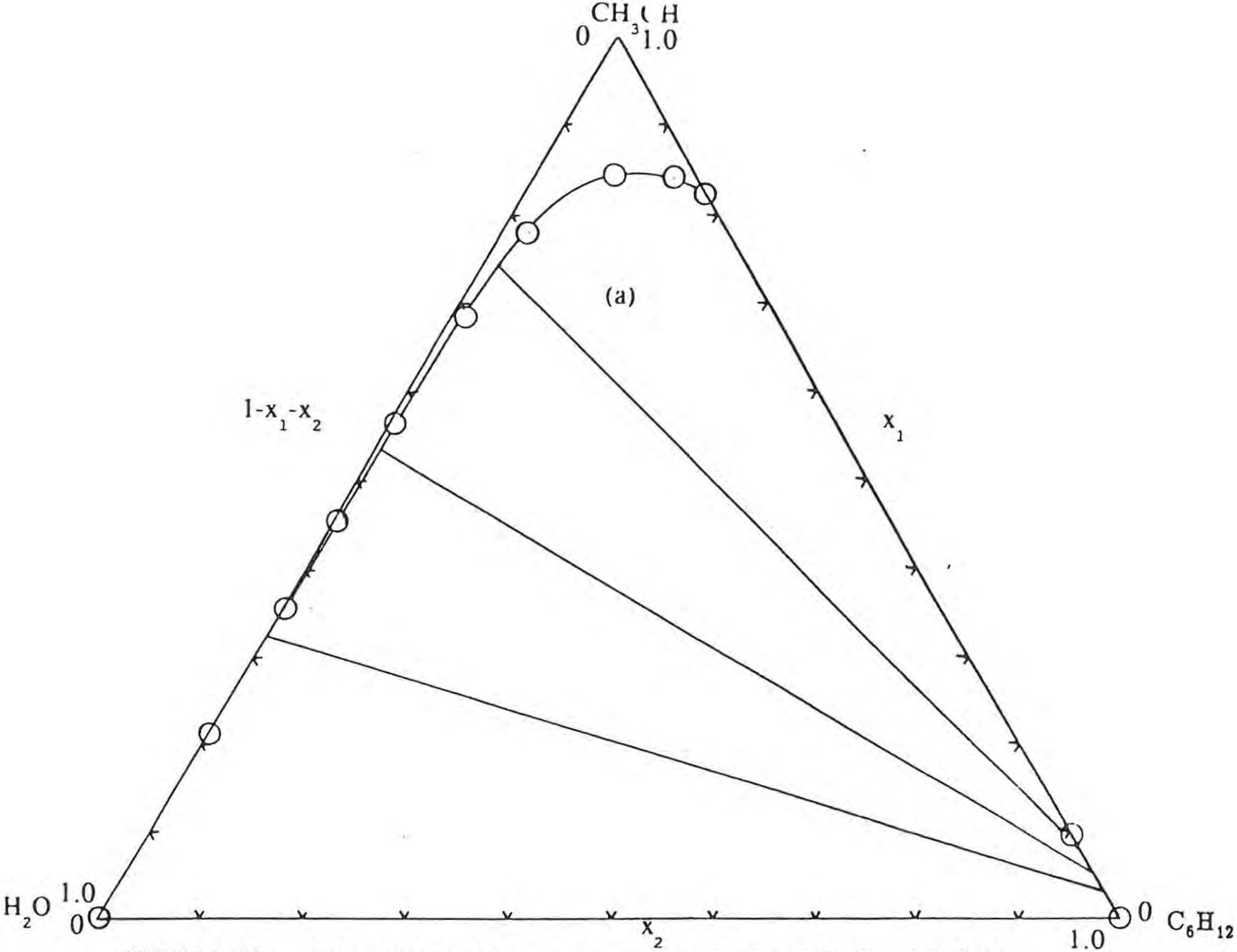


FIGURE 6.5(a) : The methanol—cyclohexane—water ternary system in mole fractions at 298.2 K

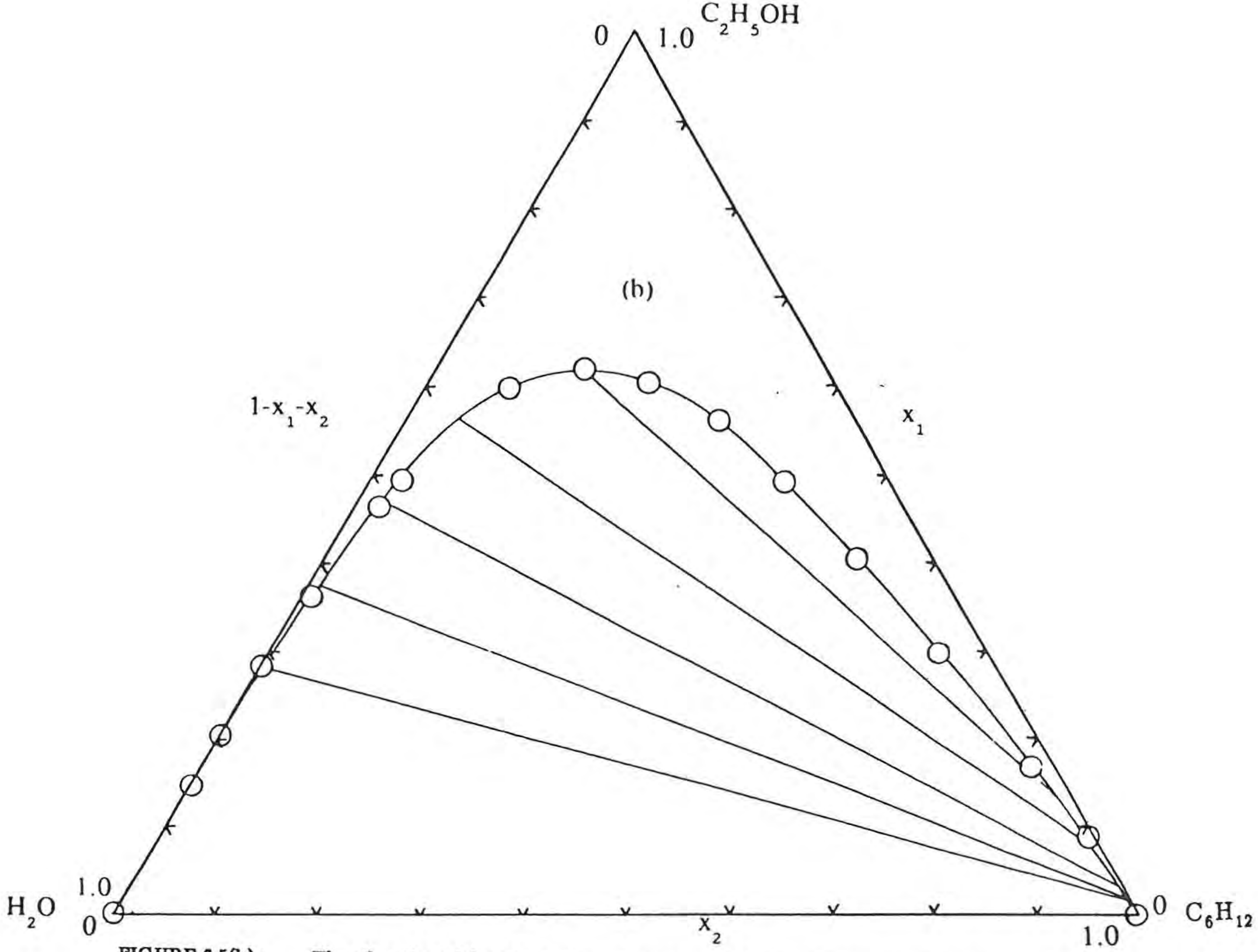


FIGURE 6.5(b) : The ethanol–cyclohexane–water ternary system in mole fractions at 298.2 K

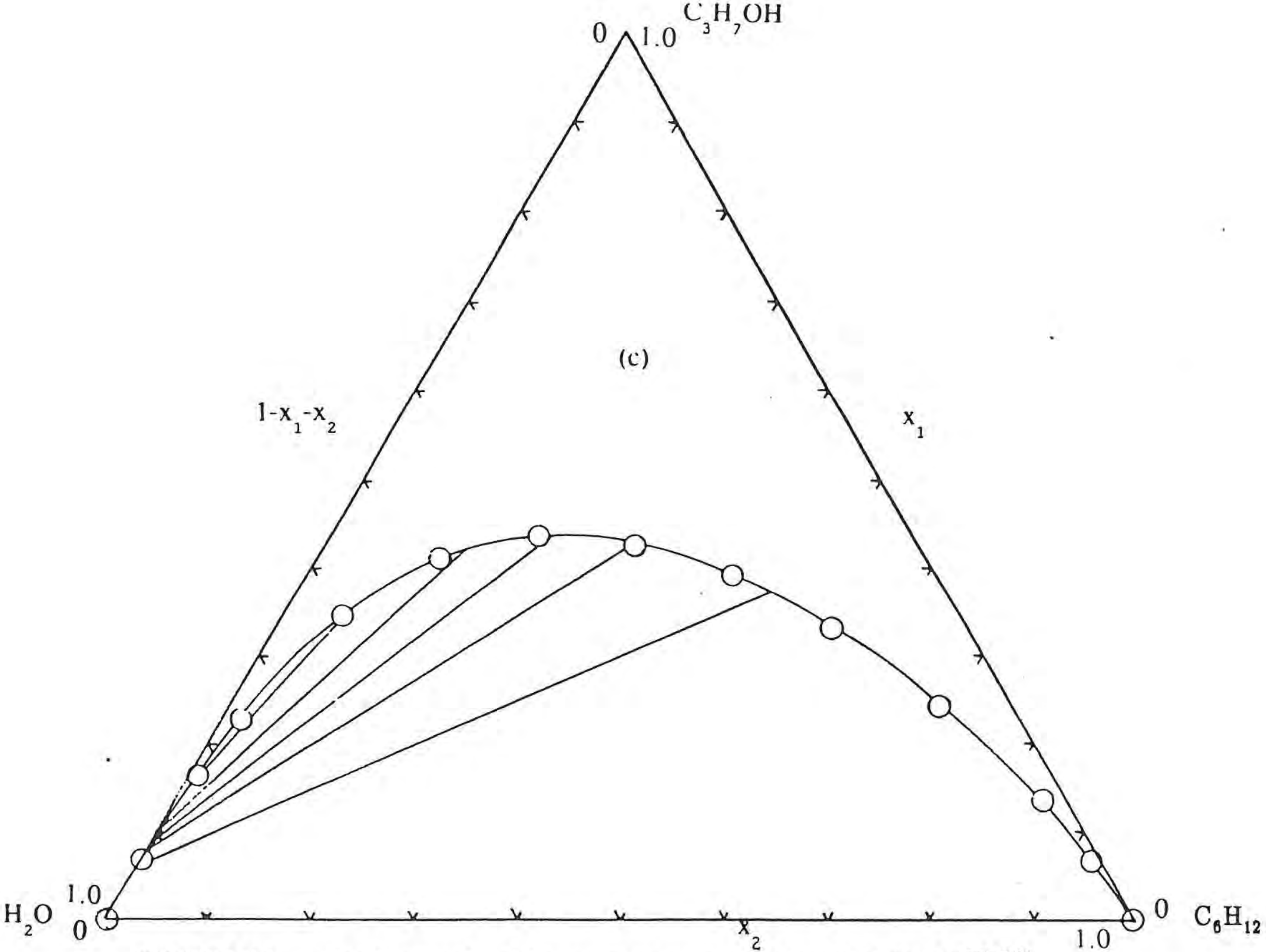


FIGURE 6.5(c) : The 1–propanol–cyclohexane–water ternary system in mole fractions at 298.2 K

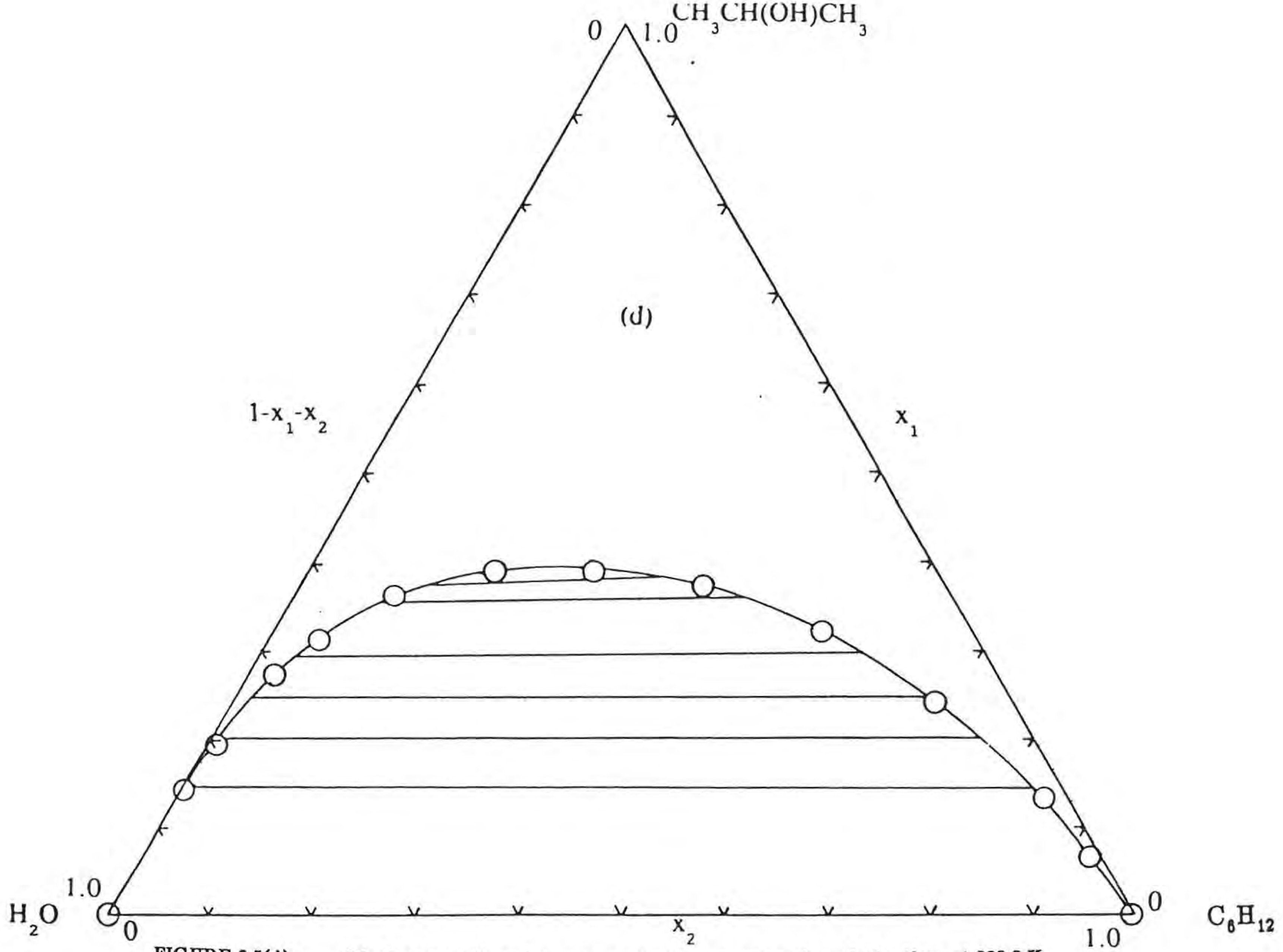


FIGURE 6.5(d) : The 2–propanol–cyclohexane–water ternary system in mole fractions at 298.2 K

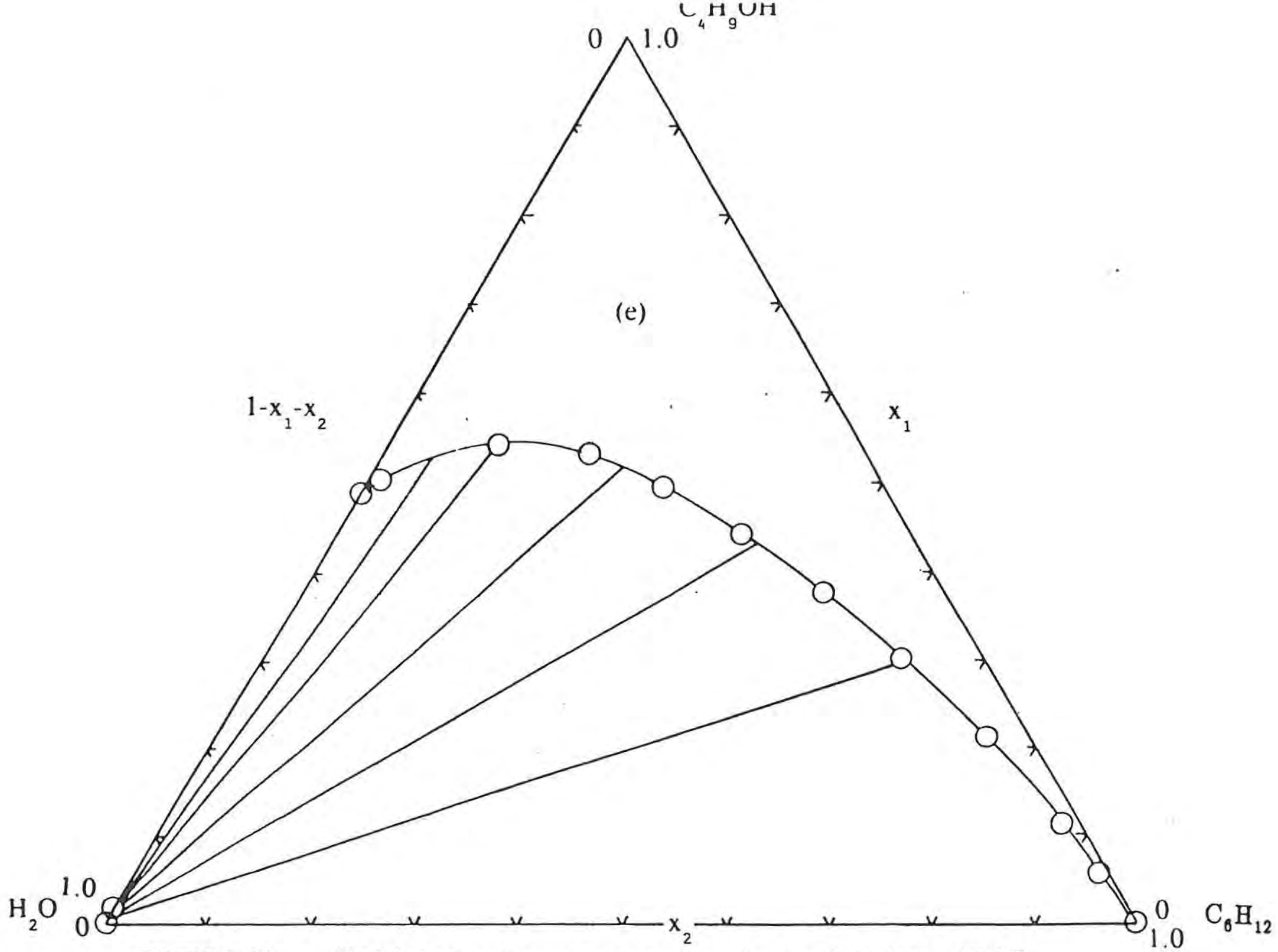


FIGURE 6.5(e) : The 1–butanol–cyclohexane–water ternary system in mole fractions at 298.2 K

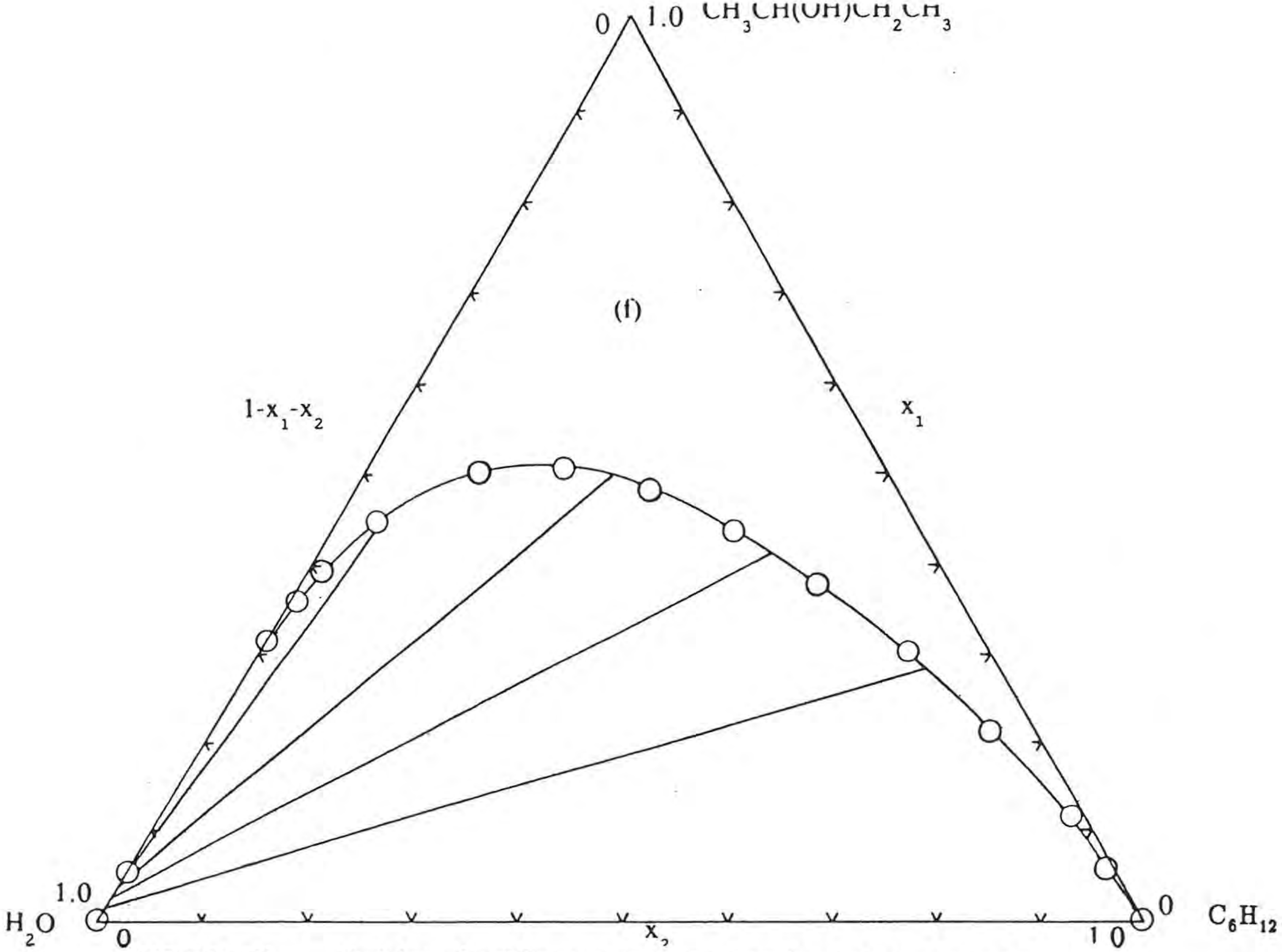


FIGURE 6.5(f) : The 2–butanol–cyclohexane–water ternary system in mole fractions at 298.2 K

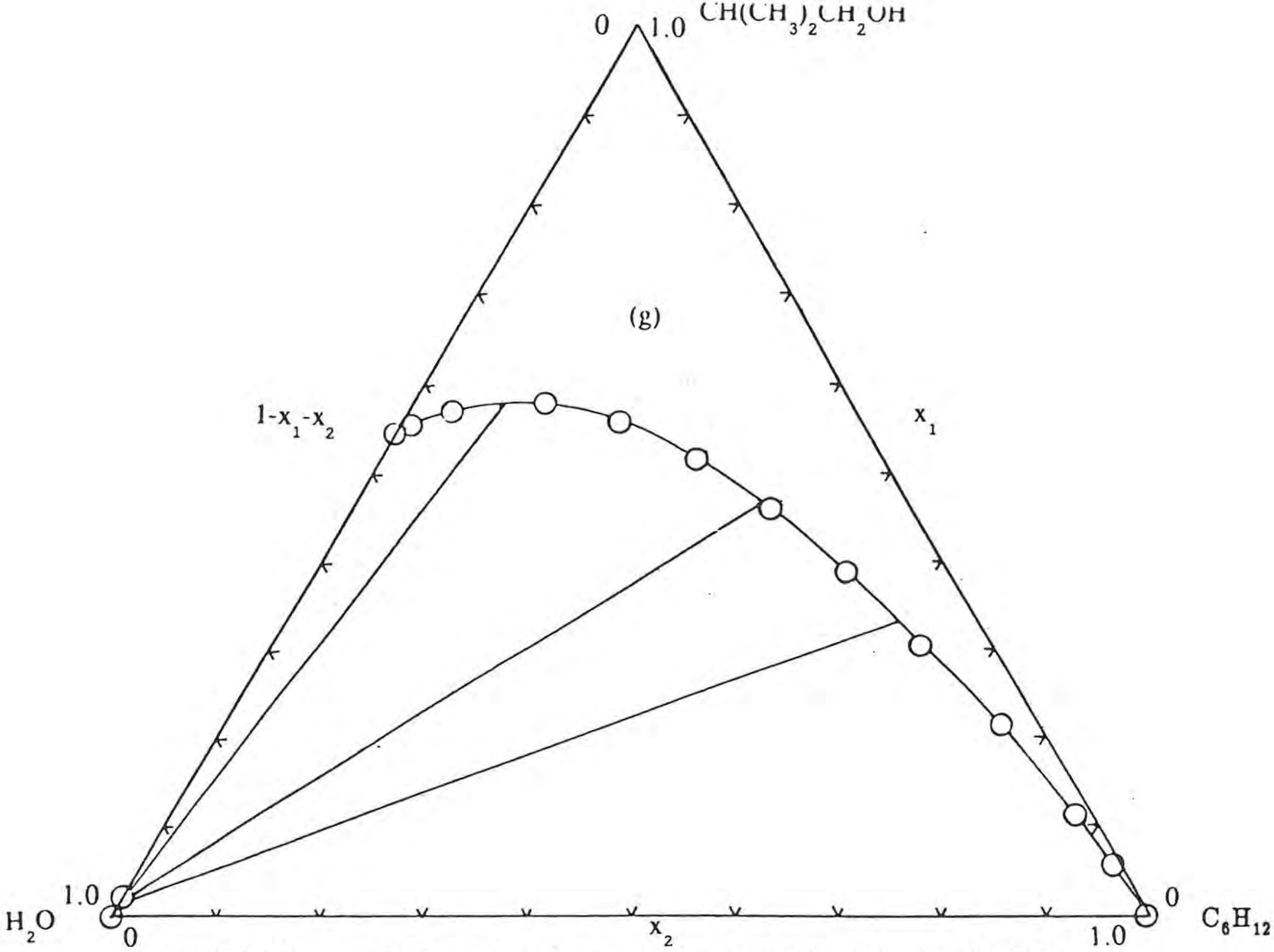


FIGURE 6.5(g) : The i–butanol–cyclohexane–water ternary system in mole fractions at 298.2 K

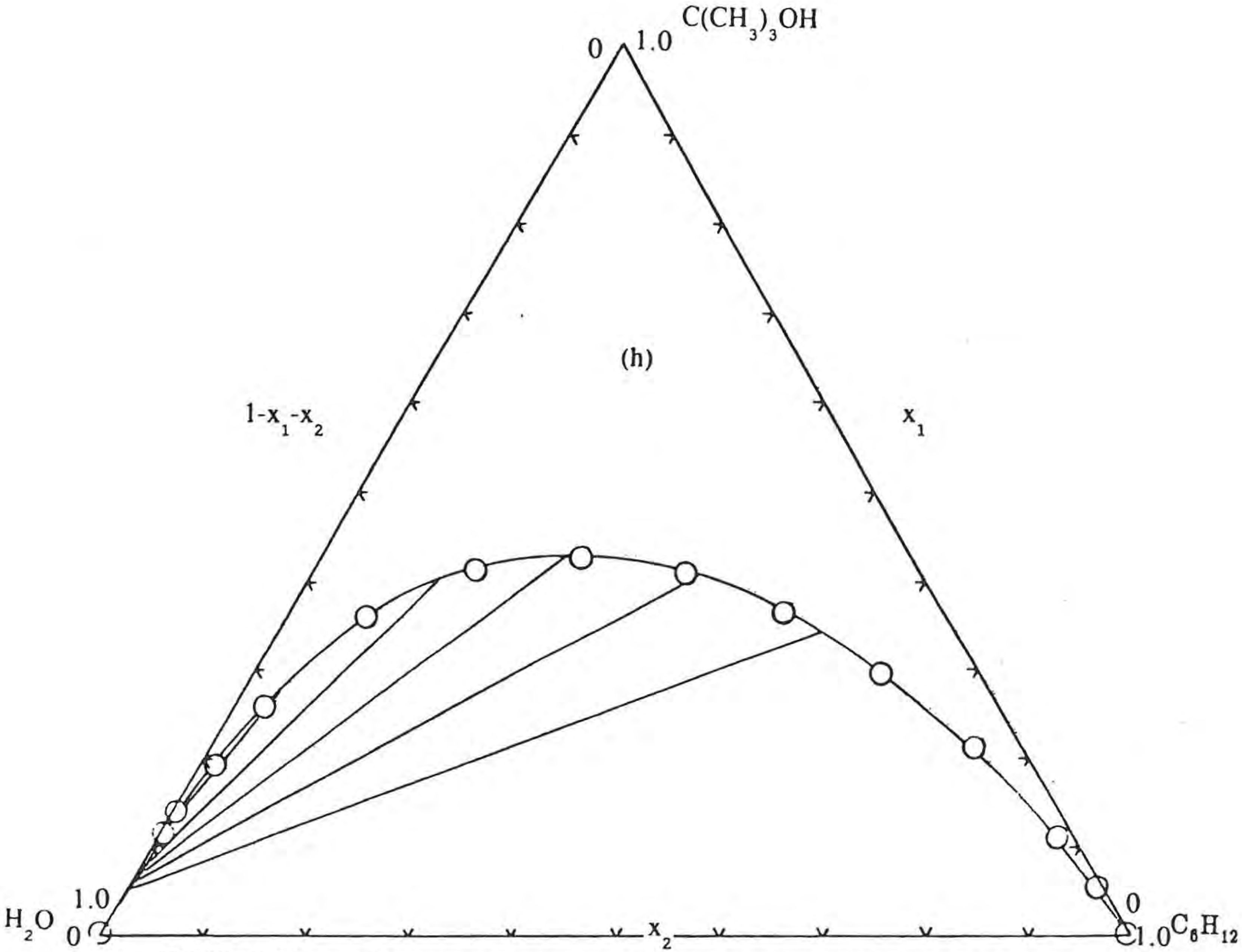
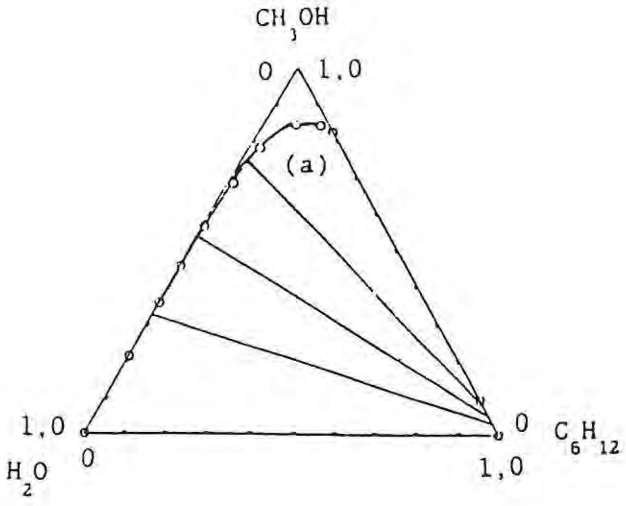
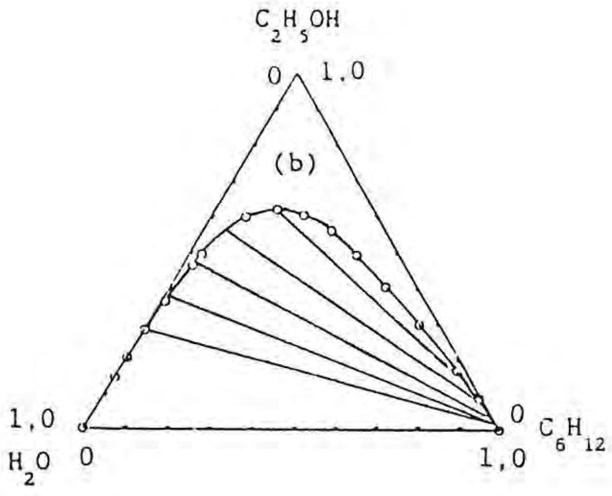
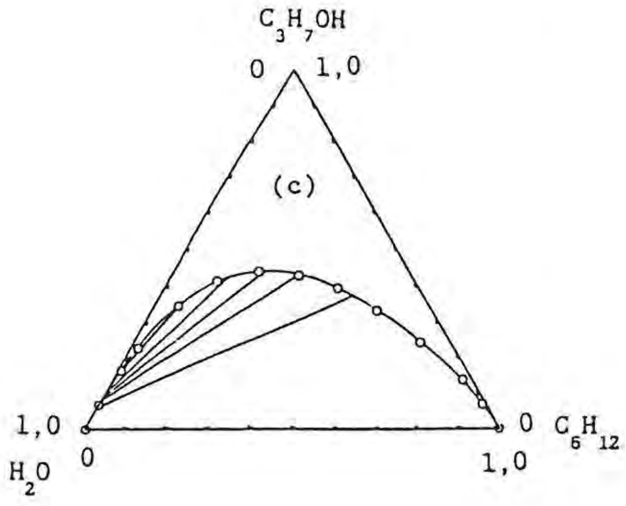
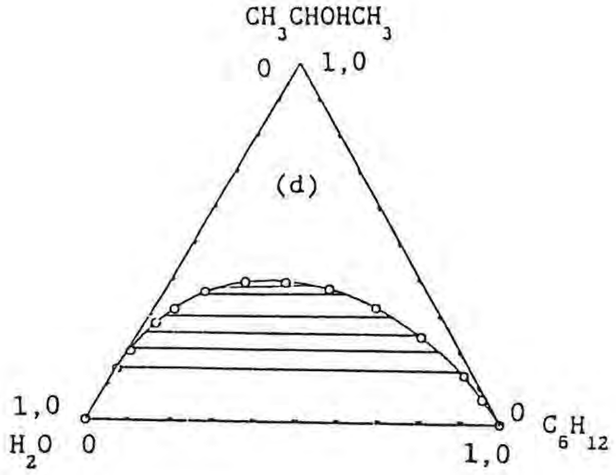


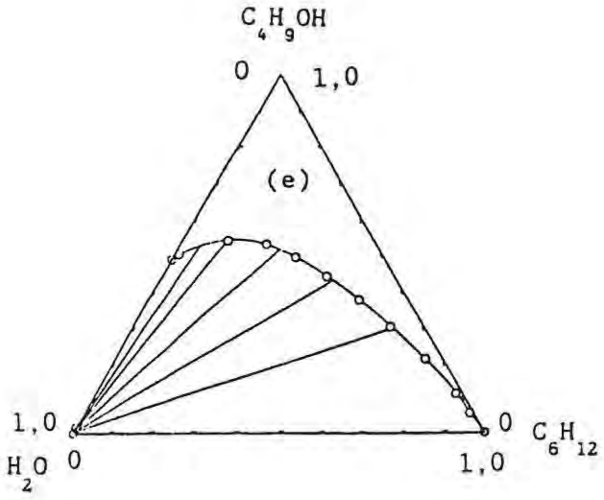
FIGURE 6.5(h) : The t—butanol—cyclohexane—water ternary system in mole fractions at 298.2 K

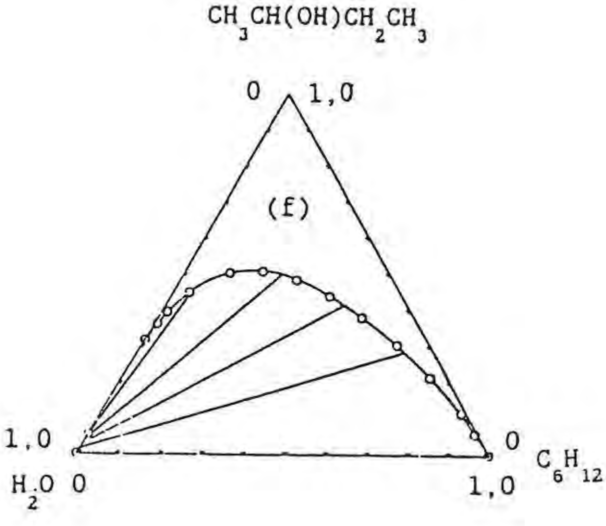

CH_3OH
0
1,0
(a)
1,0
0
H_2O
0
C_6H_{12}
1,0


C_2H_5OH
0
1,0
(b)
1,0
0
H_2O
0
C_6H_{12}
1,0


C_3H_7OH
0
1,0
(c)
1,0
0
H_2O
0
C_6H_{12}
1,0


$CH_3CHOHCH_3$
0
1,0
(d)
1,0
0
H_2O
0
C_6H_{12}
1,0


C_4H_9OH
0
1,0
(e)
1,0
0
H_2O
0
C_6H_{12}
1,0


$CH_3CH(OH)CH_2CH_3$
0
1,0
(f)
1,0
0
H_2O
0
C_6H_{12}
1,0

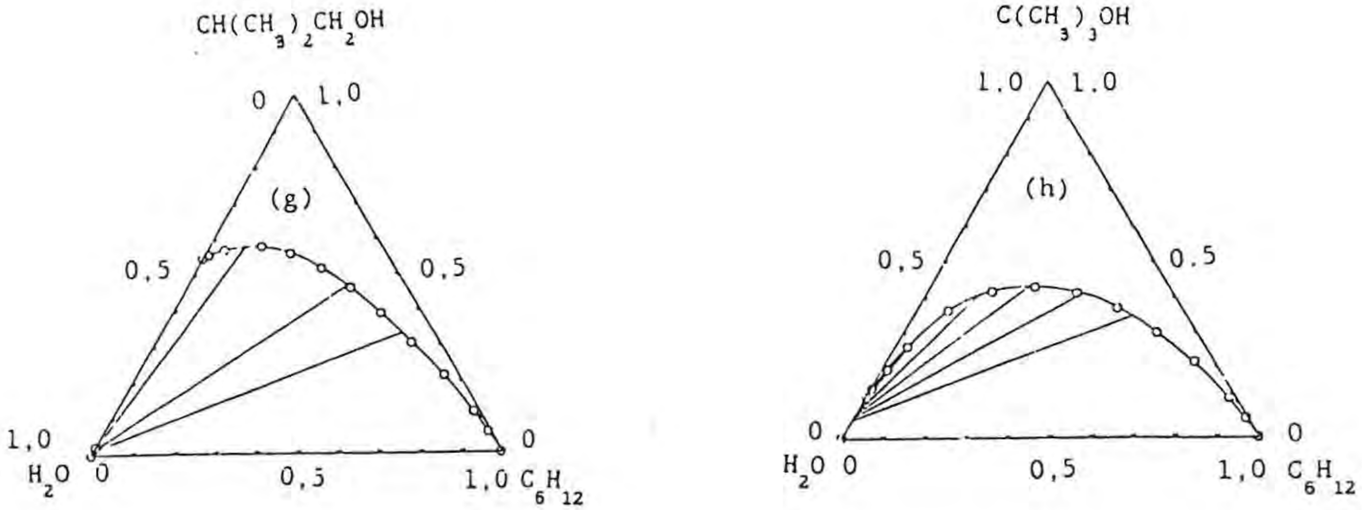


FIGURE 6.5(a–h) : Summary of liquid–liquid equilibrium curves and tielines for $\{x_1C_mH_{2m+1}OH + x_2C_6H_{12} + (1-x_1-x_2)H_2O\}$ at 298.2 K.

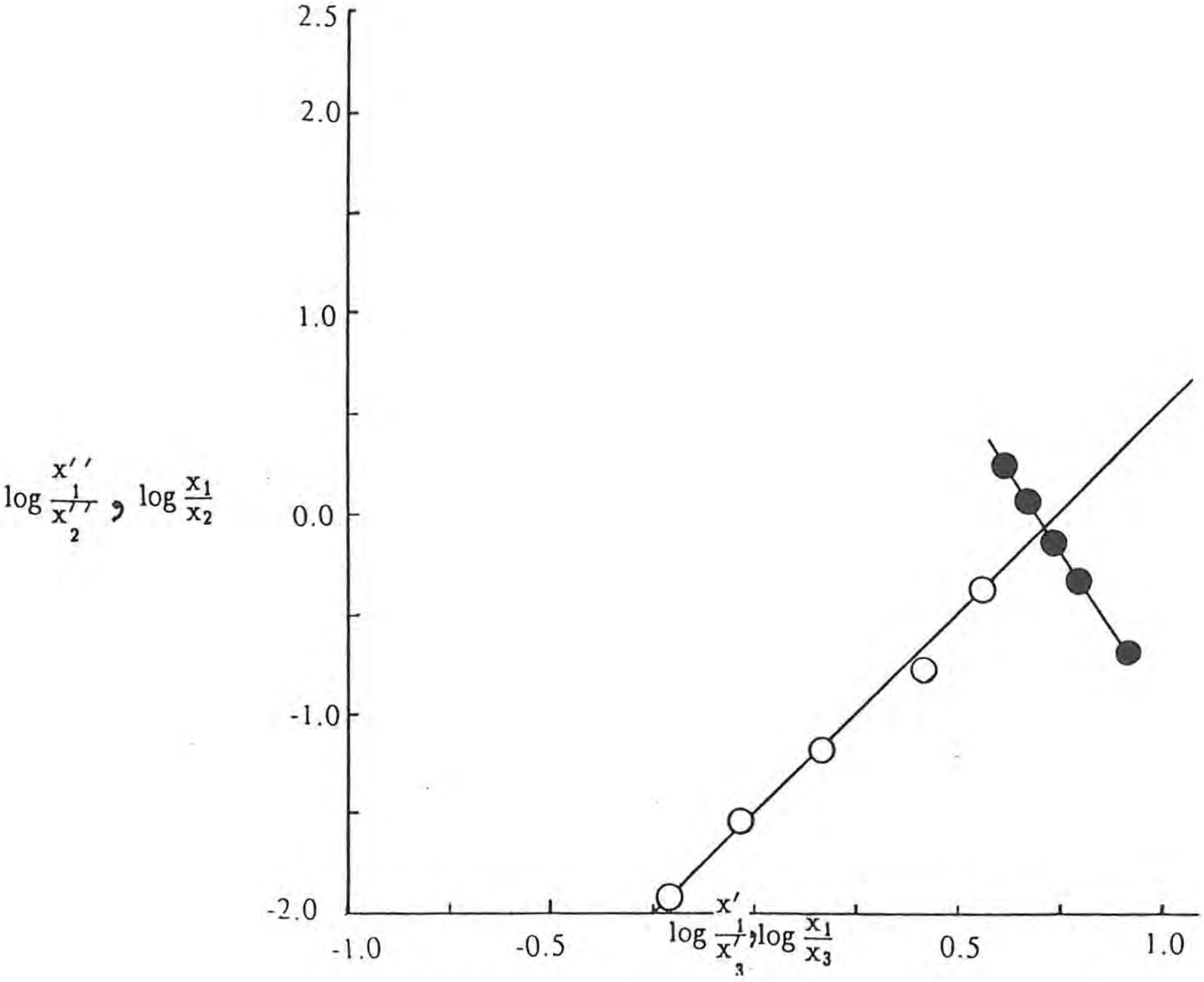


FIGURE 6.5(i) : Determination of plait point {Treybal method} : The ethanol–cyclohexane–water ternary system.

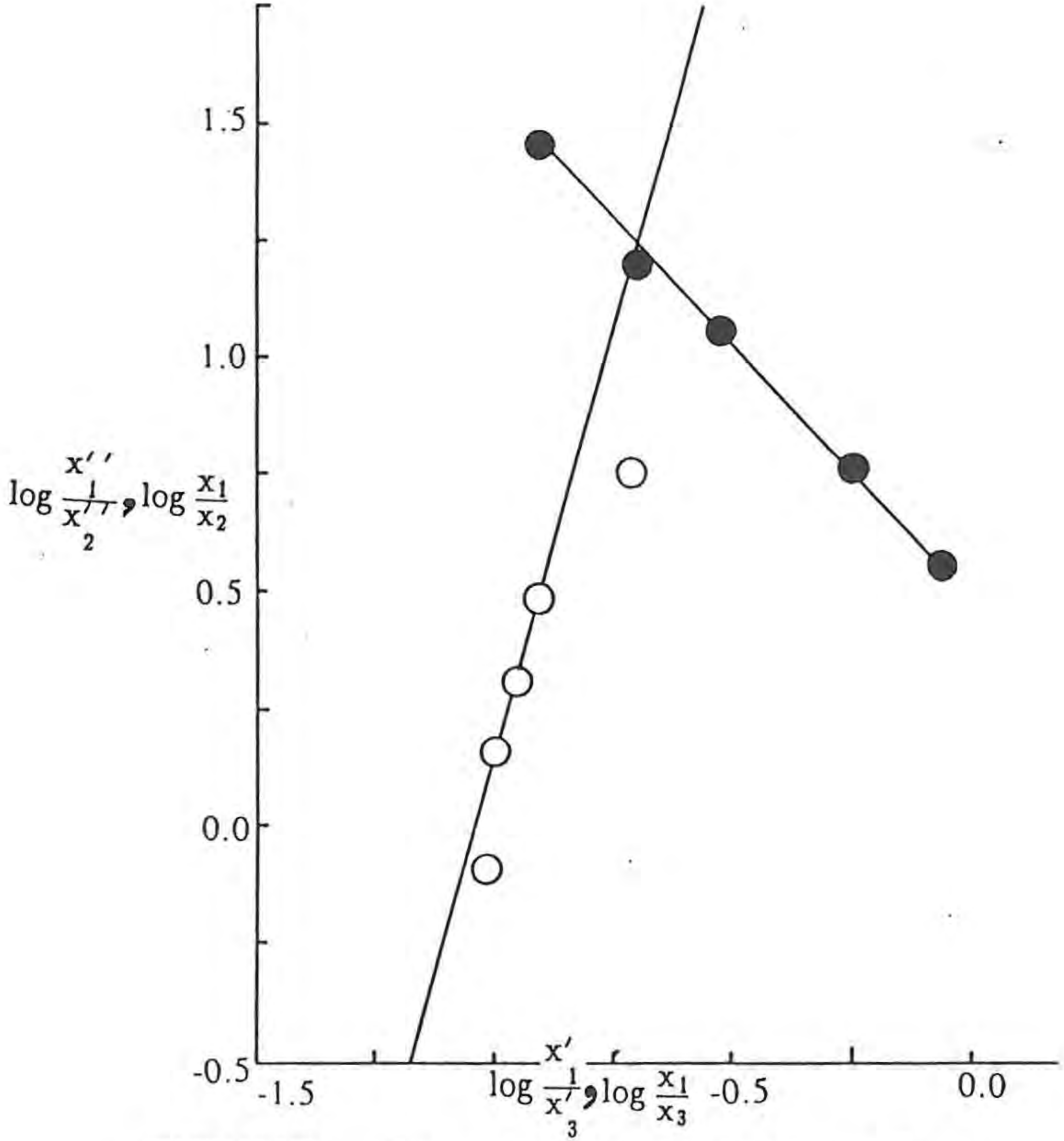


FIGURE 6.5(j) : **Determination of plait point {Treybal method} : The 1–propanol–cyclohexane–water ternary system.**

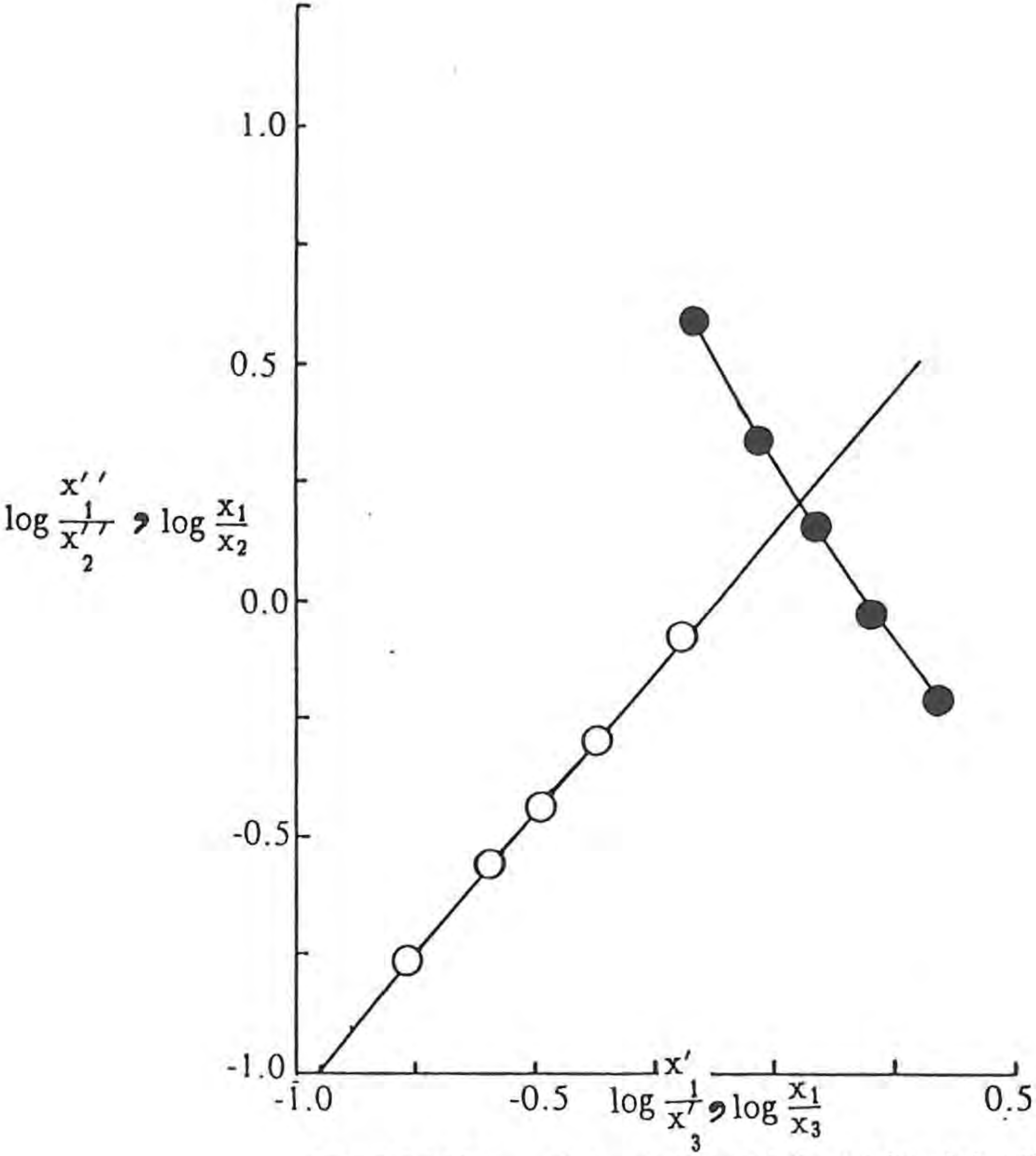


FIGURE 6.5(k) : Determination of plait point {Treybal method} : The 2–propanol–cyclohexane–water ternary system.

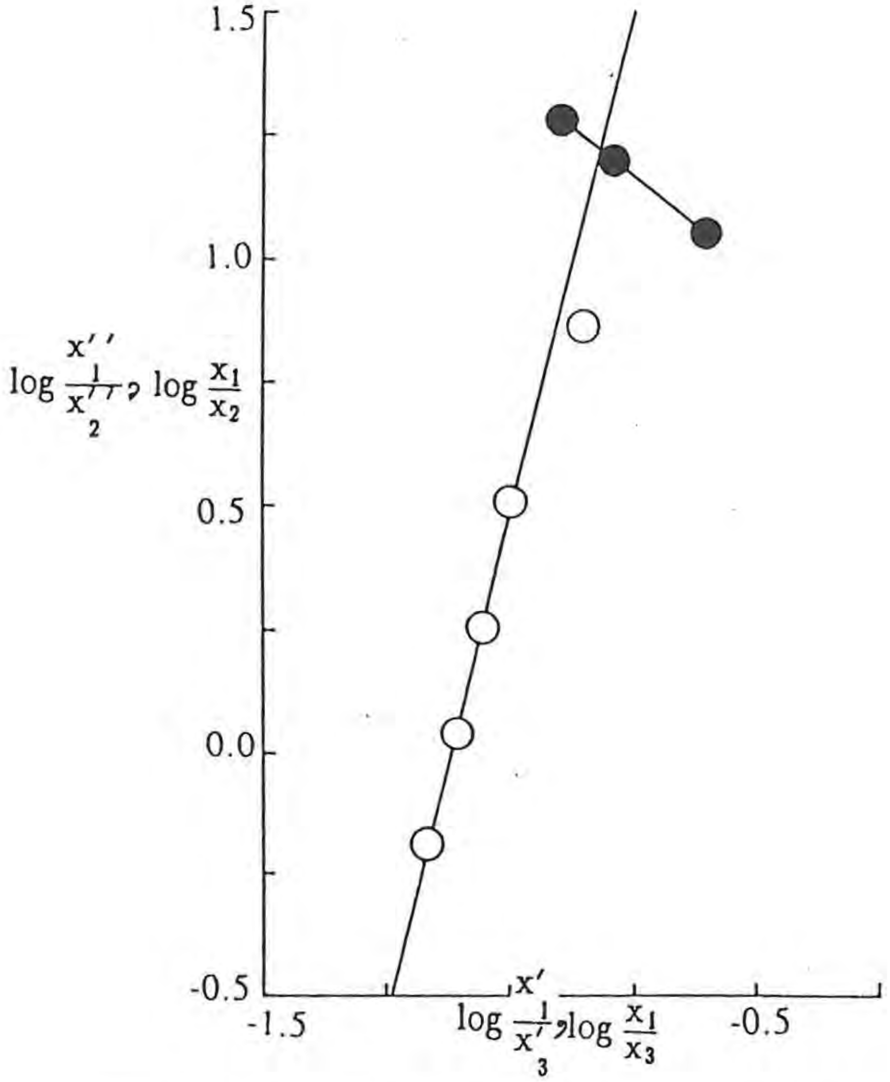


FIGURE 6.5(l) : Determination of plait point {Treybal method} : The t–butanol–cyclohexane–water ternary system.

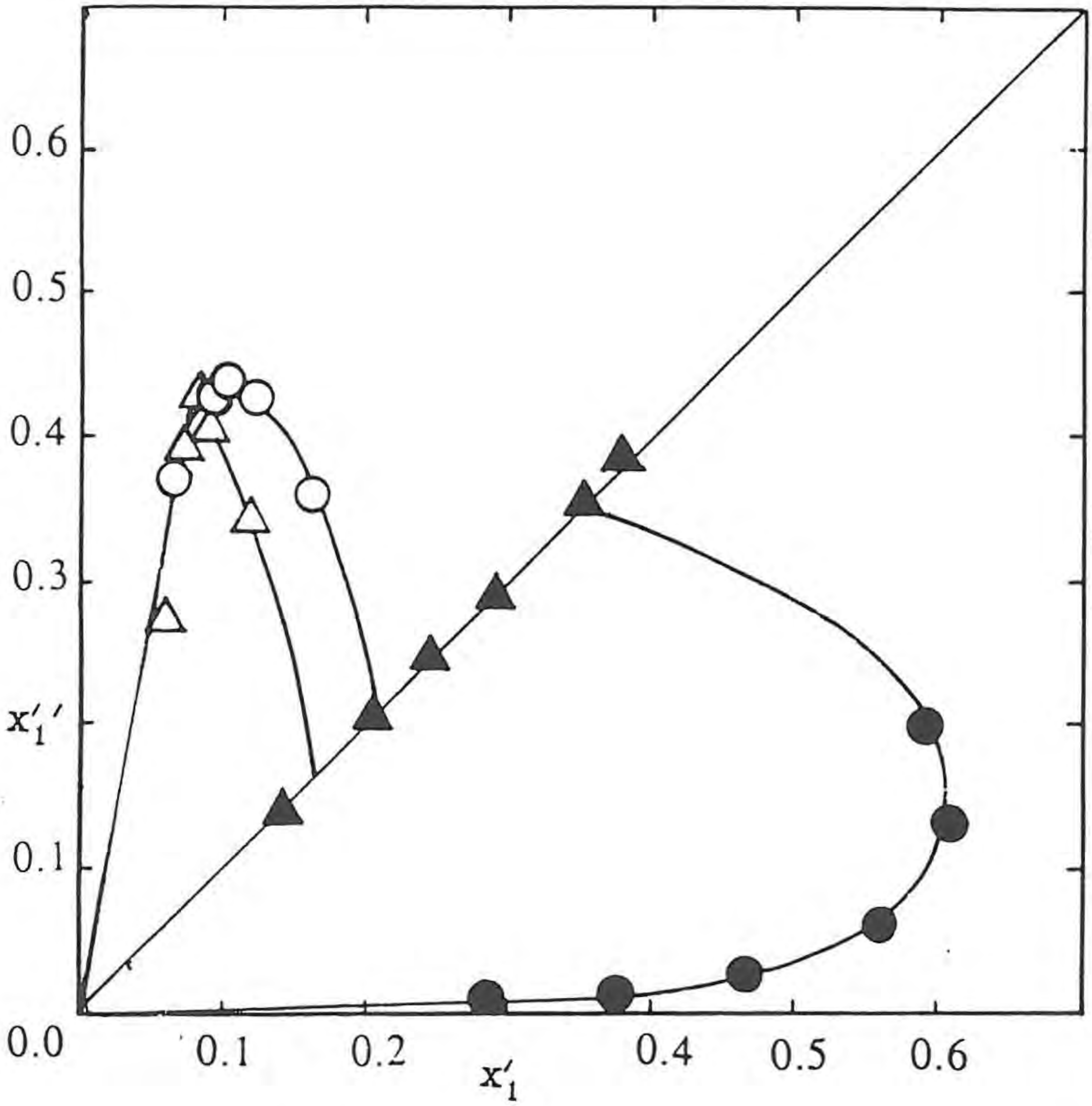


FIGURE 6.5(m) : A plot of x_1'' against x_1', showing the relative solubilities of the alkanol in the cyclohexane–rich and water–rich layers.
●, C_2H_5OH; ○, C_3H_7OH; ▲, $CH_3CH(OH)CH_3$; △, $C(CH_3)_3OH$.

6.6 : PLAIT POINTS

TABLE 6.6(a): The plait points $x_{1,p}$ and $x_{2,p}$ and the minimum concentration of alcohol $x_{1,min}$ at which the alcohol is soluble in all ratios of water and substituted benzene for the systems : $\{x_1C_mH_{2m+1}OH + x_2C_6H_{6-n}(CH_3)_n + (1 - x_1 - x^2)H_2O\}$.

	Alcohol	0	1	2–o	2–m	2–p	3
$x_{1,p}$	**CH_3OH**	0.47	0.43	–	–	0.54	0.50
$x_{2,p}$		0.44	0.50	–	–	0.49	0.47
$x_{1,min}$		0.62	0.67	–	–	0.73	0.81
$x_{1,p}/x_{1,min}$		0.76	0.64	–	–	0.74	0.61
$x_{1,p}$	**C_2H_5OH**	0.37	0.41	–	–	0.46	0.50
$x_{2,p}$		0.39	0.36	–	–	0.35	0.35
$x_{1,min}$		0.40	0.47	–	–	0.53	0.60
$x_{1,p}/x_{1,min}$		0.95	0.87	–	–	0.87	0.83
$x_{1,p}$	**C_3H_7OH**	0.11	0.19	–	–	0.26	0.20
$x_{2,p}$		0.01	0.01	–	–	0.01	0.01
$x_{1,min}$		0.43	0.44	–	–	0.44	0.43
$x_{1,p}/x_{1,min}$		0.41	0.43	–	–	0.59	0.47
$x_{1,p}$	**$CH_3CH(OH)CH_3$**	0.22	0.27	0.36	0.36	0.28	0.42
$x_{2,p}$		0.05	0.07	0.13	0.12	0.07	0.22
$x_{1,min}$		0.38	0.38	0.39	0.40	0.40	0.43
$x_{1,p}/x_{1,min}$		0.57	0.71	0.92	0.90	0.70	0.98
$x_{1,p}$	**$C(CH_3)_3OH$**	0.11	0.16	–	–	0.17	0.17
$x_{2,p}$		0.02	0.02	–	–	0.01	0.01
$x_{1,min}$		0.41	0.42	–	–	0.42	0.42
$x_{1,p}/x_{1,min}$		0.39	0.38	–	–	0.40	0.40

7. : DISCUSSION OF EXPERIMENTAL RESULTS

7.1 : DISCUSSION OF TIELINES AND BINODAL CURVES.

7.1.1 SYSTEMS INVOLVING BENZENE AND SUBSTITUTED BENZENE.

The partitioning of an alcohol between water and mesitylene or toluene or xylene or benzene compound is dependent on the length and structure of the carbon chain of the alcohol. The slope of the tielines indicate that methanol and ethanol are much more soluble in water than in any of the aromatic compounds, but the propanols and each of the butanols are much less soluble in water than in the aromatic liquids. The 2–propanol–mesitylene–water ternary system is interesting in that the alcohol is almost as soluble in water as it is in the aromatic liquid (e.g. mesitylene). The relative nature of the partitioning of an alcohol between water and mesitylene or p–xylene or toluene or benzene can also be inferred from Figures 6.1(n),6.2(p),6.3(n) and 6.4(n) where the concentrations of the alcohol in the water–rich layers, x_1' have been plotted against the concentrations of the alcohol in the conjugate mesitylene, or p–xylene or toluene or benzene–rich layer, x_1''.

The solubility of an alcohol in these substituted benzene–water systems also depends on the length and structure of the alcohol carbon chain. The minimum concentration of a primary alcohol that is soluble in any concentration $x_{1,\mathrm{min}}$, decreases from methanol to ethanol, to propanol and increases to butanol.

The secondary and tertiary alcohols have a more solubilising effect on water–hydrocarbon systems than the respective 1–alkanol of the same carbon number. For example, the minimum concentration (in mole fractions) of the butanols which are soluble in any water–mesitylene mixtures are 0.55 (butanol), 0.51 (2–butanol) and 0.43 (2–methyl–2–propanol).

The mutual solubility of each of the C_1 to C_4 alcohols in (water + methyl substituted benzene) mixtures decreases as the number of methyl groups, n, increases from 0 to 3. This can be seen in Table 6.6(a) where $(x_{1,\mathrm{min}})$, has been tabulated against n for each alcohol. This effect is most pronounced in methanol and ethanol.

The slope of a tieline, especially in the vicinity of a plait point, is an indication of the relative solubility of an alcohol in water and the substituted benzene. The position of the plait point on the liquid–liquid phase boundry is also an indication of the relative solubility. One possible way of expressing this relative solubility is to divide the alcohol concentration of the plait point $x_{1,p}$ against $x_{1,min}$. This ratio gives the relative position of the plait point on the binodal curve and should serve as a rough indicator of relative solubility. This ratio $x_{1,p}/x_{1,min}$ has been calculated for all the systems discussed in this work and is tabulated in Table 6.6(a).

The tielines in the methanol and ethanol systems slope from high concentrations of water and alcohol to low concentrations of alcohol and high concentrations of substituted benzenes. The ratio $x_{1,p}/x_{1,min}$ decreases as n increases from 0 to 3. This reflects the fact that alcohols are more soluble in water than in the substituted benzene compounds and also that this effect becomes more pronounced as n increases from 0 to 3.

In the cases of 1–propanol, 2–propanol and 2–methyl–2–propanol systems the tie–lines slope from high concentrations of alcohol and substituted benzenes to low concentrations of water and alcohol. This reflects the fact that these alcohols are more soluble in the substituted benzenes than in the water. The ratio of $x_{1,p}/x_{1,min}$ increases as n increases from 0 to 3 and reflects the increased solubility of the alcohol in the water–rich layer relative to substituted benzene–rich layer as n increases.

7.1.2 SYSTEMS INVOLVING CYCLOHEXANE

The partitioning of an alkanol between water and cyclohexane is dependent on the length and structure of the carbon chain of the alkanol. The slope of the tie–lines in Figure 6.5(a) to 6.5(h) indicate that methanol and ethanol are much more soluble in water than in cyclohexane, but propanol and each of the butanols are less soluble in water than in cyclohexane. The 2–propanol system is an interesting one in that the alkanol is as soluble in water as it is in cyclohexane. The relative nature of the partitioning of an alkanol between water and cyclohexane can also be inferred from Figure 6.5(m) where the concentrations of the alkanol in the water–rich layer has been plotted against the concentration of the alkanol in the conjugate cyclohexane–rich layer.

The solubility of an alkanol in cyclohexane–water mixtures also depends on the length and structure of the alkanol carbon chain. The minimum concentration of a primary alkanol that is soluble in any concentration of water–cyclohexane decreases from methanol (0.85 mole fraction) to ethanol (0.62) to propanol (0.44) but increases to butanol (0.55).

The secondary and tertiary alkanols have a more solubilising effect on water–cyclohexane mixtures than the respective 1–alkanol of the same carbon number. The minimum concentration of these alkanols which are soluble in any water–cyclohexane mixture are 0.39 mole fraction (2–propanol), 0.51 mole fraction (2–butanol) and 0.43 mole fraction (tert–butanol). The same pattern was evident with the alkanol + water + benzene or hexane [34,35] or heptane [36] systems.

7.2 COMPARISON OF RESULTS WITH THOSE OF OTHER WORKERS.

7.2.1 THE BENZENE AND METHYL–SUBSTITUTED BENZENE SYSTEMS

The binodal curve for the (methanol + toluene + water) system at 25°C has been reported by Mason and Washburn (1937) [37] and differ by as much as 0.04 mole fraction in the vicinity of $x_1 = 0.6$ and $x_2 = 0.3$. They did not report tie–lines in the vicinity of the plait point. The binodal curve and plait point results for the (ethanol + toluene + water) system at 25°C over the whole composition range is within 0.005 mole fraction of the binodal curve and estimated plait point results of Washburn. Beguin and Beckford (1939) [38] . The results of Baker (1955) [39] for the system (propanol + toluene + water) at 25°C differs by 0.015 mole fraction from the results of this work in the region of $x_1 = 0.3$, $x_2 = 0.6$ mole fraction.

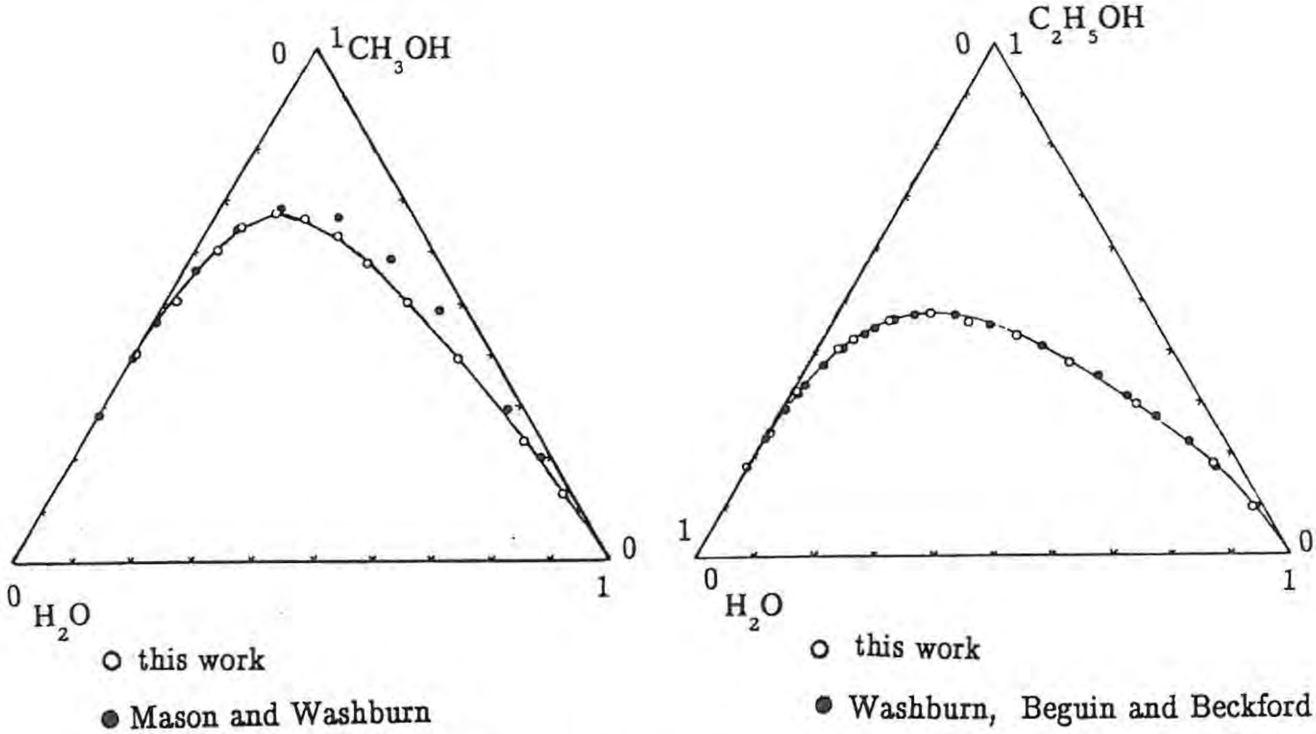


FIGURE 7.2(a) : **Literature results and the results of this work, for the methanol–toluene–water and ethanol–toluene–water ternary systems.**

The binodal curve results from this work over the whole composition range for the system (2–propanol + toluene + water) at 25°C are within 0.02 mole fraction of the results of Washburn and Beguin (1940) [40] and the plait points from this work are within 0.01 mole fraction of their result.

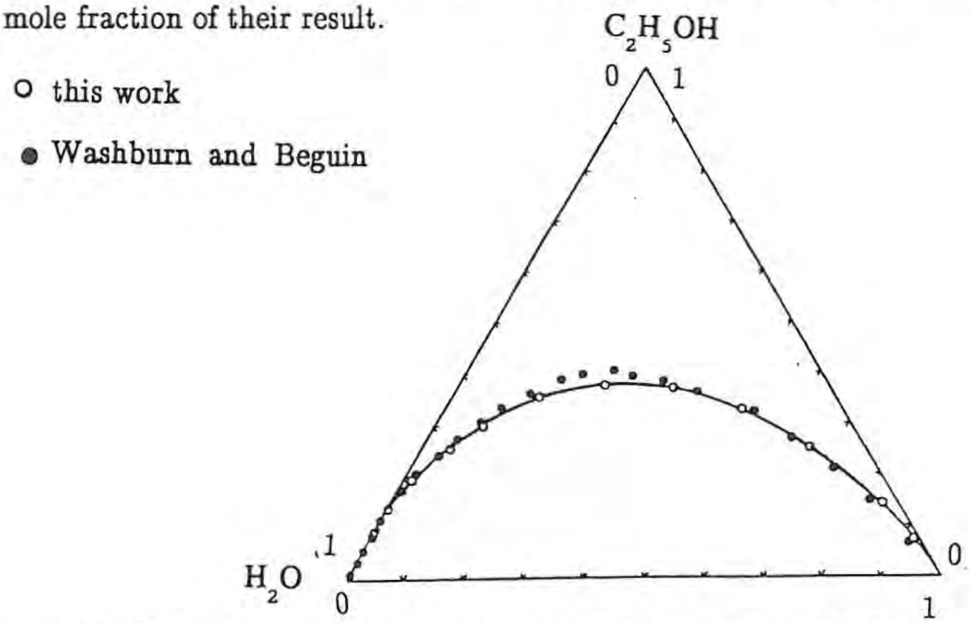


FIGURE 7.2(b) : **Literature results and the results of this work, for the 2–propanol–toluene–water ternary system.**

The binodal curve and tieline results for the (alcohol + benzene + water) systems are similar to those of Letcher (1989)[26]. The binodal curve results for (methanol + benzene + water) system at 25°C are within 0.01 mole fraction of the work published by Udovenko and Mazanko[41], but differ by as much as 0.06 mole fraction from the work of Barbaudy, Mertslin *et al*[42], and Triday[43].

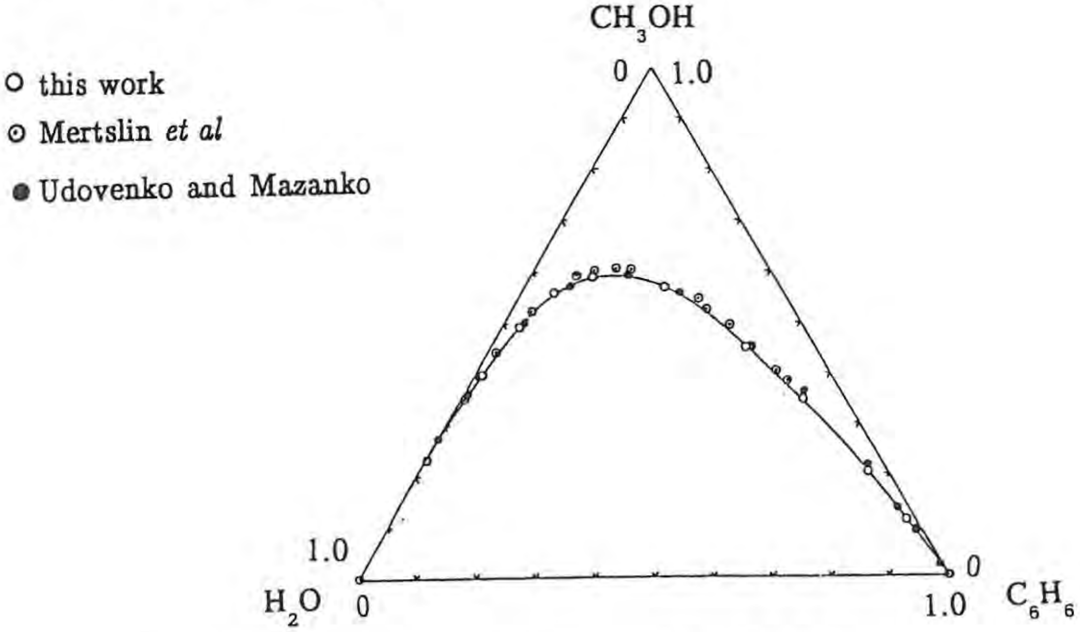


FIGURE 7.2(c) : **Literature results and the results of this work, for the methanol–benzene–water ternary system.**

The binodal curve results for (ethanol + benzene + water) compare well with those of Cassidy *et al* [44], Ross *et al* [45], and Brandani *et al* [46]. The difference in binodal curve data is to be expected since the Ross and Patterson work was done at 293.2K and the Brandani work at 303.2K. The work of Gokcen and Chang [47] was done at 338.1K and as expected, the results are very different to those reported in this work.

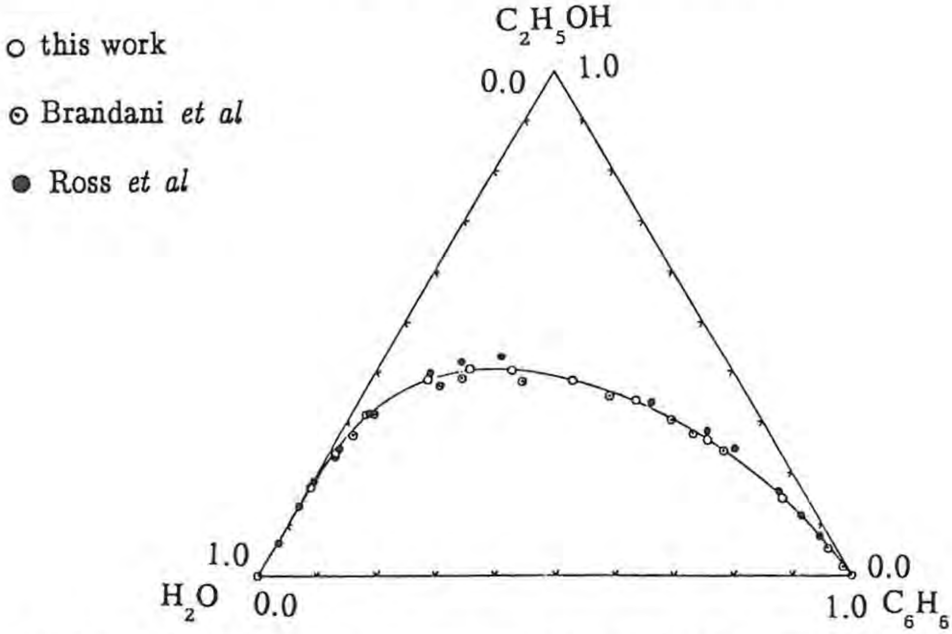


FIGURE 7.2(d) : **Literature results and the results of this work, for the ethanol–benzene–water ternary system.**

The system (1–propanol + benzene + water) has been studied by Denzler, Udovenko and Mazanko[48], and McCants *et al*[35]. The general agreement between the data reported here at 298.2K and those of Denzler[49] at 293.2K, Udovenko and Mazanko at 303.2K, and McCants *et al* at 311K, is fair.

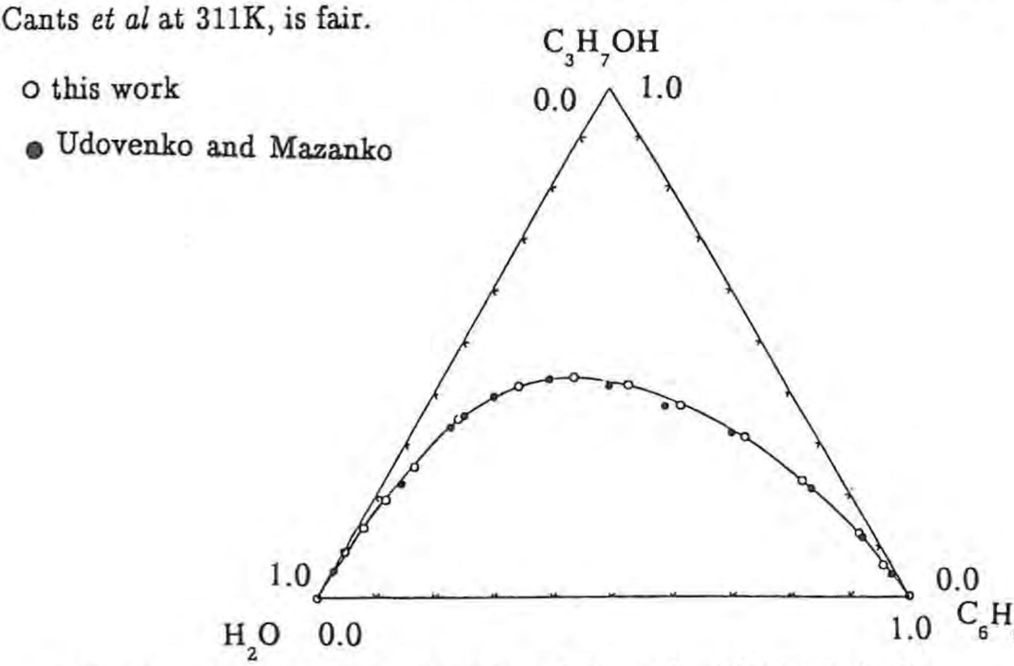


FIGURE 7.2(e) : **Literature results and the results of this work, for the 1–propanol–benzene–water ternary system.**

Udovenko and Mazanko[50] have studies the system (i–propanol + benzene + water) and their results are in good agreement with those reported in this work. The results for the (2–butanol + benzene + water) system at 298.2K differ slightly from those of Davies and Evans[51], at 303.2K. This could be a result of the temperature difference.

Only Letcher *et al* (1989) have reported work on the systems (n–butanol + benzene + water), and (t–butanol + benzene + water). Their results are very similar to those of this work. No previous work could be found for p–xylene and mesitylene.

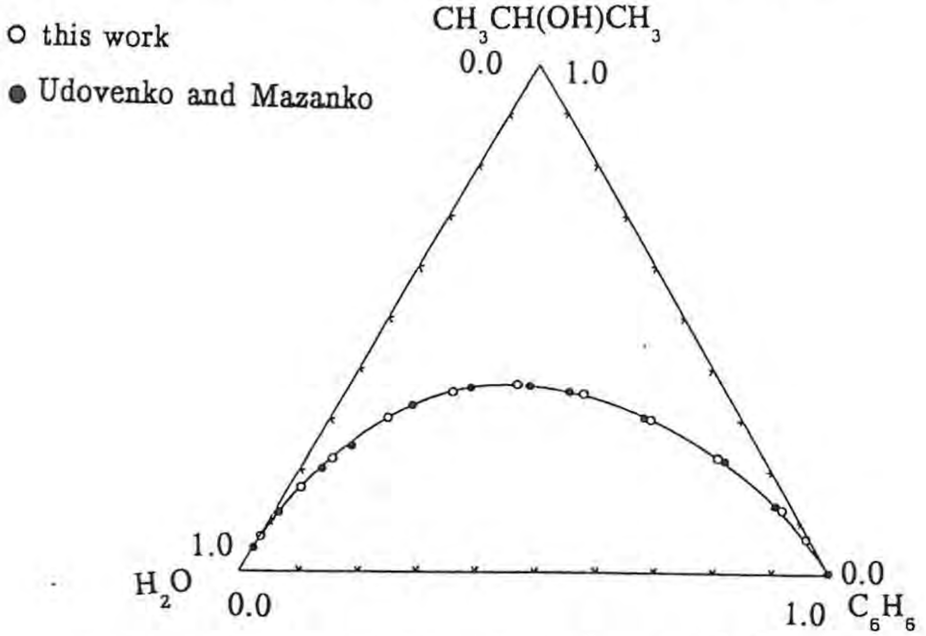


FIGURE 7.2(f) : Literature results and the results of this work, for the 2–propanol–benzene–water ternary system.

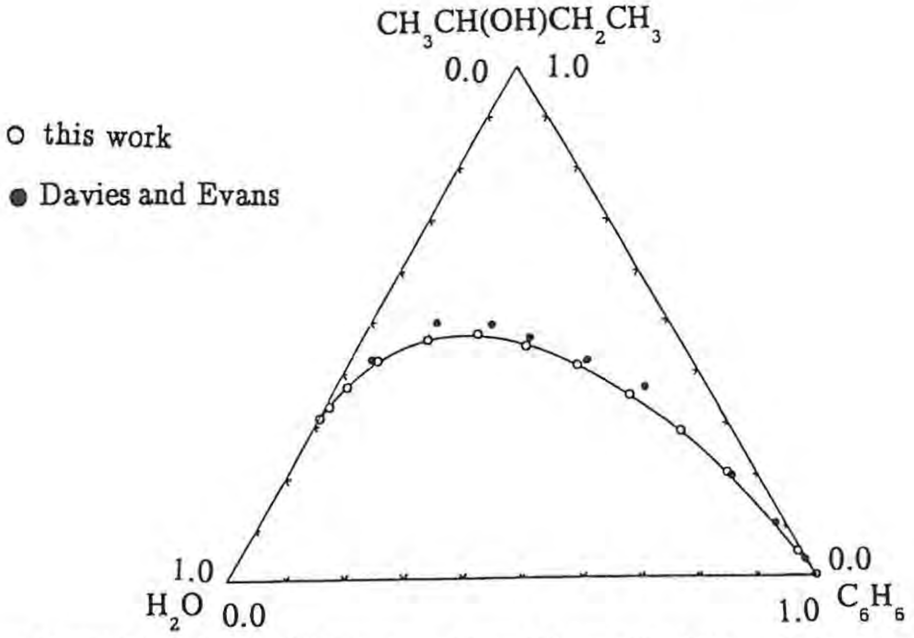


FIGURE 7.2(g) : Literature results and the results of this work, for the 2–butanol–benzene–water ternary system.

7.2.2 CYCLOHEXANE SYSTEMS

The binodal curve composition results for the methanol and ethanol systems compares well with those of Washburn and Spencer [52] and Moriyoshi *et al* [53] respectively, and in all cases are within 0.005 mole fraction of their results.

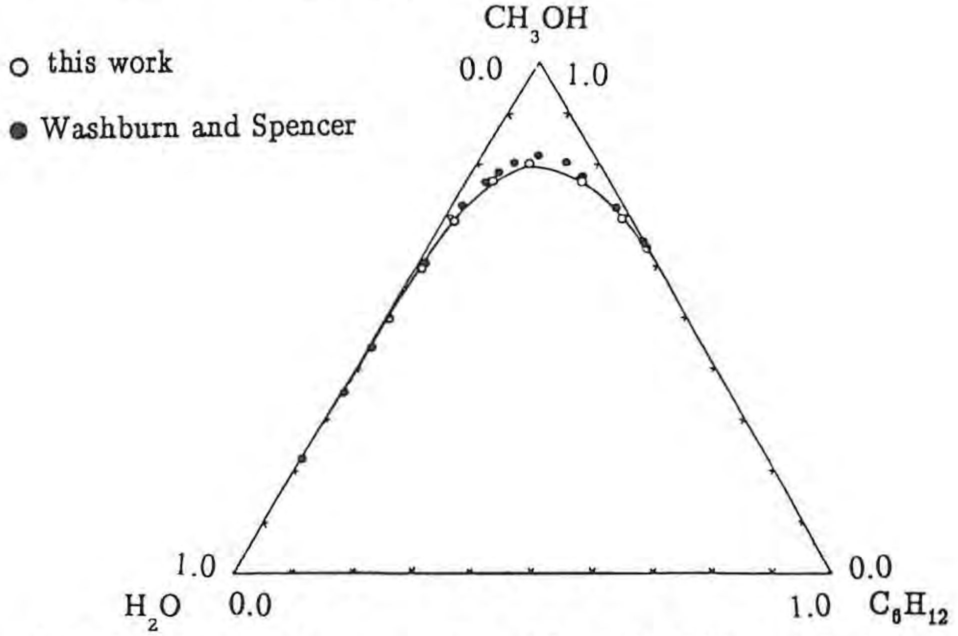


FIGURE 7.2(h) : Literature results and the results of this work, for the methanol–cyclohexane–water ternary system.

Binodal curve results for the propanols + water + cyclohexane have been reported by Washburn, Brockway and Deming [54]. The binodal curve generated from their results are in all cases within 0.01 mole fraction of the results of this work.

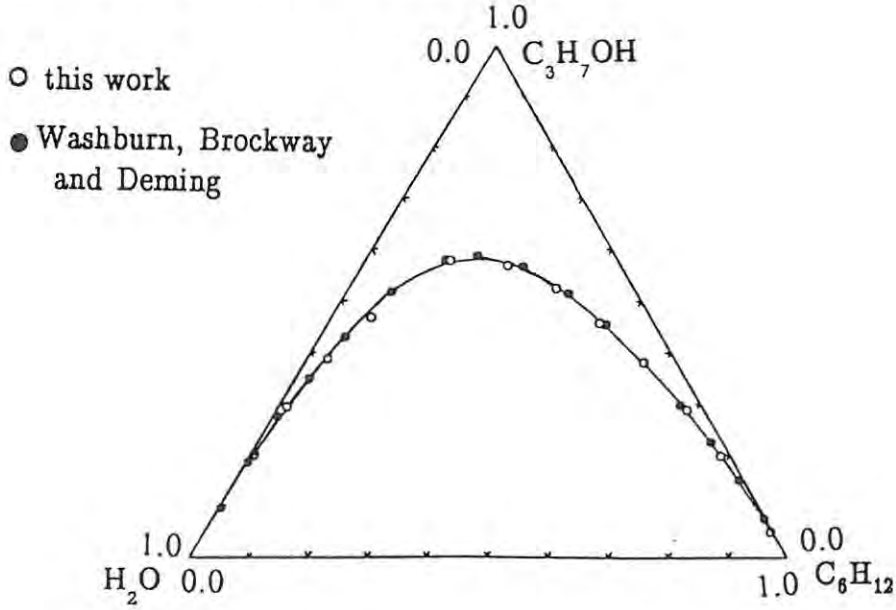


FIGURE 7.2(i) : Literature results and the results of this work, for the 1–propanol–cyclohexane–water ternary system.

No liquid–liquid equilibrium data has previously been reported for (a butanol + water + cyclohexane) mixture. A comparison of the ternary phase diagrams for the three sets of systems – (alkanols + water + cyclohexane or benzene or hexane [34,35] or heptane [36] show that water is more soluble in benzene mixtures than in the respective cyclohexane. hexane or heptane mixtures. The binodal curves for the cyclohexane systems are very similar to the binodal curves of the respective hexane systems.

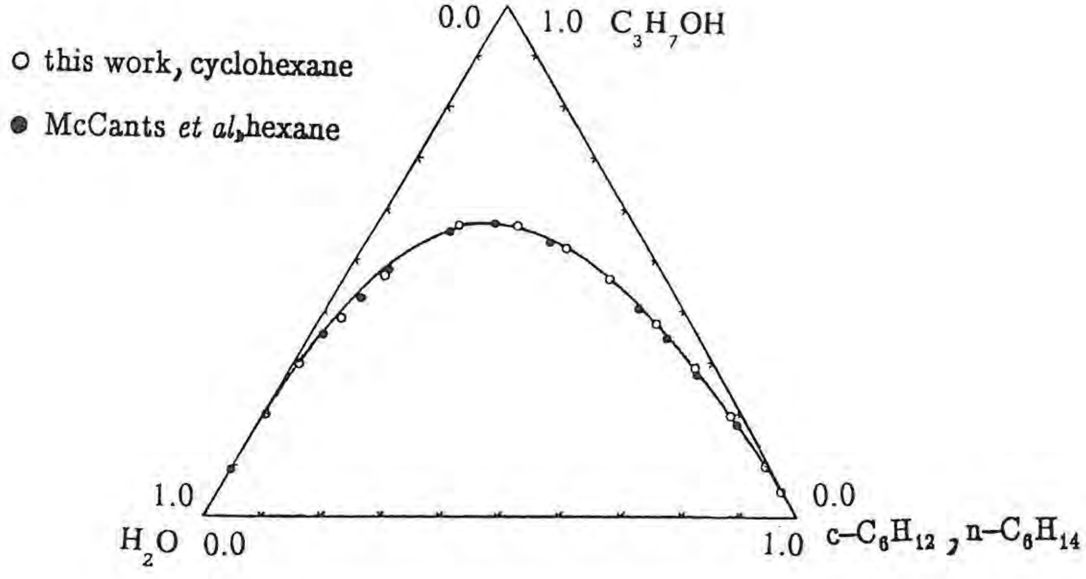


FIGURE 7.2(j) : **n–hexane results (from literature) and cyclohexane results (from this work), for the 1–propanol–water systems.**

7.3 COMPARISON OF THE PHASE EQUILIBRIA OF AROMATIC WITH NON–AROMATIC SYSTEMS.

A comparison of the ternary phase diagrams for the systems (an alcohol + benzene or a substituted benzene compound + water) with the phase diagrams for (an alcohol + cyclohexane or heptane + water) shows that water is more soluble in the methyl substituted benzene systems than in the cyclohexane or heptane systems. The order of solubility is as follows :

n–heptane < cyclohexane < mesitylene < p–xylene < toluene < benzene.

This has been shown in the diagrams below for systems involving methanol, ethanol, 1–propanol and 2–propanol. The sequence described above is clearly observed in the methanol and ethanol systems although it is not so clear for 1–propanol and 2–propanol systems.

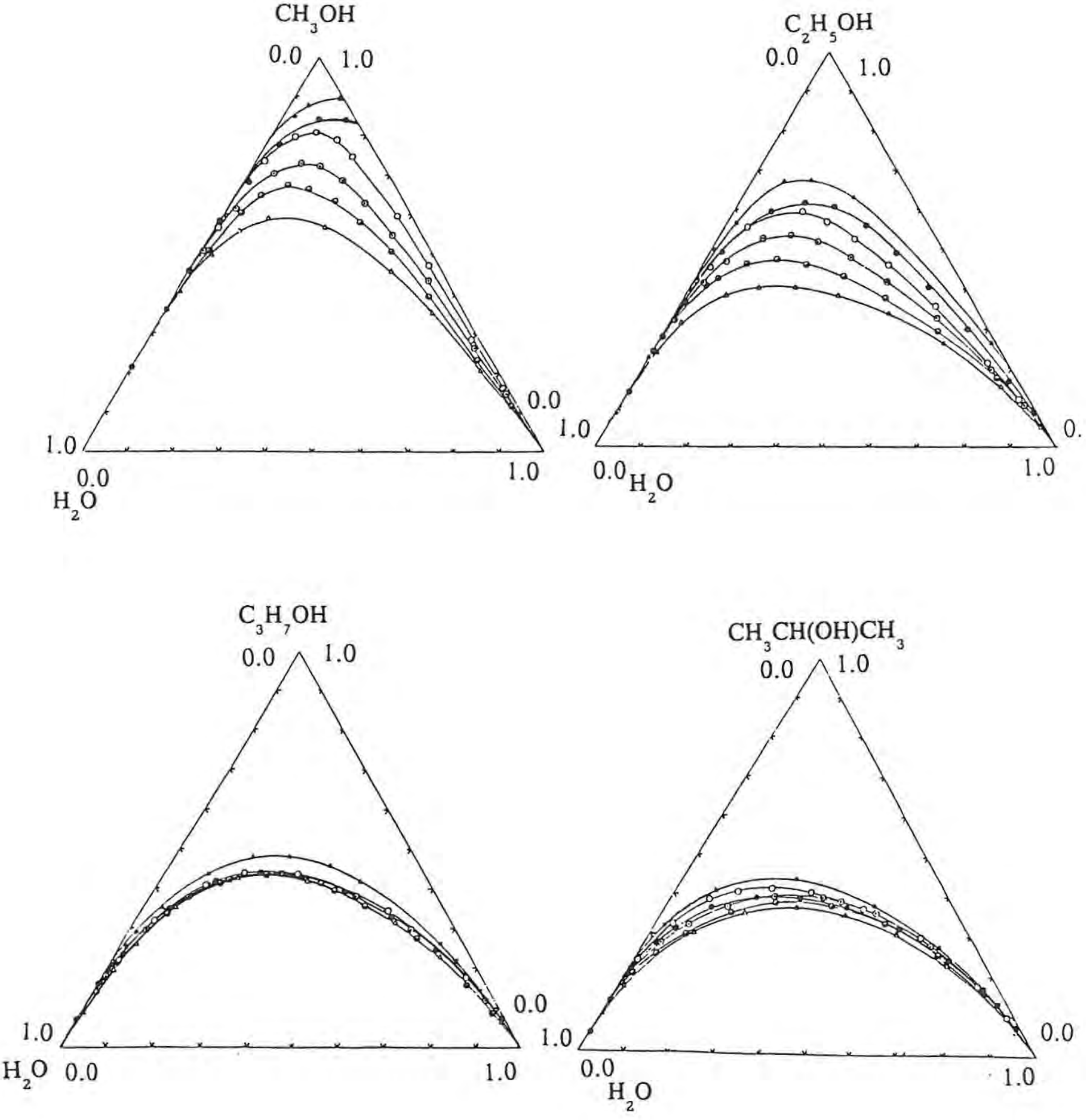


FIGURE 7.3 : **Comparison of phase equilibria of aromatic with non–aromatic systems.**

▲. n–heptane ; ●, cyclohexane ; O, mesitylene ;

Θ, p–xylene, ⊖, toluene ; Δ, benzene.

8 : LIQUID–LIQUID EQUILIBRIA IN PERSPECTIVE.

8.1 : INTRODUCTION

As mentioned in the introduction, the work carried out in this thesis is only part of a major project in the investigation of alcohol–petrol–water phase equilibria. Because petrol is a mixture of hydrocarbons involving aromatics, aliphatics and olefins, work has been done on some of these components.

In this section the alcohol–aromatics–water ternary system phase equilibrium data is discussed in relation to the alcohol–petrol–water, alcohol–aliphatics–water, and alcohol–cyclohexane–water ternary systems.

8.2 THE CORROSION PROBLEMS RELATING TO ALCOHOL–PETROL BLENDS.

In South Africa SASOL fuel alcohol (a mixture of alcohols consisting of 65% ethanol, 18% propanols and 17% higher alcohols by mass) is added to petrol in the ratio 1 : 7 i.e. 12% alcohol in the petrol.[55] Water contamination of the alcohol–petrol blends probably takes place in garage storage tanks as a result of groundwater seepage and condensation, As a result, the fuel that is pumped into tanks of cars can contain as much as 1–2 mass % of water.[56] The solubility of water in petrol is very low and is estimated to be approximately 80mg per 100g (i.e. less than 0.01 mass %)[56]. A one–phase mixture of petrol and a little water (1–2 mass %) should cause no corrosion problems, but the addition of alcohol raises water solubility significantly.

Due to the hygroscopicity of the alcohols, the alcohol–fuel blend, when left to stand. absorbs more water. This absorption process is exhanced if the mixture is heated as in a carburettor which reaches temperatures of 60 to 80°C every time the engine is switched off. On cooling, phase separation can result, and a water–rich phase forms.

For example, the water–rich layer which forms when a 12% SASOL alcohol in petrol blend separates into two phases consisting of about 70% water (see diagram).[14]

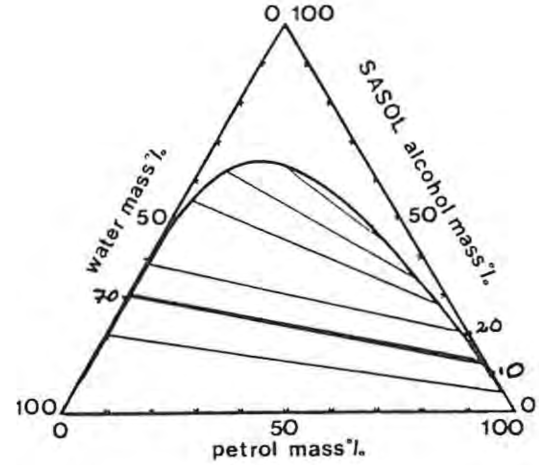


FIGURE 8.1 : **The Sasol alcohol–petrol–water ternary systems in mass%.**

It is this water–rich layer that can be responsible for corrosion problems experienced by some motorists since the introduction of alcohol–blended petrol.

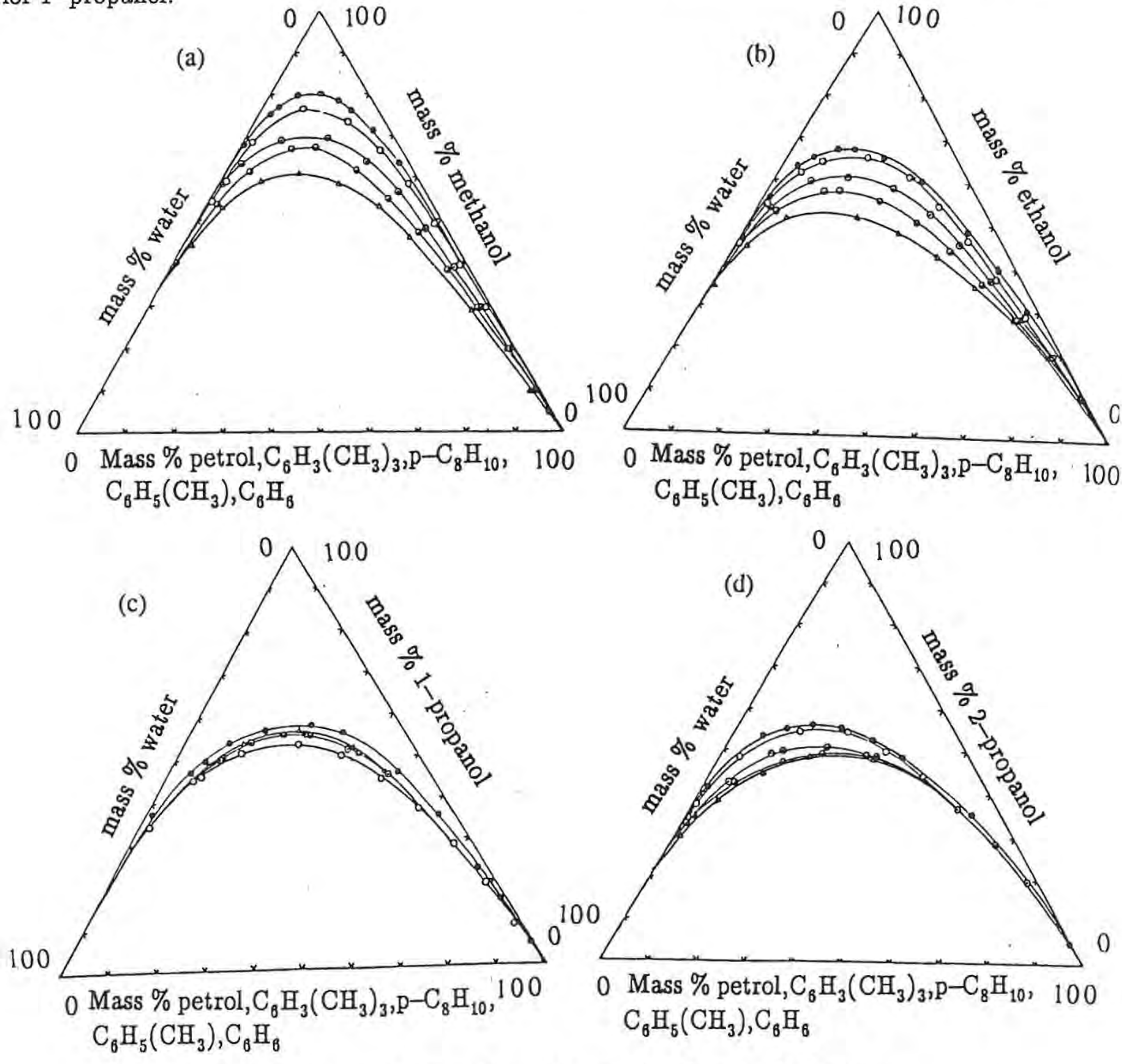
8.3 : COMPARISON OF THE SOLUBILITY PROPERTIES OF THE ALCOHOL–AROMATICS–WATER TERNARY SYSTEMS WITH THOSE OF ALCOHOL–PETROL–WATER AND ALCOHOL–N–HEPTANE–WATER.

In Figure 8.3(a) to Figure 8.3(h) below, binodal curves have been drawn in an attempt to compare the solubility properties of the systems involving the aromatic–hydrocarbons benzene, toluene, p–xylene, and mesitylene with those involving petrol and n–heptane.

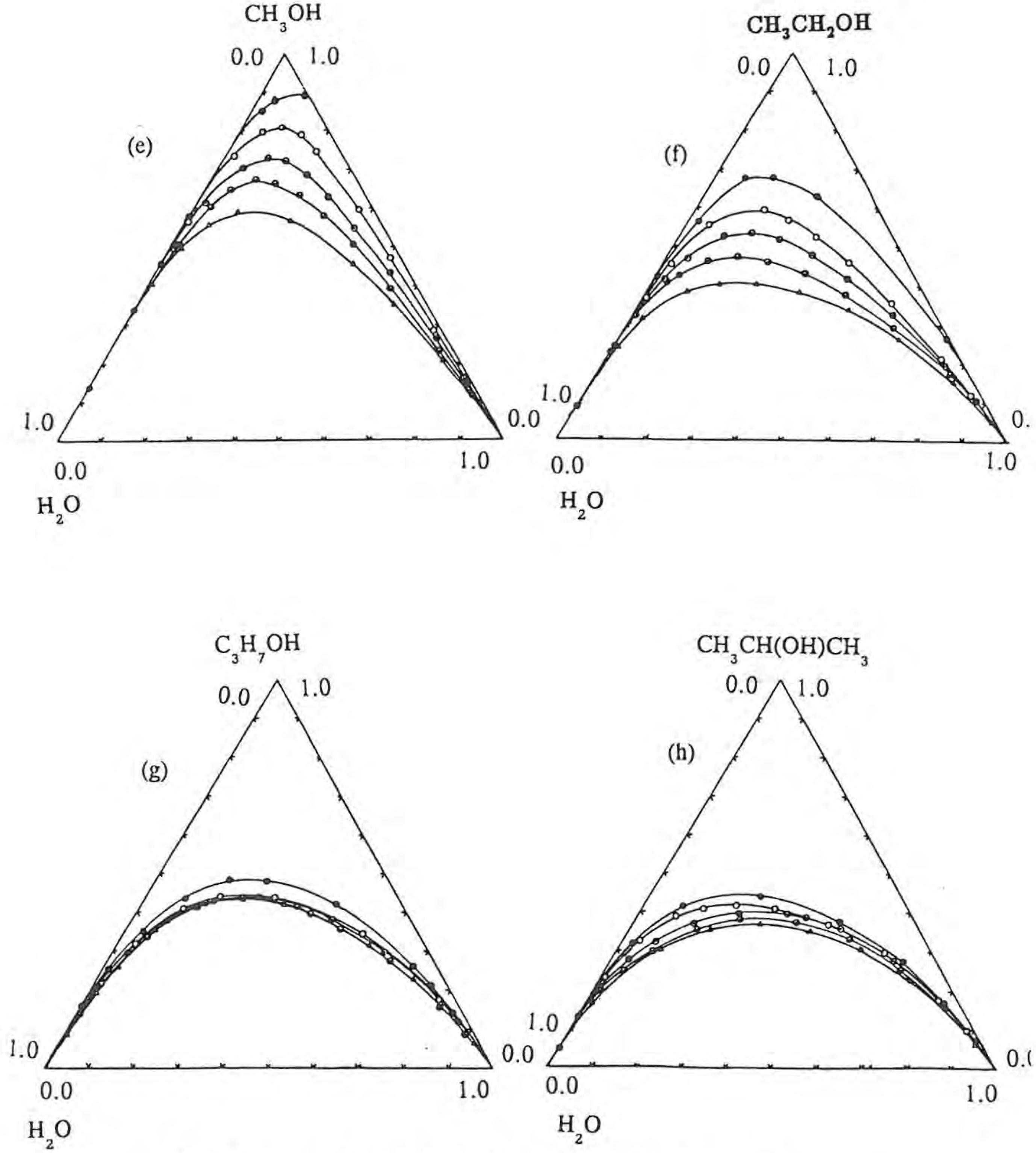
Figures 8.3(a) to 8.3(d) refer to aromatic hydrocarbon mixtures in comparison to petrol mixtures. These diagrams (Figures 8.3(a)–8.3(d)), have been drawn in mass% of compound because it is not possible to calculate the mole% of petrol(a mixture of different hydrocarbons). In Figure 8.3(a) the alcohol is methanol, in Figure 8.3(b) ethanol, in Figure 8.3(c) 1–propanol and in Figure 8.3(d) 2–propanol. Figures 8.3(e) to 8.3(h) refer to aromatic hydrocarbons in comparison to n–heptane mixtures, Figure 8.3(e) refers to methanol, Figure 8.3(f) refers to ethanol, Figure 8.3(g) refers to 1–propanol and Figure 8.3(h) refers to 2–propanol. Figures 8.3(e)–8.3(h) have been drawn in mole fractions.

Figures 8.3(a) and 8.3(b) show that solubility of water in the methanol and ethanol mixtures follow the order benzene > toluene > p–xylene > mesitylene > petrol. For the 1–propanol mixtures there is little difference in solubility of water although it seems water is most soluble in mesitylene and least soluble in petrol (see Figure 8.3(c)), Figure 8.3(d) shows that water is still less soluble in the petrol mixtures than in the aromatic hydrocarbon mixtures for 2–propanol.

In Figures 8.3(e) and 8.3(f) the same pattern as in Figures 8.3(a) and 8.3(b) is observed, with the order of solubility of water being benzene > toluene > p–xylene > mesitylene > n–heptane. for both methanol and ethanol. For 1–propanol and 2–propanol (Figures 8.3(g) and 8.3(h)) water is least soluble in the n–heptane mixtures. There is little difference in solubility of water between the aromatic hydrocarbon mixtures, especially for 1–propanol.



●, petrol ; O, mesitylene ; ⊙, p–xylene, ⊖, toluene ; Δ, benzene.



●, n–heptane ; O, mesitylene ; ⊙, p–xylene, ⊖, toluene ; Δ, benzene.

FIGURE 8.3(a–h) : The alcohol–aromatic–water ternary systems together with those of alcohol–petrol–water and alcohol–n–heptane–water.

9 : CONCLUSION

In this work, new precise phase equilibrium data (binodal curve data and tie line data) have been produced for the systems:

alcohol–mesitylene–water ternary system,
alcohol–p–xylene–water ternary system,
alcohol–toluene–water ternary system,
alcohol–benzene–water ternary system and
alcohol–cyclohexane–water ternary system.

Of the systems listed above only alcohol–benzene–water, alcohol–cyclohexane–water, methanol–toluene–water, ethanol–toluene–water, 1–propanol–toluene–water and 2–propanol–toluene–water have previously been reported.

From the experimental results the following conclusions can be made:

(i) For each hydrocarbon investigated, solubility of water in the alcohol–hydrocarbon blend increases gradually from methanol to 2–propanol. There is little difference in solubility of water among the C_4 alcohol–hydrocarbon blends.

(ii) On phase separation, the water content in the water–rich layer is far less in the ethanol and methanol blends than in the 1–propanol, 2–propanol or butanol blends.

(iii) For all the aromatic systems, the mutual solubility decreases as the number of methyl groups on the benzene ring increases, that is, benzene > toluene > p–xylene > mesitylene. Also mutual solubility is greater in the aromatic blends than in the cycloalkane and n–alkane blends (see Figure 7.3).

(iv) Only the 2–propanol–o–xylene–water and 2–propanol–m–xylene–water have been done for the o–xylene and m–xylene ternary systems. There is little difference between these and the 2–propanol–p–xylene–water ternary system.

Since it is desirable to limit phase separation to a minimum, it can be concluded that a suitable petrol for blending would be one that is rich in aromatics, especially benzene (see (iii) above). Also, since water is most soluble in the 2–propanol blends, it would seem that 2–propanol is the most suitable alcohol for blending. However when phase separation does take place the resultant water–rich layer has a very high water content. This could result in serious corrosion problems.

The application of the UNIQUAC theory to phase equilibrium problems has been tested and shown to be effective in one of the systems discussed in this thesis.

10 FUTURE WORK

Following the work done in this thesis, it is suggested that the following work be carried out .

1. Phase equilibria be determined for alcohol–hydrocarbon–water ternary systems, where the hydrocarbons are alkenes, alkynes and other cycloalkanes such as cycloheptane and cyclo–octane. These compounds are also found in petrol.

2. The effect of the addiction of oxygenates such as ethers, aldehydes and even acetic acid should also be investigated. That is, the quarternary systems alcohol–oxygenate–hydrocarbon–water should be studied. These oxygenates are currently replacing lead compounds as octane boosters in petrol.

3. Application of the UNIQUAC theory to other ternary systems discussed in this thesis and to the quarternary systems mentioned in 2 above.

BIBLIOGRAPHY

1. *The Economist*, January 1991, 76–77.
2. Flower, A.R., *Scientific American*, 1978, **338**, 42–49.
3. Duncan, R., *The Chemistry of Commerce*, 147.
4. *Ethyl Alcohol Handbook*, 5th ed., U.S.I. Chemicals, 1981.
5. Giebelhaus, A.W., *Agric. Hist.*, 1980, **154**, 178.
6. Buchanan, E.J., *Chemsa*, 1989, **15**, 352.
7. Rein, P.W., *Chemsa*, 1986, **12**, 190.
8. Riegel, E.R., *Industrial Chemistry*, The Chemical Catalog Co., Inc., New York, 1933.
9. Schlesinger, C.B., Partridge, L.J., *Chemsa*, 1983, 217.
10. Powell, T., *Racing Experiences with Methanol and Ethanol–based Motor–Fuel Blends*, Paper **750124**, Automobile Engineering Congress and Exposition, Society of Automotive Engineers, Detroit, Mich., February 1975.
11. Goodrich, R.S., *Chem. Eng. Prog.*, 1982, **78**, 29.
12. Keller, J.L., Nakaguchi, G.M., and Ware, J.C., *Methanol Fuel Modification for Highway Vehicle Use*, HCP/w**3683–18**, final report for U.S. Department of Energy, Washington, D.C., July 1978.
13. Letcher, T.M., Siswana, P.M., van der Watt, P., Radloff, S., *J. Chem. Thermodynamics*, 1989, 21, 1053–1060.
14. Letcher, T.M., Heyward, C., Wooten, S., *S.A.J. Chem.* 1986, **39**, 19
15. Vogel, A.I., *A Textbook of Quantitative Inorganic Analysis* : Longmans : London, 2nd ed., 1960, Chapter VI.
16. Briggs, S.W., Comings, E.W., *Ind. Eng. Chem.*, 1943, **35**, 411.
17. Ghildiyal, R.C., Nanoti, S.M., Kulsrestha, N.N., Rawat, B.S., Kumar, Y., Krisna, R., *Fluid Phase Equilibria*, 1989, **50**, 339–346.
18. Moriyoshi, T, Uosaki, Y, Sakamoto, T, Hayashi, Y, *J. Chem. Thermodynamics*, 1989, 21, 219–224.

19 Othmer, D.F., Tobias, P.E., *Ind. Eng. Chem.*, 1942, **34**, 693–696.

20. Bachman. I.. *Plait Point Determination.* Ind. Chem. Anal. Ed.. 1940. **12**. 38–42.

21. Brancker, A.V., Hunter, T.G., Nash, A.W., *Ibid.*, 1940, **12**, 35

22. Heric, E.L., *J. Chem. E*duc., 1960, **37**, 144.

23. Hand, D.B., *J. Phys. Chem.*, 1930, **34**, 1961.

24. Treybal. R.E.. Webber. L.D.. Daley. J.F.. *Plait Point Determination.* Ind.Eng. Chem.. 1946. **38**. 817–825.

25. Hlavaty, K., *Coll. Czech. Chem. Commun.*. 1972. **37**. 4005.

26. Letcher, T.M., Sewry, J., Radloff, S., *S.A.J. Chem.*, 1990, 43(**2**).

27. Schultz. D.M.. Crouse. C.F, S. *African Statistic J.*. 1973. **7**. 143.

28. Fredenslund, A., Gmelling, J. Rasmussen,. *Vapor–liquid Equilibria using* U*nifac* : Elsevier Scientific Publishing Company, 1977.

29. Prausnitz, J., Lichtenthaler, R. Azevedo, E. *Molecular Thermodynamics of Fluid phase equilibria*, 2nd ed., 1986.

30. Barker,J.A., *Lattice Theories of the liquid state.* New York: Macmillan Publishing Company, 1963.

31. Wilson, G.M, *J.Am.Chem.Soc.*, 1964, **86**, 127.

32. Renon, H., Prausnitz, J.M., *AIChE J.*, 1969, **14**, 135.

33. Abrams, D.S., Prausnitz, J., *AIChE J.*, 1975, **21**, 116–128.

34. Reddy, J.W., Coleman, C.F., *Ind.Eng.Chem. Fundam.*, 1981, **20**, 250.

35. McCants, J.F., Jones, J.H., Hopson, W.H., *Ind.Eng.Chem.*, 1953, **45**, 454.

36. Letcher, T.M., Wooten, S., Shuttleworth, B., Heyward, C, *J.Chem.Thermodynamics*, 1986, **8**, 1037.

37. Mason, L.S., Washburn, E.R., *The Ternary System : Methyl alcohol, toluene and water, J.Am.Chem.Soc.*, 1937, **59**, 2076–2077.

38. Washburn, E.R., Beguin, A.E, *The Ternary System : Ethyl alcohol. toluene and water at 25°C, J.Am.Chem.Soc.*, 1939, **61**, 1694–1695.

39. Baker, E.M., *The Ternary System : n–propyl alcohol, toluene and water at 25°C, J.Phys.Chem.*, 1955, **59**, 1182–1183.

40. Washburn, E.R., Beguin, A.E., *The Ternary System : Isopropyl, toluene and water at 25°C, J.Am.Chem.Soc.*, 1940, **62**, 579–581.

41. Udovenko, V.V., Mazanko, T.F., *Russ.J.Phys.Chem.*, 1963, **37**, 1256.

42. Mertslin, R.V. Kamaevslava, L.A., Nikurashina, N.I., *Russ.J.Phys.Chem.*, 1966, **40**, 1359.

43. Triday, J.O., *J.Chem.Eng.Data.*, 1984, **29**, 321.

44. Cassidy, R.M., Elchuk, S. *Anal.Chem.*, 1986, **58**, 1181.

45. Ross, S., Patterson, J., *J.Chem.Eng.Data.*, 1979, **24**, 11.

46. Brandani, V., Chianese, A., Rossi, M., *J.Chem.Eng.Data*, 1985, **30**, 27.

47. Gokcen, N.A., Chang, E.T., *J.Electrochem.Soc.*, 1972, **119**, 876.

48. Udovenko, V.V., Mazanko, T.F., *Russ.J.Phys.Chem.*, 1963, **37**, 610.

49. Denzler, C.G., *J.Phys.Chem.*, 1945, **49**, 358.

50. Udovenko, V.V., Mazanko, T.F., *Russ.J.Phys.Chem.*, 1964, **38**, 1626.

51. Davies, J.R., Evans, L.R., *J.Chem.Eng.Data*, 1960, **5**, 401.

52. Washburn, R.E., Spencer, C.H., *J.Am.Soc.*, 1934, **56**, 361.

53. Moriyoshi, T., Uosaki, Y., Takahashi, K., Yamakawa, T., *J.Chem.Thermodynamics*, 1991, **23**, 37.

54. Washburn, R.E., Brockway, C.E., Graham, C.L., Deming, P., *J.Am.Chem.Soc.*, 1942, **64**, 1886.

55. *Car*, 1985, July, 33–35.

56. Koenig, A., Menrod, H., Bernhardt, W., '*Alcohol in Automobiles*'. Alcohol fuel Conference, Inst. Chem. Eng., Sydney, August 1978.

57 Staverman, A.J., *Recl. Trav. Chim. Pays–Bas*, 1950, **69**, 163.

APPENDIX A

INPUT DATA FOR ESTM PROGRAM

```
    1
    1    1    3    3   5   3
 2000             0.0000000        0.0000000        0.0000000        0.0000000
 '1L 1U 1R'
    1    2          380.68           -64.56           -1.100
    1    3          115.13          2057.42           -1.100
    2    3         -128.88           997.41           -1.100
   -1    0   50                   1.E-5            0.
    3    0    0                   0.               0.
    5    0    0                   0.               0.
   -2    0   50                   1.E-9            0.
    5    0    0                   0.               0.
    1                  0.92             1.40       WATER
    2                  2.11             1.97       ETHANOL
    3                  3.19             2.40       BENZENE
    1    2    3    5   1   25.000
        93.0           6.9          0.4          3.5
        85.2          14.6          0.8          6.7
        73.0          25.5          2.6         10.0
        67.1          30.4          5.8         16.6
        54.3          37.8         10.2         24.4
```

APPENDIX B

OUTPUT FOR ESTM PROGRAM

```
ESTIMATED PARAMETERS :

COMPONENT I          COMPONENT J    A(I,J)        A(J,I)
                                    KELVIN        KELVIN

WATER                ETHANOL        157.07       -127.03
WATER                BENZENE        214.17        547.31
ETHANOL              BENZENE       -130.13        441.38

STEP USED TO CONSTRUCT THE BINODAL CURVE =  0.0200 MOLE FRACTION

RESULTS FOR DATA SET :
   LEFT  COMPONENT = WATER
   UPPER COMPONENT = ETHANOL
   RIGHT COMPONENT = BENZENE
```

APPENDIX C

RESULTS USING ESTM FOR THE ETHANOL—BENZENE—WATER TERNARY SYSTEM — CALCULATED TIE LINES IN MOLE PERCENT

(FOR INTERPOLATION)

NUMBER OF ITERATIONS	LEFT COMPONENT PHASE 1	LEFT COMPONENT PHASE 2	UPPER COMPONENT PHASE 1	UPPER COMPONENT PHASE 2	RIGHT COMPONENT PHASE 1	RIGHT COMPONENT PHASE 2
4	99.8168	1.8853	0.0000	0.0000	0.1832	98.1147
2	97.5000	2.0799	2.2426	0.9439	0.2574	96.9762
1	95.5000	2.2532	4.1618	1.7520	0.3382	95.9948
1	93.5000	2.4324	6.0629	2.5574	0.4371	95.0101
1	91.5000	2.6185	7.9436	3.3638	0.5564	94.0177
1	89.5000	2.8125	9.8013	4.1744	0.6987	93.0131
1	87.5000	3.0156	11.6333	4.9925	0.8667	91.9919
1	85.5000	3.2291	13.4368	5.8211	1.0632	90.9498
2	83.5000	3.4545	15.2091	6.6632	1.2909	89.8823
1	81.5000	3.6934	16.9470	7.5219	1.5530	88.7848
1	79.5000	3.9476	18.6477	8.4000	1.8523	87.6523
1	77.5000	4.2193	20.3080	9.3007	2.1920	86.4800
1	75.5000	4.5108	21.9247	10.2270	2.5753	85.2622
2	73.5000	4.8248	23.4945	11.1820	3.0055	83.9931
1	71.5000	5.1646	25.0142	12.1691	3.4858	82.6662
1	69.5000	5.5338	26.4802	13.1920	4.0198	81.2742
1	67.5000	5.9369	27.8891	14.2544	4.6109	79.8088
1	65.5000	6.3790	29.2374	15.3606	5.2626	78.2604
1	63.5000	6.8667	30.5214	16.5153	5.9786	76.6180
1	61.5000	7.4076	31.7376	17.7237	6.7624	74.8687
1	59.5000	8.0114	32.8821	18.9918	7.6179	72.9968
2	57.5000	8.6901	33.9513	20.3260	8.5487	70.9839
1	55.5000	9.4588	34.9413	21.7334	9.5587	68.8078
2	53.5000	10.3366	35.8483	23.2206	10.6517	66.4428
2	51.5000	11.3468	36.6682	24.7933	11.8318	63.8598
2	49.5000	12.5176	37.3973	26.4524	13.1027	61.0300
2	47.5000	13.8784	38.0313	28.1885	14.4687	57.9331
2	45.5000	15.4534	38.5661	29.9731	15.9339	54.5735
2	43.5000	17.2468	38.9975	31.7505	17.5025	51.0027
2	41.5000	19.2300	39.3205	33.4404	19.1795	47.3295
2	39.8184	21.0000	39.5046	34.7331	20.6769	44.2669
2	37.9689	23.0000	39.6105	35.9749	22.4207	41.0251
2	36.1256	25.0000	39.6104	37.0063	24.2640	37.9937
2	34.2560	27.0000	39.4970	37.8459	26.2470	35.1541
2	32.3387	29.0000	39.2555	38.5087	28.4057	32.4913
0	30.6773	30.6773	38.9387	38.9379	30.3840	30.3848

APPENDIX D

RESULTS FOR THE ETHANOL—BENZENE—WATER TERNARY SYSTEM USING ESTM – DEVIATION BETWEEN CALCULATED (INTERPOLATED) AND EXPERIMENTAL CONCENTRATIONS IN MOLE PERCENT :

	LEFT COMPONENT		UPPER COMPONENT		RIGHT COMPONENT		CALC–
	PHASE 1	PHASE 2	PHASE 1	PHASE 2	PHASE 1	PHASE 2	RMS
EXP. TIE LINE	93.0000	0.4000	6.9000	3.5000	0.1000	96.1000	
CALC. TIE LINE	93.1021	2.4694	6.4370	2.7178	0.4608	94.8127	
CALC—EXP	0.1021	2.0694	−0.4630	−0.7822	0.3608	−1.2873	1.0729
EXP. TIE LINE	85.2000	0.8000	14.6000	6.7000	0.2000	92.5000	
CALC. TIE LINE	85.2794	3.2539	13.6323	5.9139	1.0883	90.8321	
CALC—EXP	0.0794	2.4539	−0.9677	−0.7861	0.8883	−1.6679	1.3634
EXP. TIE LINE	73.0000	2.6000	25.5000	10.0000	1.5000	87.4000	
CALC. TIE LINE	74.0718	4.7351	23.0457	10.9090	2.8825	84.3560	
CALC—EXP	1.0718	2.1351	−2.4543	0.9090	1.3825	−3.0440	1.9889
EXP. TIE LINE	67.1000	5.8000	30.4000	16.6000	2.5000	77.6000	
CALC. TIE LINE	65.7575	6.3221	29.0638	15.2181	5.1787	78.4598	
CALC—EXP	−1.3425	0.5221	−1.3362	−1.3819	2.6787	0.8598	1.5102
EXP. TIE LINE	54.3000	10.2000	37.8000	24.4000	7.9000	65.4000	
CALC. TIE LINE	53.3566	10.4090	35.9070	23.3334	10.7363	66.2576	
CALC—EXP	−0.9434	0.2090	−1.8930	−1.0666	2.8363	0.8576	1.5511
CALC—EXP RMS.	0.8784	1.7424	1.5839	1.0103	1.9000	1.7424	1.5266