THE SYNTHESIS AND PROPERTIES OF SOME POLYMER HYDROGELS

Dissertation

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BRYN HIRD

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CONTENTS

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ABSTRACT

The interactions between water molecules and polyelectrolyte species in aqueous solutions are reviewed and are used to infer interactions occuring in swollen crosslinked polyelectrolyte hydrogels. Linear poly(acrylic acid) and derivatives neutralised to varying degrees with alkali-metal hydroxides are prepared and characterised. Samples of these compounds are crosslinked by γ-irradiation to form hydrogels. Hydration studies on linear polymers, crosslinked material and a commercial polyacrylate hydrogel indicate a possible hydration structure and provide some insight into the nature of water-polymer interactions within a swollen polyacrylate gel.

1 INTRODUCTION

1.1 Hydrogels

1.1.1 Definition and Classification

Hydrogels consist of hydrophilic polymers which have been crosslinked (covalently, ionically or by molecular association (See Section 1.1.2)) to varying degrees in order to form insoluble three-dimensional network structures. These three-dimensional matrixes are capable of absorbing up to several hundred times their own mass of water, the extent of water uptake being governed by factors such as the charge density of the polymer chains, degree of crosslinking and presence of small electrolyte ions.

Hydrogels may be classified as being natural (e.g. gelatin, starch, carrageenan, agar-agar etc.), or synthetic (e.g. crosslinked poly(acrylic acid), poly(hydroxyethyl methacrylate), poly(vinyl alcohol), poly(vinyl pyrrolidene) etc.), although a number of semi-synthetic hydrogels have been made by grafting synthetic side-chains onto a natural polymer backbone e.g. starch - poly(acrylonitrile). [1]

1.1.2 Crosslinks

The mechanical strength of a hydrogel depends on the number and nature of the crosslinks. A high degree of crosslinking reduces the ability of the polymer matrix to swell and hence inhibits water absorption, but leads to a physically stronger hydrogel than in the case of a lightly crosslinked system. The crosslinks

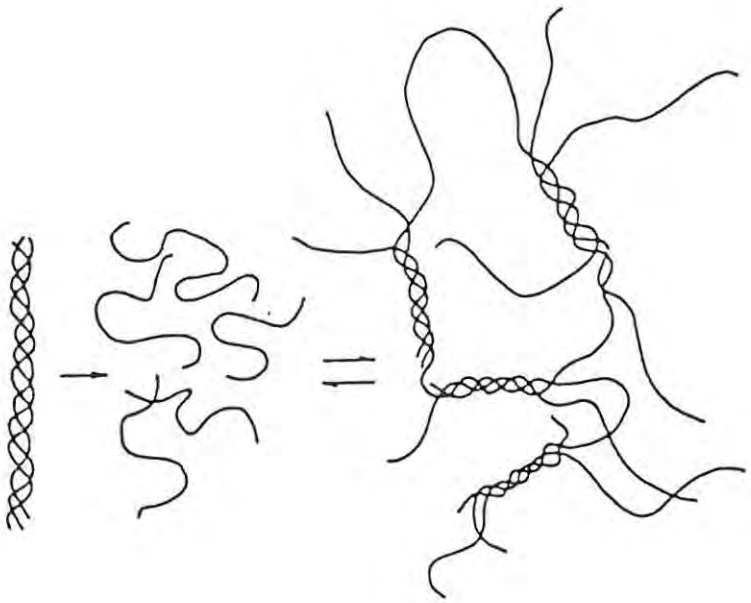

Fig. 1 a: Schematic representation of the collagen ⟶ gelatin solution ⟶ gelatin gel transformation, showing triple-helix molecular associations. Reproduced from ref. 2.

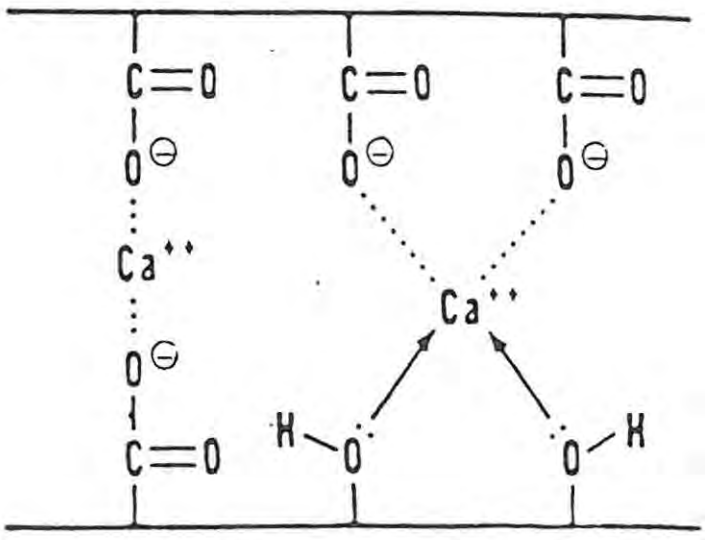

Fig. 1 b: Schematic representation of ionic crosslinking by divalent calcium ions in algin gels. Reproduced from ref. 1.

may be simple molecular associations, ionic bonds or covalent bonds. The mechanically strongest hydrogels result from numerous strong covalent crosslink bonds.

Intermolecular associations may take the form of double helixes, (e.g. carrageenan) or triple helixes (e.g. gelatin). Ionic crosslinks are formed by polyvalent ionic species bonding ionically to more than one polymer chain.[1,2] (See fig. 1). Covalent crosslinking can be achieved by the incorporation of polyfunctional monomers during polymerisation, or by irradiation after polymerisation.[3] The latter technique was used in the present study. This yields a hydrogel free of crosslinking agent 'impurities', but may lead to some degradation of the gel. (See section 3.3.1).

1.1.3 Applications

As a result of their superabsorbent properties, hydrogel polymers are potentially very useful in applications such as absorbent disposable towels, absorbent dressings for medical applications , moisture retaining soil additives or seed coatings, and general drying agents.[1] Other properties of these gels such as slow diffusion rates [4,5] of large molecules through the swollen matrix have made them useful in applications such as battery separators, dialysis and reverse osmosis membranes, and controlled drug release agents.[6,7,8] They are also commonly used for optical contact lenses,[8,9] prosthesis and adhesives, as well as rheological control agents in foods and paints.[1]

A major problem encountered in the practical application of these materials is the marked reduction of their absorbing capacity in the presence of simple salts.[10,11] Many of the potential applications of hydrogels require the absorbence of dilute solutions of various salts (body fluids and plant nutrients). Although it is possible to remove the ions from solution by means of ion exchange resins,[12,13] recovery and regeneration of the resin is impracticable in many instances thus making this technique prohibitively expensive.

Water absorbencies of up to 1250 grams per gram of dry polymer have been reported for acrylate hydrogels.[14] The properties of the gel can be altered by using different homopolymers or copolymers of controlled composition. Polymerisation is usually effected using a free-radical mechanism initiated by compounds such as 2,2′ azo bis-(2-methylpropionitrile) (AIBN) or benzoyl peroxide,[15] or by ionising radiation such as ^{60}Co γ-rays.[16,17,18] Homopolymers and copolymers of varying monomer ratios of acrylates , acrylamides, maleates and vinyl alcohols have been reported.[19-22] Crosslinking agents (polyfunctional species) used include allyl acrylate and ethylene glycol [14,15] or polyvalent ionic salts such as aluminium nitrate.[23]

1.2 Water

A detailed understanding of the interaction of water and electrolyte ions with the polymer is of obvious commercial importance. Although it has been possible to construct gels of

improved properties or to modify existing natural polymers to improve their gel qualities, the structure of the hydrogel and the mechanism of water immobilisation is still incompletely understood.[1]

In the swollen state, a firm hydrogel can contain up to several hundred times the mass of polymer present in the gel. This can be equivalent to several thousand molecules of water per repeat unit of the polymer. Thus, by far the greater proportion of a swollen hydrogel consists of water, and hence an understanding of the nature of the interaction of the water molecules with themselves and the polymer chains would greatly assist an investigation into the fundamental characteristics of such a gel.

1.2.1 The Flickering Cluster Model

Many theories have been proposed to account for the anomalous behaviour of water based on the fundamental properties of the water molecule,[24-26] one of the currently most accepted theories being the 'flickering cluster' model of Frank and Wen.[27] This theory proposes that substantial forces of attraction exist between the molecules of water in the liquid state.[28] This is evidenced by the unusual physical properties of water relative to chemically similar compounds such as ammonia and hydrogen sulphide. Frank and Wen pointed out that when a hydrogen bond forms between two molecules, considerable polarity is developed. The dipole produced makes it more probable that a second hydrogen bond will form, then a third, and so on. In this way, several

hydrogen bonds can form very rapidly in a small volume of liquid. A short time afterwards, this hydrogen bonded volume will 'melt' due to kinetic energy in the liquid. Thus small elements of volume are rapidly transformed into ice-like clusters and are rapidly melted.[29]

The model predicts an average second-neighbour hydrogen bond length of 2,85 Å . It would therefore be expected that any molecule capable of forming hydrogen bonds of this length, submerged in liquid water, would perturb the equilibrium between the solidlike cluster components and the fluidlike components of the water with a net result of considerably enhancing the overall hydrogen bond structure.[29-31]

1.2.2 Polarized Multilayer Theory

In order to explain reduced partial molar volumes of water [32] and other observed effects in the neighbourhood of a hydrophilic surface, it has been proposed that water exists as polarized multilayers covering such a surface.[33,34] The first layer of water molecules is attracted strongly by the surface, the second layer being adsorbed essentially not by the surface, but by the first adsorbed layer. The adsorption thus propagates from layer to layer with the forces of attraction becoming progressively weaker for each successive layer as the distance from the surface increases.[35]

There is a great deal of experimental evidence in support of the polarized multilayer theory and some researchers have postulated

that many layers may exist and that they may extend over relatively large distances from the surface of a hydrophilic macromolecule.[33,34]

1.3 Water-Polymer Interactions

There is an obvious interaction between the water molecules in a swollen hydrogel and the hydrophilic polymer matrix. Because water is a highly polar liquid, the hydrophilic polymer involved in gel formation must also be polar in order to interact with the water molecules. Polar functional groups which are attached to the polymer backbone tend to ionise to varying degrees in the presence of water to form charged polymeric functionalities. (See section 1.3.1.1.1.2)

A study of such a polyelectrolyte before crosslinking is a great deal simpler than a study of the gel, as the linear polymer is soluble and many of the fundamental properties of gels may be inferred from results of experiments performed on polyelectrolyte solutions. The more lightly crosslinked the polymer, the more closely the hydrogel will approximate a true polyelectrolyte solution. When only a few crosslinks per polymer molecule exist, the chains in the swollen hydrogel can be assumed to behave in a similar fashion to those in a solution of comparable concentration, except for obvious differences such as the translational motion of the macroions.

1.3.1 Linear Polyelectrolytes in Solution

Although a number of detailed theoretical treatments of polyelectrolyte solutions are available, they invariably omit or oversimplify some of the complexities of the real system by adopting idealised models.[36] The pertinence of approximations inherent in such models can be judged by assessing how well they can account for various experimental observations.

The presence of a large number of charged species attached to a macromolecule produces some striking effects that are not generally observed in solutions containing uncharged macromolecules of similar chemical composition, or in solutions containing an equivalent concentration of unpolymerised charged molecules.[36] The superimposition of contributions from these charges produces a strong electric field which does not diminish in accordance with the inverse square law for point charges. High molecular mass macroions tend to develop an ordered structure in solution even at relatively high dilution, thus demonstrating the existence of strong long-range electrostatic forces exerted by the overall polymeric charge.[2]

Most of the distinctive features of polyelectrolyte solutions can be explained at least qualitatively in terms of the field arising from the polyion charges. In dilute solutions, the primary variables that determine the strength of this field are the charge density of the polyion and the concentration of added simple electrolyte.[36]

In this study, poly (acrylic acid) and it's derivatives obtained

by partial or complete neutralisation were investigated. Poly (acrylic acid), PAA, is a typical example of a synthetic water soluble polyelectrolyte which can be crosslinked to form an absorbent gel. The charge density, and hence the resultant electric field of the polyion can easily be controlled over a wide range without extensive modification of the polymer, by neutralisation of the acidic side-groups with a suitable base. The selection of PAA was further justified by the fact that it is the simplest model polymeric substance for the determination of the hydration of the carboxyl groups. [37]

1.3.1.1 Factors affecting the polyion Field

1.3.1.1.1 Linear Charge Density

1.3.1.1.1.1 Number of charges per unit length

The number of charges per unit length of a polyion can be altered synthetically by incorporating monomers with different numbers of ionic groups in the polymer backbone, or by ionising some of the functional groups attached to the backbone. The greater the ratio of ionised groups to unionised groups on a polymer molecule, the smaller will be the average distance between charged species. However, the relationship between the degree of ionisation and the average distance between charges on a flexible polyion such as PAA, tends to be non-linear. The Coulombic repulsion between charges increases as the average distance between them decreases, thus causing the dimensions of the polyion to change with change in ionisation level. [38]

In the case of a weak polyacid such as PAA, ionisation of the carboxylic groups can be achieved by neutralisation with a suitable base (See section 1.3.1.1.1.2). Because PAA is a weak acid, relatively few of the carboxylate groups dissociate or ionise to form charged species in an unneutralised PAA solution. For a degree of neutralisation greater then $\alpha = 0,2$, where α is the fraction of neutralised acid groups on the polyion, the degree of ionisation can be considered equal to the degree of neutralisation [37]. This shows that the Coulombic forces between segments are greatly affected by neutralisation. These forces are strongest between neighbouring charges on the chain [39], but long-range forces have also been shown to be important. [40]

From titration and viscosity behaviour,[41,42] it appears that in the PAA molecule nearest-neighbour interaction is a large part of the total interaction and must be taken into account in models and theories correlating phenomena observed experimentally.

There have been numerous attempts to describe the shape of dissolved polyions in terms of analagous models with various modifications to include the effects of the macromolecular charge that must alter the interactions of both adjacent and distant pairs of segments in the chain.[36]

In principle, Coulombic repulsion between charges on adjacent segments of a polymer molecule may cause a change in the local conformational distribution, hence altering both the distance between neighbouring charges and the overall dimensions of the polyion chain.[2]

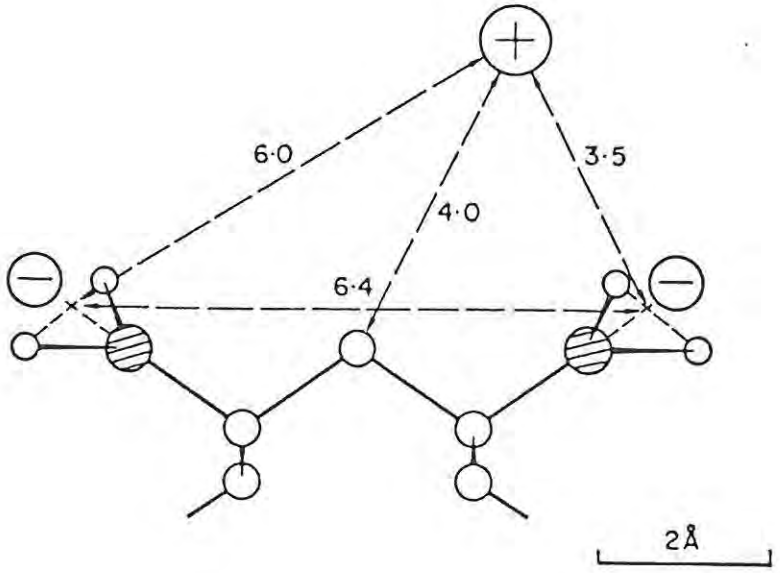

Fig. 2 a: Charge distribution which minimises the coulombic energy for a GG conformation of a racemic pair of monomer units.

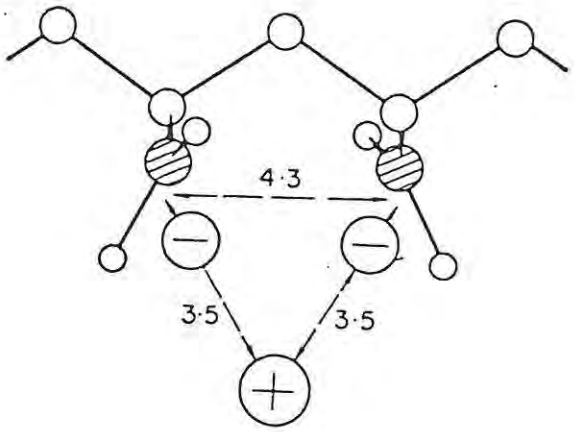

Fig. 2 b: Charge distribution which minimises the Coulombic energy for a TT conformation of a racemic pair of monomer units. Reproduced from ref. 39.

Lifson [43] has shown theoretically that the distance between charged species in fully ionised PAA can vary from 2,51 to 6,01 Å depending on the rotation of the skeletal bond between charges, larger distances between adjacent charges corresponding to more twisted states of the macromolecule.[43] (See fig. 2). Thus it was expected that the effect of ionisation of the polyelectrolyte would be to increase the repulsion between neighbouring charges and therefore induce the molecule to twist or coil, in order to maximise the distance between charges. However, experimental observations indicate that the PAA molecule expands with increasing degree of neutralisation.[38,44] This was attributed to the uneven distribution of ionic charges inside and outside the molecular coil giving rise to a relatively high intramolecular osmotic pressure which tends to expand the molecule.[43] More recently the expansion of the polyion with neutralisation has been attributed to the lowering of the effective charge density by the 'condensation' of hydrated counterions onto the polymer.[39] (See section 1.3.1.1.2)

However, some researchers have postulated that the macroscopic dimensions of the polyion molecules change on neutralisation without significant alteration of the local conformation of the polymer segments.[45,46] A small difference was detected in the titration curves of isotactic PAA, which was suggested to have a local helical structure, and syndiotactic PAA, which was assumed to have a planar zigzag conformation.[47] (See fig. 3)

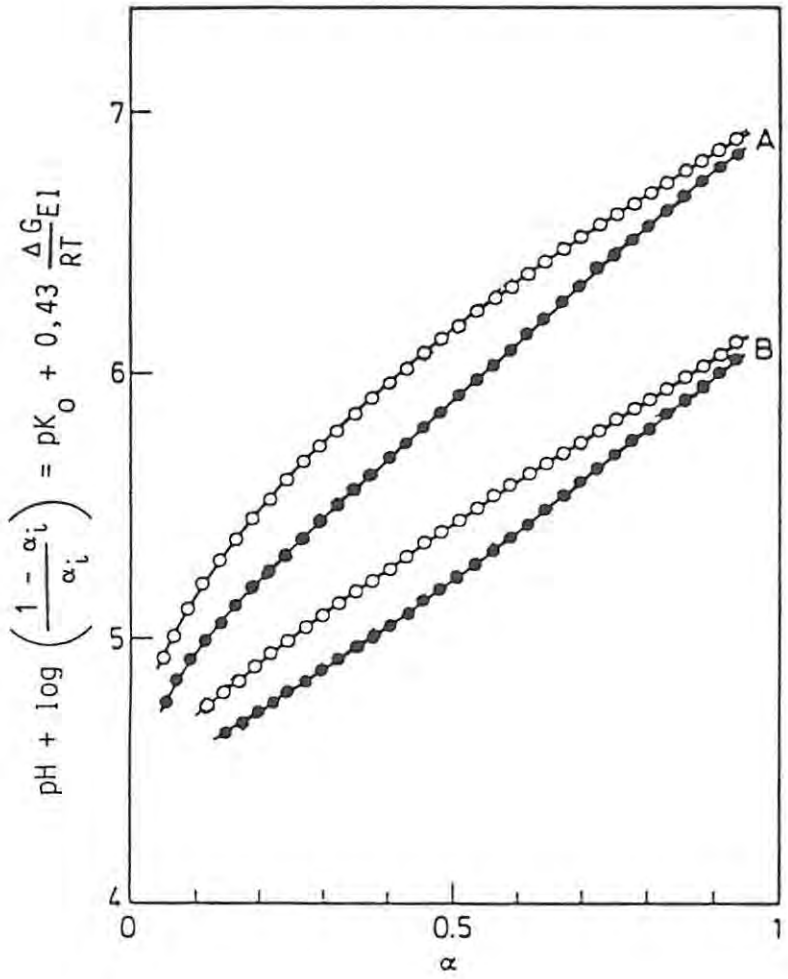

Fig. 3: Potentiometric titration curves of isotactic and syndiotactic poly(acrylic acid)s at 25 °C. A: 0,01 N NaCL ; B: 0,10 N NaCl solns. The white and black circles show expermental data of the isotactic and syndiotactic forms respectively. Reproduced from ref. 42.

NOTE : $K_{app} = \frac{\alpha_i [H^+]}{1 - \alpha_i}$ (See section 1.3.1.1.2)

$$-\log K_{app} = -\log [H^+] + \log \left(\frac{1 - \alpha_i}{\alpha_i} \right)$$

$$pK_{app} = pH + \log \left(\frac{1 - \alpha_i}{\alpha_i} \right)$$

$$pK_{app} = pK_o + 0,43 \frac{\Delta G}{RT} El$$

$$pH + \log \left(\frac{1 - \alpha_i}{\alpha_i} \right) = pK_o + 0,43 \frac{\Delta G}{RT} El$$

It is clear from these curves that isotactic PAA is a weaker acid than syndiotactic PAA at all degrees of neutralisation except as α tends to 1. The upward inflection at high degrees of neutralisation was attributed to the free energy change accompanying the expansion of the flexible macromolecule, rather than that due to a local conformational change, contributing to the total free energy change for dissociation. The coincidence of the titration curves for both stereoregular forms of PAA at complete neutralisation was also proposed to occur due to the added free energy from macroscopic expansion rather than local conformational change.[48]

These deductions were supported by NMR studies in which a change in the local conformation of PAA with neutralisation could not be detected.[11] This led to the conclusion that the local conformations of PAA segments are fixed, and independent of the degree of neutralisation. The expansion of the macromolecule was attributed predominantly to a change in the long-range interactions between charged segments of the polyion rather than a change in nearest neighbour interactions.[45] However, these conclusions were based on the assumption that the short-range interactions between segments are not affected by the presence of charge. No theoretical or experimental foundation was proposed for this assumption. Furthermore, subsequent NMR studies have shown a dependence of the degree of local coiling on the degree of neutralisation in deuterated isotactic PAA.[42]

Recent Raman spectroscopic studies on PAA exhibited changes in the C-C stretching region of the spectra with degree of neutralisation.[49] This was ascribed to the randomisation of the local conformations of segments of the molecular chain as the degree of neutralisation increases. The randomisation of local conformations also accounts for the convergence of the titration curves of isotactic and syndiotactic PAA at complete neutralisation.

The titration curve of PAA exhibits an upward inflection which is not observed in the titration curve of poly (methacrylic acid).[48] This, and other marked differences in the properties of these two polyelectrolytes demonstrate the fact that small structural differences which are difficult to model theoretically can have a profound influence on the behaviour of a polyelectrolyte. The differences in the titration curves of the two polyacids have been explained by assuming that the hydrophobic methyl group of poly(methacrylic acid) reduces the flexibility of the polymer chain in aqueous solution, which implies that the conformation of the flexible PAA backbone is more easily changed. Hence the change in free energy associated with the conformational change should be added to the electrostatic free energy change for ionisation in determining the total free energy change on neutralisation.[48]

1.3.1.1.1.2 Ionic Strength of Structural Charges

In order to preserve the electroneutrality of a polyelectrolyte substance, the polyion charges must be compensated by

counterions; typically ions of low molecular mass such as H^+ or Na^+. [36] In the case of PAA, the H^+ ions can be substituted for metal cations by titration with the required metal hydroxide or by ion-exchange methods. In solution, these counterions can dissociate from the carboxylate anion on the polymer backbone leaving a strong anionic charge on the polyion. Undissociated carboxyl groups are regarded as being non-ionic and are only slightly polar, thus making little contribution to the overall polyion field. Because PAA is a weak acid, relatively few of the carboxylic acid groups ionise in aqueous solution. Neutralised carboxylate groups tend to ionise more easily and the degree of ionisation of the polymer, α_i , may thus be increased by neutralisation.[2]

$$\sim\!\!\sim COOH \rightleftharpoons \sim\!\!\sim COO^- + H^+$$

$$\alpha_i = \frac{[\sim\!\!\sim COO^-]}{[\sim\!\!\sim COO^-]+[\sim\!\!\sim COOH]}$$

$$K_o = \frac{[\sim\!\!\sim COO^-][H^+]}{[\sim\!\!\sim COOH]}$$

α_i is the fraction of ionised groups on the polymer and

K_o is the equilibrium dissociation constant for the dissociation of a monomeric charge.

The apparent dissociation constant, K_{app}, is a function of the degree of ionisation of the polymer α_i .

$$K_{app} = \frac{\alpha_i [H^+]}{1 - \alpha_i}$$

The magnitude of K_{app} is determined not only by the free energy

required to dissociate an isolated monomeric charge, but also by ΔG_{El}, the electrostatic free energy change associated with the removal of the counterion from the field established by other charges on the polyion.[36,42,48]

$$\Delta G_{app} = \Delta G_{o} + \Delta G_{El}$$

$$-RT \ln K_{app} = -RT \ln K_{o} + \Delta G_{El}$$

$$pK_{app} = pK_{o} + \frac{0,43\ \Delta G_{El}}{RT}$$

For a weak polyacid such as PAA, ΔG_{El} is positive, it's magnitude depending on all the factors that determine the electric field surrounding the polyion.[36]

In the titration curves for PAA represented in fig. 3, as the degree of neutralisation of the polymer is increased in the absence of added salt, the polyion becomes a much weaker acid than its monomeric analogue. This effect is due to the increase in the strength of the polyion field.[42]

1.3.1.1.2 Counterion Binding

If a polyelectrolyte molecule were completely ionised, i.e. all of the functional groups on the polymer dissociated, it would provide a region of exceedingly high charge density when compared to charge densities encountered in similar non-polymeric ionic solutions.[39,50] The increased strength of the polyion field due to ionisation causes the counterions to cluster around the polymeric charges thereby effectively reducing the charge density

of the polyion. Dilution of the polyelectrolyte solution has little effect on the concentration of counterions in the neighbourhood of the polyion.[51] Even at infinite dilution, self-ionization of the solvent leads to appreciable counterion concentrations in regions close to the polyion.[2]

The counterions within the domain of the polyion field are regarded as being bound to the polymer as opposed to free ions in the bulk solution. The bound ions reduce the charge density of the polyion and the resulting effective charge density, ξ , is an important parameter in models that have been proposed to account for observed phenomena in polyelectrolyte solutions.[52] When the effective charge density of a weak polyacid is lowered by counterion binding, the apparent dissociation constant, K_{app}, is affected, and the titration curve of the polyacid is shifted to a lower pH. This gives rise to the curvature of the titration curves of PAA in fig. 3. (See section 1.3.1.1.1).

Various properties such as ion migration , diffusion rates, counterion activity etc. have been studied in order to determine the extent of counterion binding in polyelectrolyte solutions.[50] However, different values for the fraction of bound counterions have been obtained for the same system depending on the experimentally determined parameter. These differences are thought to be due to varying strengths of ion-binding to the polymer. Some of the observed parameters are dependent only on the fraction of tightly bound ions, while others are influenced by more loosely bound counterions as well.[53]

Counterions which are in direct contact with one or more charged groups on the polyion with no intervening water molecules are said to be 'site bound'.[54] If the hydration layer of the counterion remains intact, or if the counterion in it's free state is only slightly hydrated, then it's interactions with specific locations on the polyion will be sufficiently weak to be dominated by the overlapping Coulombic fields of neighbouring charged groups. In this case, the counterion will be drawn to the polyion as a whole by the strong polyanionic field, but will not be bound to a specific group and will be free to move about the polyion surface. Such counterions are said to be territorially bound.[54]

Although a continuum of bound states may exist ranging from covalent complexation to complete territoriality,[54] a two-state model is generally employed in theoretical treatments of polyelectrolyte solutions for simplicity.[55] With few exceptions, theoretical treatments have been based on either the Poisson-Boltzmann equation,[56,57] or the counterion condensation formulation proposed by Imai and Onishi and developed primarily by Manning.[2,58]

The counterion distributions obtained by the Poisson-Boltzmann theory account only for the mean electrostatic field due to the small-ion environment and neglect other short-range forces among the small ions. The counterion condensation theory is based on free energy minimisation using a simple two state model, and despite obvious approximations,[2] there is little question that

the counterion condensation theory does capture the qualitative structural features of polyelectrolyte solutions.[58]

This theory proposes that as the effective charge density is increased by neutralisation, a critical value of ξ is reached above which counterions can be said to 'condense' onto the polyion. This may be represented as

$$f = (N\xi)^{-1} \quad \text{when} \quad \xi > N^{-1}$$

and

$$f = 1 \quad \text{when} \quad \xi < N^{-1}$$

where f is the ratio of structural charge which is uncompensated by bound counterions to the total structural charge on the polyion, and N is the counterion valence.[59,60]

The critical charge density (ξ =1) for the condensation of Na^+ ions onto PAA corresponds to a degree of neutralisation α = 0,35 i.e. one ionic charge per 7 Å of the polyion.[2] It is clear from quadrupole relaxation data on the ^{23}Na nucleus that Na^+ condensation on PAA does not occur at ξ = 0,8 and does occur at ξ = 1,1 hence supporting the counterion condensation theory.[61,62] (See fig. 13, Section 3.4.2).

The fact that the ratio of the net charge density to the linear charge density of the polyion, f, depends on no specific properties of the counterion and polyion other than the valence of the former and the linear charge density of the latter, indicates that only long-range interactions between the constituents of the solution are involved.[54] Since site binding is determined by specific short-range interactions, the theory

predicts that all bound univalent ions should be territorially held. There is strong evidence in support of this in the Na^+, PAA system.[59,63,64] However, complexation with multivalent cations is known to occur.[49,52,65]

The counterion condensation theory also predicts that the extent of counterion binding is independent of the concentration of free counterions in solution or the ionic strength of the solution in a univalent system.[54]

It is well established that the degree of binding of univalent counterions to a polyelectrolyte molecule such as PAA is not significantly affected by the concentration of added simple univalent salt under non-extreme conditions.[4,44,66,67] The effect of added salt is greater at low degrees of neutralisation due to the high covalent contribution to the binding free energy.[68]

In order to account for deviations from the predictions of simple theory at high polymer concentrations, scaling concepts have recently been introduced to account for polymer-polymer interactions. These interactions reduce the effective flexibility of the polymer chain and may thus affect the dimensions of the polymer at high concentrations.[69,70]

1.3.1.1.3 Addition of Salt

Although the presence of simple univalent salt does not affect the degree of counterion association in a polyelectrolyte

solution to a large extent [10,11], the high polyion field causes oppositely charged electrolyte ions to accumulate in the volume of solution surrounding the polyion. This high local concentration of unbound ions affects every process in which the polymeric charges are involved, effectively reducing the Coulombic interactions among the polyion charges themselves and with other charged species in solution, by forming a screening atmosphere around each polymer chain.[71] Thus the presence of salt has the same effect as counterion binding by diminishing Coulombic interactions of the polymer charges, therefore lowering ΔG_{El} and reducing the apparent pK value of the polyion for every value of α, i.e. increasing the strength of the polyacid.

Hence, although the local characteristics of the segments of the macromolecule (local configuration, short-range electrostatic repulsion, distance between neighbouring charges etc.) are not significantly affected by the addition of univalent salts, the change in long-range effects is quite marked. Variation in the average end-to-end distance of the polymer chains and hence the viscosity of polyelectrolyte solutions, has been shown to be markedly dependent on the ionic strength of the solution.[86] Viscosity data of polyelectrolyte solutions containing no added salt are complicated by long-range polymer-polymer interactions. If the polyelectrolyte solution is diluted with salt solution of a concentration such as to keep the ionic atmosphere surrounding the polyions unchanged during the dilution process, inter-molecular forces are effectively screened while intra-molecular forces remain unchanged therefore maintaining the dimensions of

the polyelectrolyte molecule.[2] This procedure, known as 'isoionic dilution', yields linear plots of reduced viscosity against polyelectrolyte concentration, which can be extrapolated to zero concentration in order to determine the molecular mass of the polymer. (See section 3.2.4).

The screening of inter-molecular interactions by simple electrolyte ions allows the macromolecules to approach each other more closely, therefore showing a reduction in the volume of solution associated with each polyion molecule.[66]

1.4 Crosslinked polyelectrolytes in the presence of water

Although the detailed structure of a swollen hydrogel is incompletely known,[1] various studies have been undertaken in order to investigate the forces involved in causing the observed high water sorption and rigidity of such a system.[28,72-74]

1.4.1 Factors Responsible for Gel Swelling

1.4.1.1 Osmotic Forces

In a system containing crosslinked polyelectrolyte molecules and pure water, the three dimensional polymer network can be considered to act as a permeable membrane.[66] Because the anions ($\sim\!\!\sim COO^-$) are fixed to the polymer matrix, they are unable to diffuse through the system. In order to preserve electrical neutrality, the cations therefore also tend to remain within the polymeric structure. Hence the ionic concentration within the insoluble network tends to be greater than that in the

surrounding medium, and osmosis of water into the gel occurs, causing swelling. The osmotic pressure in such a system is relatively large, and the resultant internal pressure of the gel on swelling has been thought to be responsible for the rigidity of the gel.[1]

The addition of salt to such a system [51] reduces the difference between the concentrations of ionic species inside the gel and in bulk solution, thereby reducing the osmotic pressure and inhibiting swelling of the gel. The internal pressure of the gel is known as the Donnan osmotic pressure and is equal to the hydrostatic pressure required to maintain equilibrium of a polyelectrolyte solution, through a membrane permeable to both salt and water, if the concentrations of polyelectrolyte molecules and simple salts are equal on either side of the membrane.[66]

At equilibrium, the concentrations of the simple salt will be unequal on the two sides of the membrane, but the potential difference across the membrane will be zero.[75,76] In the case of an unneutralised weak polyacid gel, the pH of the bulk solution can be adjusted so that the concentrations of H^+ ions inside and outside the gel are equal. This is known as the isoelectric point.[77] Although water uptake is a minimum at this point, the fact that considerable swelling is still observed under these conditions indicates that Donnan osmotic effects are responsible for only part of the swelling.[51,77] In this study, osmotic effects are critically evaluated.

1.4.1.2 Electrostatic Forces

Local electrostatic forces exerted on neighbouring molecules by each individual charge on the polymer are known as short-range forces. These forces are relatively strong and are responsible for the primary hydration of the polymer. The polymer charges are also thought to act cooperatively and exert long-range forces on species beyond the primary hydration region. (See section 1.3.1)

The importance of electrostatic effects in the sorption process can be demonstrated by applying a potential difference across a sample of a swollen polyelectrolyte gel. An infinitesimal change in electric potential across the gel causes the gel to collapse, the volume of the collapsed gel being up to several hundred times smaller than that of the swollen gel.[78] This discrete, reversible volume change at a particular applied potential indicates that there exists a critical stress below which the gel is swollen and above which the gel collapses.[78]

1.4.2 Bound Water

Water which is enclosed in the three-dimensional structure of the hydrogel can be classified as bound water or free water. Free water can be defined as that portion of the water held which has physical properties indistinguishable from those of ordinary liquid water, whereas there is a detectable difference between the properties of bound water and those of free or bulk water.[73]

Many methods have been used for determining the degree of binding in gels, including studies of equilibrium vapour pressure, partial molar volumes, nuclear magnetic resonance and differential scanning calorimetry.[31] Unfortunately, differences in the sensitivity of measurement of each of these characteristics give rise to different values for the amount of bound water in a particular system depending on the technique employed.

The strength of binding of the water may depend on how the water molecules are associated with the polymer matrix. Several types of bound water have been postulated :[28]

i) Water which is strongly chemically bound, such as in the hydration of salts

ii) Water adsorbed on hydrophilic sites of the molecule by hydrogen bonding

iii) Water attracted to ionic sites by the molecular dipole of the water molecule

iv) Water held by capillary forces between the surfaces of the insoluble network

v) Water held within an amorphous network due to supersaturation of dissolved molecules

vi) Water held in solution or suspension by 'long-range' forces

Although it is not possible to determine the relative amounts of water bound by each specific set of forces, it is evident that the first three types are bound by short-range forces and are the most firmly held. However, they do not constitute a significant proportion of the bound water in a hydrogel as there are only a limited number of sites available for direct interaction with

water molecules. Most of the bound water in a swollen gel is comprised of the remaining three types.

1.4.2.1 Primary Hydration

At very low degrees of hydration, discrete binding energies may be experienced, a particular binding energy being associated with a specific type of binding of the water molecules to the polymer. Once all the sites associated with a particular binding energy are filled, a change in properties, such as molar volume of the adsorbed water, on further hydration of the polymer, may be detected.

In recent hydration studies of sodium polyacrylates at various degrees of neutralisation, at a constant relative humidity of 73%, it was observed that the equilibirium water uptake increased only slightly with increasing neutralisation up to $\alpha = 0,3$. [79] At higher degrees of neutralisation, the molar equilibrium water content increased linearly with α to give a maximum hydration number per repeat unit of 4. This led to the hypothesis that the sodium ion exists in an octahedral coordination state with the coordination sites occupied by the polymeric carboxyl oxygen atoms or by the oxygen atoms of water molecules. Carboxyl oxygen atoms would be in excess when less than one third of the acid groups were neutralised.[79] Above 33% neutralisation, vacant sites in the octahedron would appear which would be available for coordination with oxygen atoms of water molecules.[80] (See fig. 12, section 3.4.2)

Similar studies with Li^+, K^+, Cs^+ and Rb^+ by the same authors have led to analagous models being proposed for these systems, but with different coordination structures and therefore different primary hydration numbers for each ion. [81-83]

On the basis of enthalpy and entropy data for protein systems,[34] it has been suggested that water molecules in the hydrated shell of a counterion, in the region of a hydrophilic polymer chain, merge with water molecules in the polarized multilayers surrounding the macromolecule mutually reinforcing the hydration structures of the polyion and the counterion. [34] As the hydrated diameter of a cation such as Na^+ is thought to be relatively large (5 Å ; sixteen water molecules in the hydration shell)[84,85], structuring effects may exist at substantial distances from the polyion.

1.4.2.2 Water Held by Long-Range Forces

Beyond the highly structured region surrounding each polyion, long-range forces exerted by the cooperative effect of the polyion charges may perturb the equilibrium between ice-like clusters and free water molecules thus enhancing the structural properties of the water.

Whenever water is restricted in a channel of molecular dimensions, it adopts a particular structure which is not present in the bulk liquid. Water constrained by microscopic glass capillaries of up to 10 μm in radius has a vapour pressure considerably lower than would be expected on geometric grounds,

thus suggesting that it's liquid structure is more highly organised. [86,87]

In a fully neutralised sodium polyacrylate gel containing 1 g of polymer per 1000 g of water, approximately $1,56x10^{-22}$ l of water is associated with each repeat unit. As the highly charged polyions tend to be distributed as far apart from each other as possible, it is reasonable to assume that the polymer chains are evenly distributed throughout the gel. Employing a cylindrical-cell model for the water surrounding each polymer segment of length 0,25 nm, permits calculation of the cell radius, i.e. the distance of the furthest water molecules associated with a polymer segment from that segment.[55] A simple calculation shows this distance to be in the region of 14 nm, but subtracting the radius of the rod-like polymer segment itself and the thickness of the structured hydration layer surrounding the rod, yields an effective cell radius of less than 10 nm. [55] Thus it is evident that some of the water furthest from the polymer chains in a swollen hydrogel may be influenced by so-called capillary forces. The channels between macromolecules in the swollen state of the gel have been termed 'transient capillaries' as they vary in dimension with the extent of swelling of the gel.[35]

The purpose of the present study is to investigate more fully the molecular interactions occuring in a swollen acrylate hydrogel at various degrees of crosslinking, neutralisation and added salt concentration in order to gain an insight into the structure of the gel.

2 EXPERIMENTAL

Linear poly(acrylic acid) was prepared by free radical polymerisation of acrylic acid. Derivatives of the PAA were obtained by neutralisation to varying degrees with alkali solution. The PAA and its derivatives were then characterised by various analytical techniques, and samples of each material were crosslinked by γ-irradiation to form hydrogels. The water uptake properties of both linear and crosslinked material under controlled conditions were investigated by gravimetric techniques. A commercial, crosslinked, polyacrylate hydrogel, Aquakeep SH4, was also studied in this fashion.

2.1 Synthesis

2.1.1 Reagents

Acrylic acid was distilled between 50 and 53 ^{o}C at 0,1 mm Hg to remove inhibitor, and was kept frozen until required. 2,2′ azo-bis-(2-methylpropionitrile) (AIBN) was recrystallised from methanol and stored at 0 ^{o}C.

2.1.2 Polymerisation

Due to the hygroscopic nature of poly(acrylic acid), recovery of the polymer from aqueous solution is extremely difficult. Hence polymerisation of acrylic acid was carried out in a dilute solution of the momomer in benzene, the insoluble polymer precipitating from solution.

Thus 0,229 g ($1,39 \times 10^{-3}$ mol) AIBN was dissolved in 98,2 g (1,36 mol) acrylic acid and added dropwise over one hour to 1000 ml dry distilled benzene purged with nitrogen at 60 °C with stirring. Approximately 1,5 hours after the start of the polymerisation, PAA precipitated to give a thick slurry. This was filtered, washed with dry benzene and vacuum dried at 60 °C. The yield of dry material was approximately 96 g (98%).

2.1.3 Neutralisation

Four PAA samples of approximately 10 g each were dissolved in water (50 ml) and neutralised to 32, 50, 67 and 100 mole percent by dropwise addition of the calculated amount of a standard 2,65 molar sodium hydroxide solution with stirring. Recovery of the polymers in a form convenient for handling was effected by freeze-drying each solution from a thin film on the walls of a 250 ml flask evacuated to 0,1 mm Hg. The polymers thus obtained had an eggshell-like appearance. Each of the four samples was treated by cold soxhlet extraction with a 95:5 ethanol:water mixture for 12 hours to remove possible traces of low molar mass salt, and redried under vacuum at 60 °C. An attempted extraction of a sample of unneutralised PAA in a similar fashion was unsuccessful due to the high solubility of the polyacid.

A standard caesium hydroxide solution was obtained by eluting a solution of 5 g A.R. caesium iodide in a small volume of water through a 50 ml column of swollen Amberlite IRA-400 anion exchange resin in the hydroxide form. The resulting caesium hydroxide solution was shown to be free of halide by addition of

a few drops of silver nitrate solution to a small aliquot, then standardised against hydrochloric acid using methyl orange as the indicator. A standard potassium hydroxide solution was prepared from a commercial ampoule. These solutions were used to prepare fully neutralised poly(caesium acrylate) and poly(potassium acrylate) salts by addition of the calculated volume of standard solution to a weighed sample of PAA dissolved in a small amount of water. The products were obtained by free-drying as before.

2.2 Analysis

Preliminary experiments indicated that the polymers were extremely hygroscopic and absorbed water even when stored in a dessicator. All samples were therefore dried in a vacuum oven at less than 0,01 mm Hg at 60 ^{o}C for 24 hours immediately prior to being weighed.

2.2.1 Microanalysis

Samples of unneutralised PAA and samples neutralised to 32, 50, 67 and 100 mole percent with sodium hydroxide viz. designated NaPAA 32, NaPAA 50, NaPAA 67 and NaPAA 100 respectively, were sent to the National Chemical Research Laboratories of the Council for Scientific Industrial Research for microanalysis. (See section 3.2.1, Table 2)

2.2.2 Titration

In order to determine the percentage purity of the polyacid, a vacuum dried sample was dissolved in water and titrated against a standard sodium hydroxide solution under nitrogen using a pH meter to determine the end point. The extent of neutralisation of the partially neutralised samples was determined experimentally by titration of the remaining acid groups with standard sodium hydroxide solution potentiometrically as before. The proportion of unneutralised acid groups in a sample of the commercial, crosslinked acrylate hydrogel, Aquakeep SH4, was also determined in this manner.

2.2.3 Flame Emission Spectroscopy

Using a Varian Techtron 1000 spectrophotometer, a calibration curve for standard sodium chloride solutions in the range 4 to 10 ppm Na^+ was plotted. From this, the concentration of sodium ions in a standard polymer solution could be determined which yielded the extent of neutralisation of the polymer. (See section 3.2.3)

2.2.4 Viscometry

Viscosity measurements were carried out on standard solutions of PAA and NaPAA 100 in dry distilled 1,4-dioxane and 0,5 M Sodium bromide solution respectively. Using a Technico ASTM D.445 Otswald-type viscometer with a nominal constant of 0,01 cS/s, the intrinsic viscosities of the polymer solutions in the concentration range 0,1 to 1,0 grams of polymer per 100 ml, at

30,0 ^{o}C, were determined. Extrapolating curves of the intrinsic viscosity of each solution vs. concentration to zero polymer concentration yielded the limiting viscosity number, $[\eta]_{\theta}$, which could be related to the viscosity average molecular mass of each polymer. (See section 3.2.4)

2.3 Crosslinking

Five samples each of PAA, NaPAA 50 and NaPAA 100 were sent for irradiation in an Atomic Energy of Canada Ltd. Gamma Cell 220 ^{60}Co irradiator with a nominal capacity of $4,1x10^{14}$ $Bq(s^{-1})$ and a dose rate of 2,5 KGy/hr which was determined by Fricke dosimetry. 1 Gray (Gy) corresponds to 1 Joule of energy absdorbed per kilogram of sample. (1 Mrad = 10 KGy). The five samples of each neutralisation level were irradiated to 10, 25, 50, 100 and 200 KGy total dose. The irradiations were carried out on dry solid state powder samples in glass containers under vacuum.

The irradiated samples were removed from the glass containers, placed in flasks with excess water and allowed to equilibrate for several days in order to detect any gel formation. Only the samples which received the highest dose showed very slight gel formation. All other samples were completely soluble.

It has been shown that crosslinking of water soluble polymers by irradiation occurs readily in relatively dilute aqueous solutions due to radicals being formed in the water and promoting radicals on the polymer.[88] Hence solutions of PAA, NaPAA 50 and NaPAA 100 in the concentration range 2% to 10% were made up in glass

ampoules such that each ampoule contained approximately 100 mg of polymer. The solutions were then degassed by several freeze-thaw cycles, the ampoules sealed under a low pressure of N_2, and sent for irradiation in the dose range 30 to 50 KGy as before. Unfortunately, a large proportion of breakages was sustained in transit due to strain induced in the glass ampoules on sealing. However, the remaining samples afforded a preliminary estimate of the relationship between the degree of neutralisation, concentration of solution and irradiation dose. (See section 3.3, Table 5)

The gel fraction in each sample was obtained by decanting any supernatant fluid, dried in a vacuum oven at 60 ^{o}C for 48 hours, and weighed. Water was then added to each sample in 5 ml portions until no more water was taken up by the gel over a period of several days. Each sample was then drained on a 100 mesh copper wire screen and the gel remaining on the screen after 4 minutes was weighed.[89] Although no quantitative measurement of the mechanical strengths of the gels was made, their relative degrees of firmness could be estimated by inspection and by stirring with a glass rod. The mass of gel samples and their estimated relative mechanical strengths gave an initial estimation of the optimum concentration and dose ranges for the formation of a firm gel with high water absorbing capacity.

Based on these preliminary results, two further batches of PAA, NaPAA 32, NaPAA 50, and NaPAA 100 samples of approximately 100 mg each were prepared in the concentration range 1% to 15%. These

solutions were degassed as before, sealed in glass ampoules under vacuum and despatched for irradiation in the dose range 3 KGy to 75 KGy. After irradiation, the ampoules were carefully opened, and the contents swollen in a slight excess of water for several days before being drained on a 100 mesh nylon screen [19] to determine the mass of swollen gel in each sample. (See section 3.3, fig. 6; Appendix 1)

Each gel sample was then washed, dried as before and weighed. However, the results showed that there was no correlation between concentration of solution, radiation dose and amount of dry material present in each gel. It was therefore apparent that efficient removal of uncrosslinked material from the gel was not being accomplished by the technique employed. Hence selected samples were stirred for 24 hours in a vast excess of water (approx. 1 l per 100 mg polymer), drained, dried and weighed. The mass of dry material thus obtained was a function of solution concentration and total dose.(See section 3.3.2, fig. 7)

2.4 Water Uptake

2.4.1 Rate of Water Uptake

A sample of each of PAA, NaPAA 50, NaPAA 100 and SH4, of approximately 100 mg was weighed into a shallow flat-bottomed dish immediately after being dried at 60 ^{o}C for 24 hours in a vacuum oven. The dish was placed in a small cell through which air at 75% relative humidity was passed at a rate of approx. 2 ml per second. The humidity of the air was controlled by passing it

through a saturated sodium chloride solution.[90] The apparatus was immersed in a water bath of which the temperature could be controlled to within ± 0,5 °C. (See fig. 4). The relative humidity of the air passing through the cell was assumed to be constant over the temperature range employed as it is known that the change in relative humidity with temperature under these conditions is approximately 0,02% per °C.[90]

The dish was removed from the cell at appropriate intervals, rapidly weighed to ± 0,1 mg and immediately returned to the cell. From the mass increase, the water uptake per repeat unit of polymer as a function of time could be determined for each polymer over a range of temperatures. Samples of PAA, NaPAA 50 and NaPAA 100 were studied at temperatures of approximately 20 °C, 30 °C and 42 °C in this way. Condensation of moisture on the lid of the sample cell at higher temperatures was observed.

2.4.2 Equilibrium Water Uptake

2.4.2.1 Relative Humidity Studies on Linear Material

Dry samples of approximately 100 mg each were weighed into shallow flat-bottomed dishes which were then each suspended in a static atmosphere of controlled relative humidity. The humidities were controlled in the range 10% to 90% relative humidity by employing saturated solutions of A.R. grade salts in closed vessels in a temperature controlled environment at 25,0 ± 0,1 °C.[90,91] (See fig.5).

The samples were allowed to equilibrate for several days until no

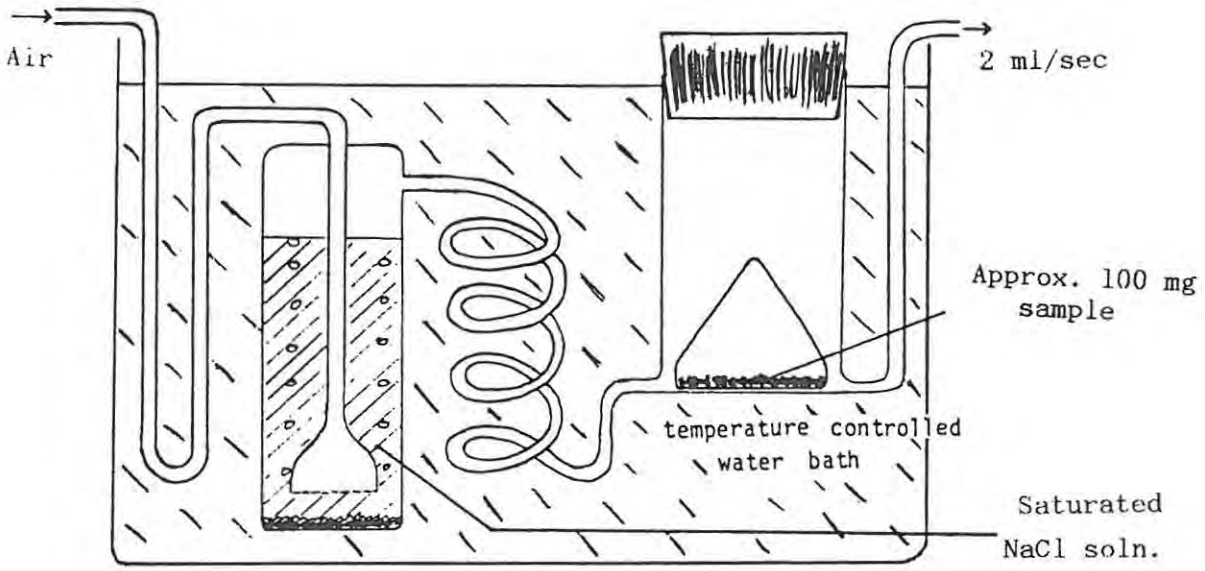

Fig 4: Apparatus for determining rate of hydration of polyacrylates at constant relative humidity and controlled temperature.

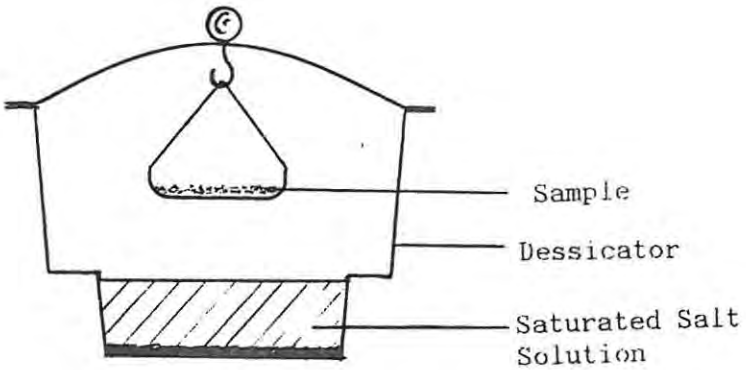

Fig. 5: Apparatus for determining equilibrium water uptake of polyacrylates under controlled conditions.

increase in mass of the sample could be detected over a period of 24 hours. Each sample was then removed from the humidity vessel and rapidly weighed to ± 0,1 mg. From the mass increase, the equilibrium water uptake per mole of repeat unit of each sample as a function of relative humidity could be determined. The water uptake of samples of PAA, NaPAA 32, NaPAA 67, NaPAA 100, KPAA 100, CsPAA 100 and Aquakeep SH4 were studied using this method.

2.4.2.2 Saturated Water Uptake of Crosslinked Hydrogel

The dry material obtained from extracted samples (See section 2.3) was assumed to be free of uncrosslinked polymer and was reswollen in excess water. Remaining acid groups in the gel were neutralised by adding calculated amounts of a standard sodium hydroxide solution, saturated water uptake of the gel being measured at stages during the neutralisation. (See section 3.4.2.2, fig. 14).

2.5 Effect of Salt on Gel Deswelling

Volumetric solutions of various A.R. grade salts were made up in the concentration range 0,02 to 0,7 normal and a 100 ml aliquot of each solution added to an approximately 100 mg sample of dry Aquakeep SH4. The mixtures were allowed to stand for several days at room temperature in order to reach equilibrium, then centrifuged at 4500 r.p.m for 10 min. on a Hattich Universal 1200 centrifuge with an average radius of 8 cm. Supernatant fluid was

decanted and the mass of precipitated gel determined. From the mass of dry material in each sample and the mass of swollen gel, a graph of water uptake vs. conc. of salt solution could be plotted for each of the salts used. The salts used are given in Table 1.

TABLE 1: Salts Used in Gel Deswelling Experiments

Univalent Cationic Salts	Divalent Cationic Salts	Trivalent Cationic Salts
Sodium Fluoride	Calcium Chloride	Ammonium Chloride
Sodium Chloride	Magnesium Chloride	Chromium III Chloride
Sodium Bromide	Barium Chloride	
Sodium Iodide		
Sodium Salicylate		
Sodium Formate		
Potasium Chloride		
Potassium Bromide		
Ammonium Chloride		
Sodium Sulphate		
Sodium Phosphate		

3 RESULTS AND DISCUSSION

3.1 Synthesis

The synthesis of linear PAA as described in section 2.1 gave a high yield of a white powdery product (approx. 98% yield) which was extremely hygroscopic. The product was found to have a high degree of purity and a relatively high degree of polymerization. Chapiro has shown that the free radical polymerisation of acrylic acid in reaction mixtures of low monomer concentration such as that employed in the synthesis of PAA in the present study (c.a. 10%), in a solvent such as benzene, gives rise to a polymer which is completely atactic.[92] Hence stereospecific effects have been disregarded in the analysis and interpretation of observed experimental phenomena.

3.2 Analysis

3.2.1 Microanalysis

The results obtained by microanalysis for the percentage of carbon, hydrogen and sulphated ash was in reasonable agreement with the expected values which were calculated assuming 100% purity of each sample. (See Table 2). The deviations from the expected values could be due to small amounts of moisture absorbed during transit and handling.

TABLE 2: Microanalysis Results for Uncrosslinked Polymers

		Expected value	Obtained value
PAA	%C %H % Sulphated ash	47,5 5,8 0,0	48,12 5,53 <0,30
PAA (extracted)	%C %H % Sulphated ash	47,5 5,8 0,0	48,12 5,53 <0,30
NaPAA 32 (extracted)	%C %H % Sulphated ash	44,0 5,0 23,17	43,52 4,77 22,68
NaPAA 50 (extracted)	%C %H % Sulphated ash	40,7 4,5 43,87	38,70 4,63 39,3
NaPAA 67 (extracted)	%C %H % Sulphated ash	38,7 4,1 56,53	36,87 4,64 49,62
NaPAA 100 (extracted)	%C %H % Sulphated ash	36,4 3,6 71,67	33,05 3,93 64,80

3.2.2 Titration

Potentiometric titration of a sample of linear PAA showed the polymer to be almost 100% pure. Titration of remaining acid groups in the partially neutralised samples yielded values for the extent of neutralisation, α, which were in good agreement with those expected. Titration of fully neutralised samples was obviously not possible. (See Table 3).

TABLE 3: Titration Data for Polyacrylates

	End Point /ml (0,0960 M NaOH)	Sample Mass /g	Degree of Neutralisation
PAA	27,10	0,1875	0%
NaPAA 32	26,75	0,3060	33%
NaPAA 50	27,75	0,4507	51%
NaPAA 67	25,25	0,6980	69%
Aquakeep SH4	14,50	0,5752	70%

3.2.3 Flame Emission Spectroscopy

Standard solutions of NaPAA 32, NaPAA 50 and NaPAA 100 were prepared in order to determine the percentage of sodium present in each sample. An attempt was made to compensate for matrix effects by the addition of sodium-free PAA to the standard NaCl solutions such that the concentration of polymer in the standard reference and sample solutions corresponded appropriately. However, it is known that the viscosities of polyacrylate solutions depend significantly on the degree of neutralisation of the polymer and the concentration of simple salt in solution.[4,93] Hence matrix effects could not be adequately compensated for and the results were thought to be viscosity dependent.

3.2.4 Viscometry on uncrosslinked PAA and NaPAA 100

Limiting viscosity numbers, $[\eta]_\theta$,for PAA and NaPAA were obtained by extrapolating the experimentally determined intrinsic viscosities to zero concentration. The values thus obtained

were applied to the intrinsic equation [4,93]

$$[\eta]_\theta = K\bar{M}_v^a$$

in order to determine $\bar{M}_v$, the viscosity average molecular mass for each polymer. K and a are constants for a particular polymer/solvent system.[4,93] (See Table 4). The calculated molecular mass values for the two polymers correspond to average degree of polymerisation values, Z, of 2700 and 2800, which are well within experimental error limits of each other.

TABLE 4 : Viscosity Data for PAA and NaPAA 100

Sample	PAA	NaPAA 100
Solvent	1,4-Dioxane	0,5 M NaBr (aq.)
$[\eta]_\theta/dl^{-1}$	0,38	1.77
$K/10^{-3}dl^{-1}$	0,85	0,506
a	0,50	0,506
$M_v/10^5$	2,0 0,2	2,5 0,2
Z	2800	2700

3.3 Crosslinking and Gel Formation

Preliminary irradiation experiments on polymer solutions indicated that gel formation is a function of degree of neutralisation of the polymer, concentration of the solution and total dose. (See Table 5).

The viscosity of all NaPAA 100 samples appeared to decrease with increasing dose suggesting degradation rather than crosslinking.

This is in keeping with the findings of other workers that degradation occurs more readily at higher degrees of neutralisation.[94]

TABLE 5: Gel Formation of Polyacrylates on Irradiation

Dose /KGy	Sample	Solution Concentration 10%	5%	2%
50	PAA	gel + sol	gel + sol	-
	NaPAA 50	gel	gel	-
	NaPAA 100	sol	sol	-
25	PAA	gel + sol	gel + sol	gel + sol
	NaPAA 50	-	-	-
	NaPAA 100	sol	sol	sol
10	PAA	gel	gel	-
	NaPAA 50	sol	sol	sol
	NaPAA 100	sol	sol	-
5	PAA	gel	sol	-
	NaPAA 50	-	-	-
	NaPAA 100	sol	-	sol
3	PAA	-	sol	-
	NaPAA 50	sol	sol	-
	NaPAA 100	sol	sol	sol

Values obtained for the mass of swollen gel per gram of polymeric material present in the gel were in poor agreement with those obtained in later experiments under similar conditions. This was attributed to differing pressures of nitrogen in the sealed ampoules and to gel collapse due to contact with the copper wire screen used to drain the samples. Nevertheless, the values obtained gave an indication of the optimum concentration and dose ranges for the formation of highly absorbent gels in each system.

Subsequent polymer solutions were irradiated under vacuum and the resulting gels drained on a nylon screen. The mass of swollen

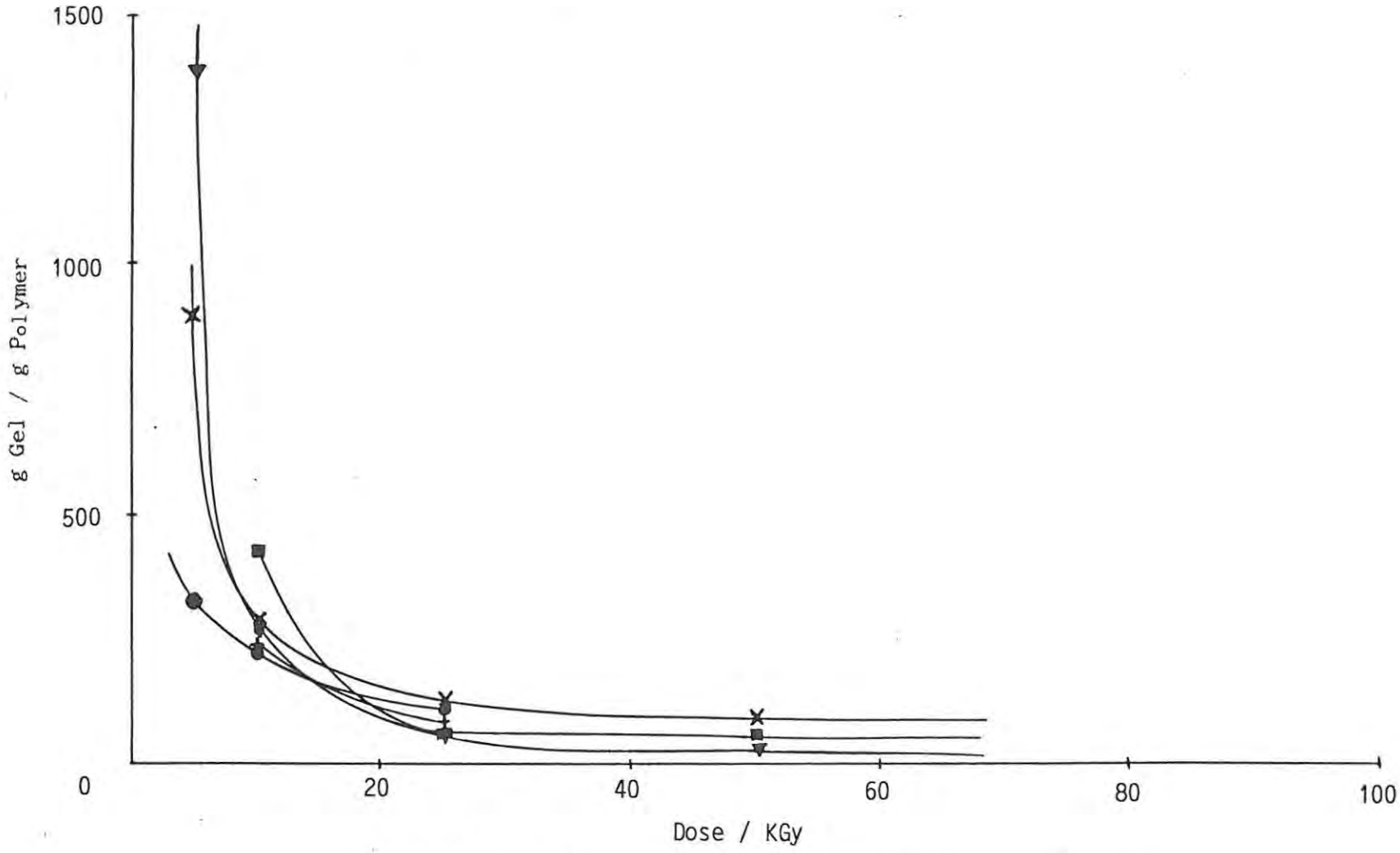

Fig. 6 a: Saturated water uptake vs. dose curves for PAA.
Concentration of irradiated solutions: ✕ = 1% ; ▼ = 2% ; ■ = 5%
● = 10% and + = 15% by mass.

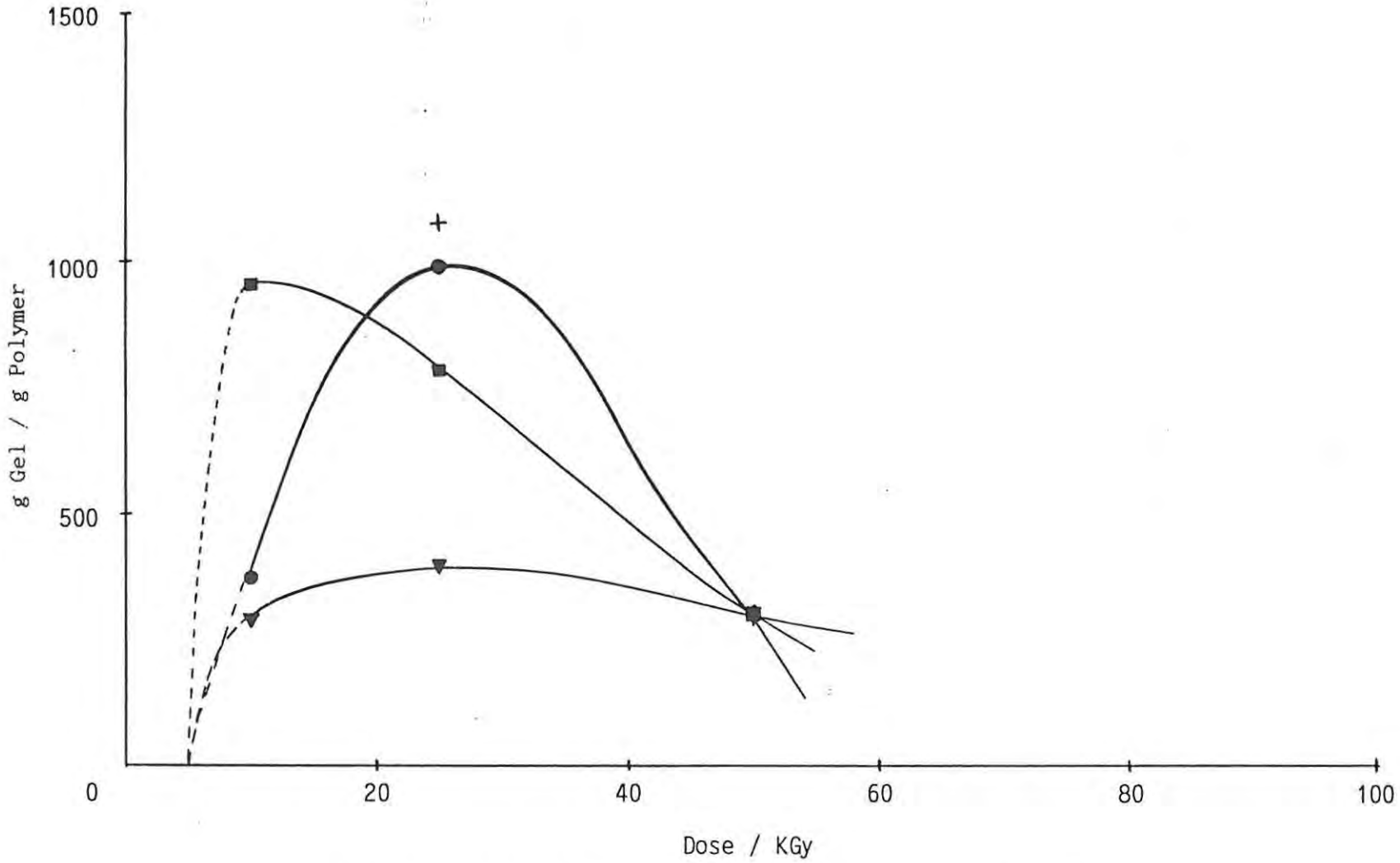

Fig. 6 b: Saturated water uptake vs. dose curves for NaPAA 32.
▼ = 2% ; ■ = 5% ; ● = 10% and + = 15%

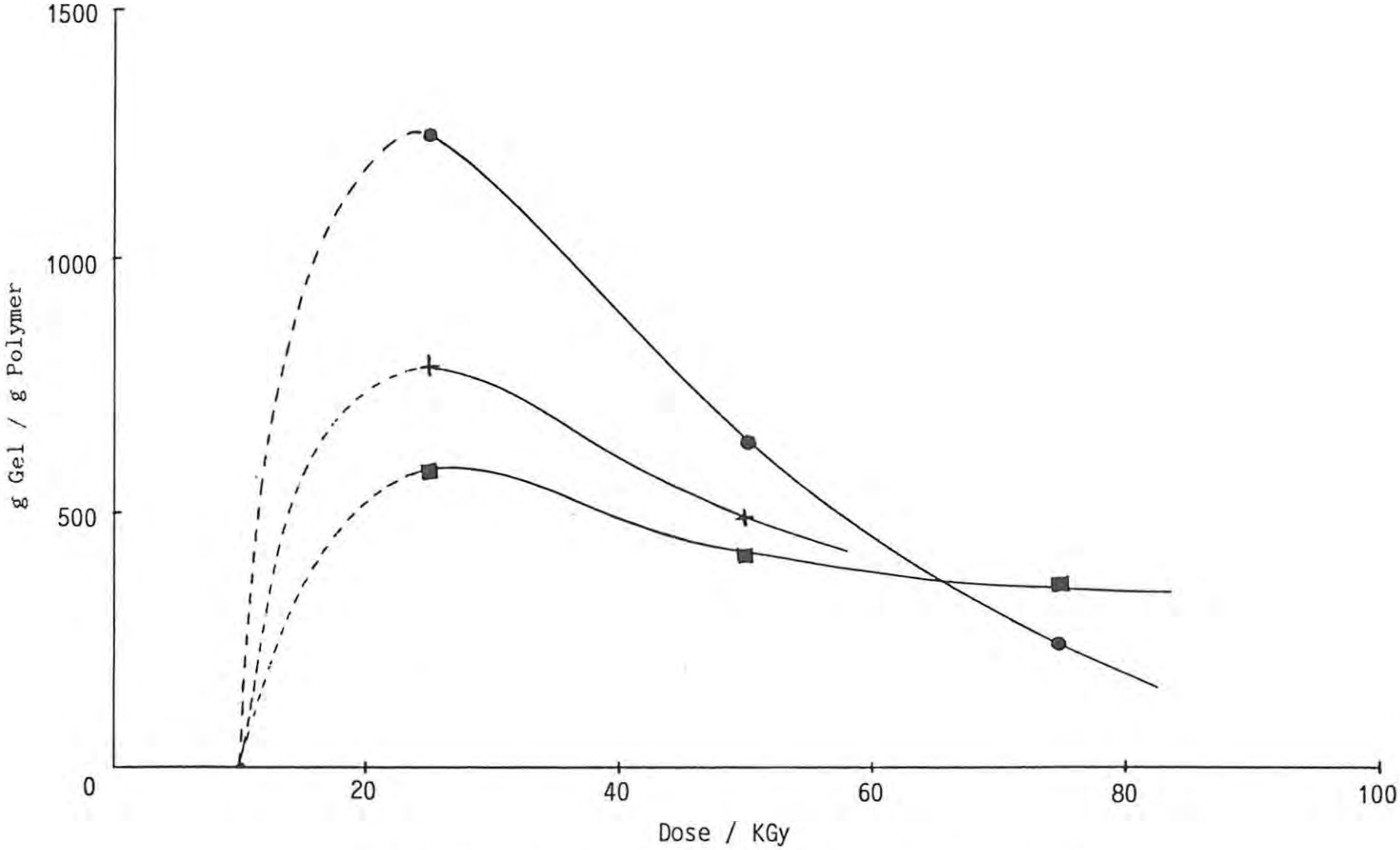

Fig. 6 c: Saturated water uptake vs. dose curves for NaPAA 50.
■ = 5% ; ● = 10% and + = 15%

gel obtained per gram of polymer present initially in the polymer solution, in these experiments, is plotted against the irradiation dose in fig. 6. (See appendix 1). Although the errors in these data are relatively large, particularly for soft gels, general tends may be observed.

For PAA samples (See fig. 6a), no gel formation was observed at doses lower then 5 KGy. At irradiation doses of 5 KGy and above, water uptake values decreased with increasing dose but rigidity of the gel appeared to increase with increasing dose. No pattern for concentration dependence could be distinguished.

For both NaPAA 32 and NaPAA 50, the optimum dose for the formation of a gel with high absorbing capacity is in the region of 25 KGy , NaPAA 32 showing increasing water uptake with increasing concentration and NaPAA 50 having an optimum concentration of approximately 10%. No gel formation was observed for doses less than 5 KGy or concentrations less than 2% for NaPAA 32 solutions, whereas doses less than 10 KGy or concentrations less than 5% precluded gel formation in the case of NaPAA 50 solutions.

Thus it appears that for a polyacrylate solution above a certain minimum concentration, gel formation occurs above a critical irradiation dose. Below this critical dose, insufficient crosslinking occurs for gel formation regardless of the concentration of the solution. As the dose in increased above that required for incipient gel formation , more crosslinks are formed thus giving rise to mechanically firmer (more rigid) gels

with reduced water uptake. At even higher doses, degradation of the gel occurs thus reducing both the rigidity of the gel and it's absorbing capacity. The minimum dose for gel formation is dependent on the degree of neutralisation of the polymer, crosslinking being less efficient at increased neutralisation levels.[94] No gel formation was observed for samples neutralised to more than 50%.

Between the concentration extremes of solid samples and very dilute solutions, for which no gel formation was observed, there appears to be an optimum concentration for the formation of water absorbent gels by gamma irradiation dependent on the degree of neutralisation. This is not unexpected as the repulsive forces between the macromolecules are known to increase with increasing neutralisation, and changing the concentration changes the distance between macromolecules. (See section 1.3.1.1.2)

3.3.1 G Values

The number of events occurring per 100 eV of radiation energy absorbed by the sample gives an indication of the efficiency of the radiation for that event and is known as the G value. A dose of 1 KGy (0,1 Mrad) corresponds to an energy absorption of $0{,}625 \times 10^{19}$ eV per gram of sample. Although a number of G values have been determined for crosslinking and scission events in polyacrylate solutions, there is some uncertainty regarding the absolute values due to the inherent contribution of the G value for water which itself is the subject of some controversy.[95]

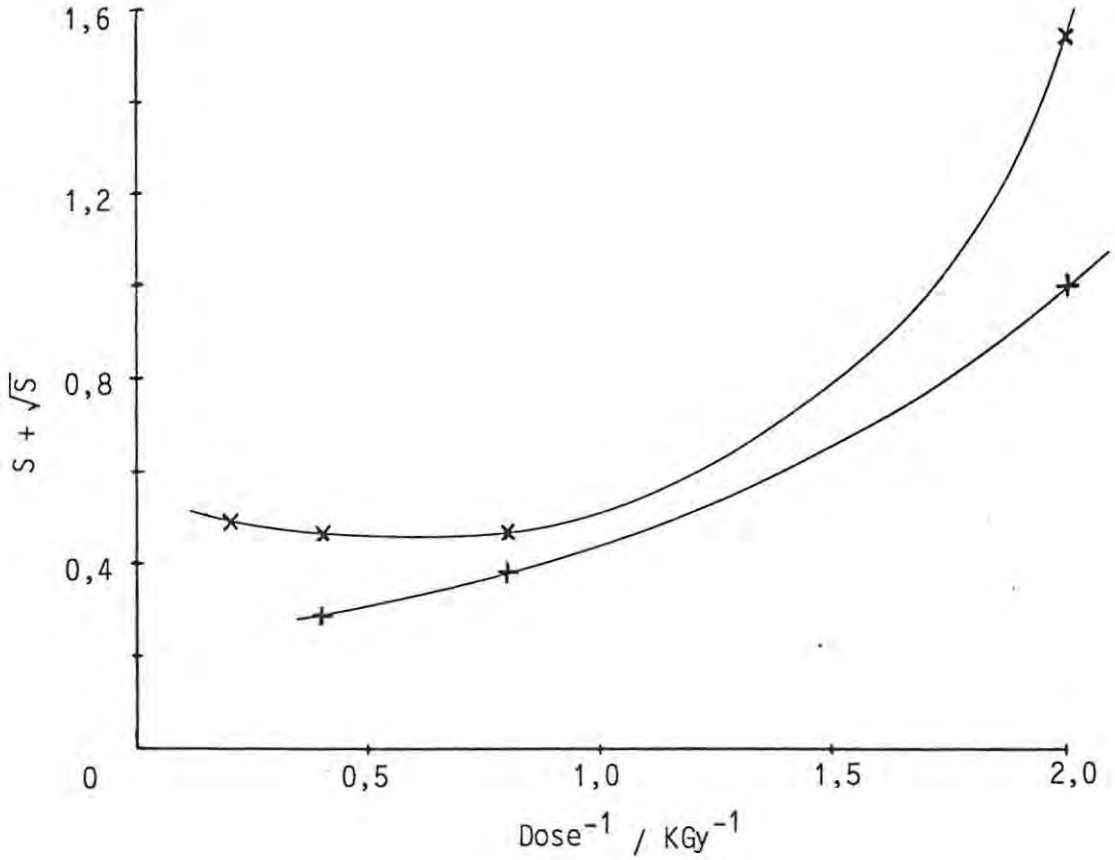

Fig. 7: Plot of $S+\sqrt{S}$ vs. reciprocal irradiation dose. (S = Sol fraction). × = PAA ; + = NaPAA 32

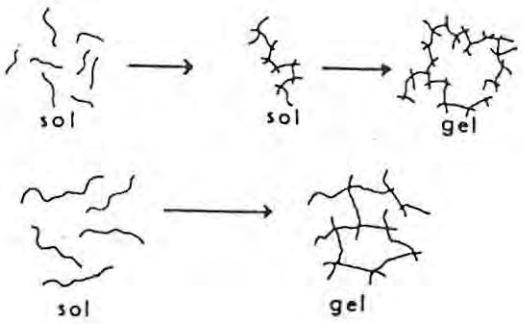

Fig. 8: Schematic representation of the influence of initial molecular mass on critical crosslink density for gel formation.[16]

Disregarding the absolute G values, an attempt was made to determine the ratio of the G value for crosslinking to the G value for scission for certain systems by determining the fraction of insoluble crosslinked material present in selected samples. (See section 2.3). This gives a measure of the number of crosslinks formed per main-chain scission event. According to theories proposed to account for gel formation by irradiation, the G value ratio may be determined from the slope of a plot of $S+\sqrt{S}$ vs. $1/r$, where S is the soluble fraction of the irradiated polymer and r is a measure of the total dose.[96] However, plots of $S+\sqrt{S}$ vs. $1/r$ determined experimentally were found to be non-linear (see fig. 7) in conflict with these theories. The proposed theories assume a random distribution of the initial molecular mass of the polymer and a high enough dose for most of the material present to be included in the crosslinked network. For non-random distributions, the theory only holds at doses high enough to cause three main-chain scission events per macromolecule. The theories have been extended to include other initial molecular mass distributions such as Poisson distributions,[97] but as the mass distribution of polymer used in the present studies was not determined, and only relatively low doses were employed, no useful information could be obtained in this regard.

3.3.2 Crosslink Density

The results obtained in this study are similar to those obtained for polyacrylamides by other workers,[16] and show a minimum sol

fraction (maximum gel fraction) at a dose called the gel-saturation dose. The gel fraction decreases at higher doses due to degradation of the polymer matrix. The dose required to achieve the minimum sol fraction is dependent on the molecular mass of the starting material, but the crosslink density (proportion of monomer units which are crosslinked) is independent of the initial molecular mass for a particular system.[88] (See fig. 8).[16]

The molar concentration of crosslinks (number of moles of crosslinks per unit volume), φ , has been related to the swelling ratio, S, of a polyacrylate gel containing no uncrosslinked polymer by the equation [98]

$$\varphi = \frac{1}{v_1} \frac{-[\ln(1 - 1/S_v) + (1/S_v) + \chi(1/S_v)^2]}{[(1/S_v)^{1/3} - (1/S_v)/2]}$$

where

V_1 is the molar concentration of the solvent (18,02 cm^3/mol for water),[80]

χ is the solvent-polymer interaction parameter (0,5 for PAA - water),[98]

and S_v is the volume swelling ratio, defined as the volume of swollen gel divided by the volume of original sample.

S_v can be related to the mass of the swollen gel, M, and the mass of polymeric material present in the gel, M_o , by the relation [99]

$$S_v = (\rho_p/\rho_s)S_w + (1 - \rho_p/\rho_s)$$

where ρ_p is the density of polymer (1,48 g/cm^3 for PAA)

and ρ_s is the density of solvent (0,997 g/cm^3 for water at 25 ^oC).[80]

The results of M and M_o obtained for the four extracted PAA samples (See sections 2.4.2.2 and 3.4.2.2) could be used to calculate φ in each case. Assuming the polymer chains to be evenly distributed throughout the swollen gel and knowing the number of moles of polymer molecules present initially in the sample permits calculation of the number of crosslinks per original mass average molecule, ζ . (See Table 6).

TABLE 6: Swelling Data for Irradiated Poly(acrylic acid) Samples

Dose /KGy	50	25	10	5
M_o /g	0,0935	0,0837	0,0888	0,0233
M /g	3,26	6,54	23,32	125,0
S_v	51,3	110,7	472,8	7960
φ /mol l^{-1}	$5,36x10^{-7}$	$6,71x10^{-8}$	$1,18x10^{-9}$	$1,38x10^{-10}$
Polymer conc. / mol l^{-1}	$1,42x10^{-7}$	$6,62x10^{-8}$	$1,89x10^{-8}$	$9,20x10^{-10}$
ζ	3,8	1,0	0,08	0,15

ζ values of less than 1 were derived for the two samples which received the lowest irradiation doses thus indicating that not all of the macromolecules present are bonded to the three-dimensional polymer structure. This could be explained by assuming incomplete removal of uncrosslinked material from the gel. On the other hand, it would be expected that extraction of unbound polymer from these highly swollen, lightly crosslinked gels would be more easily accomplished than extraction from the

highly crosslinked samples. The results obtained at very low doses (below the gel-saturation dose) may be influenced by uncrosslinked material of high molecular mass. It has been shown that PAA of molecular mass $2x10^5$, such as used in this study, is readily soluble in water, whereas PAA of molecular mass $2x10^6$ is almost completely insoluble.[88] Precipitation of such high molecular mass material which is not bound to the polymer network would contribute to the measured parameter M_o in the crosslink density analysis.

Hence, owing to the difficulties encountered in determining the ratio of crosslinking to scission events and the crosslink density of a PAA gel, it was not possible to determine gel formation as a function of irradiation dose, concentration, initial molecular mass and degree of neutralisation.

3.4 Water Uptake

3.4.1 Rate of Water Uptake

The results of rate of water uptake studies at 75% relative humidity are shown in fig. 9 as a function of neutralisation and temperature.

Both the initial rate of sorption and the equilibrium water uptake values were found to increase with increasing degree of neutralisation. For any given degree of neutralisation, the initial rate of water uptake was seen to increase with increasing temperature whereas the equilibrium water content decreased.

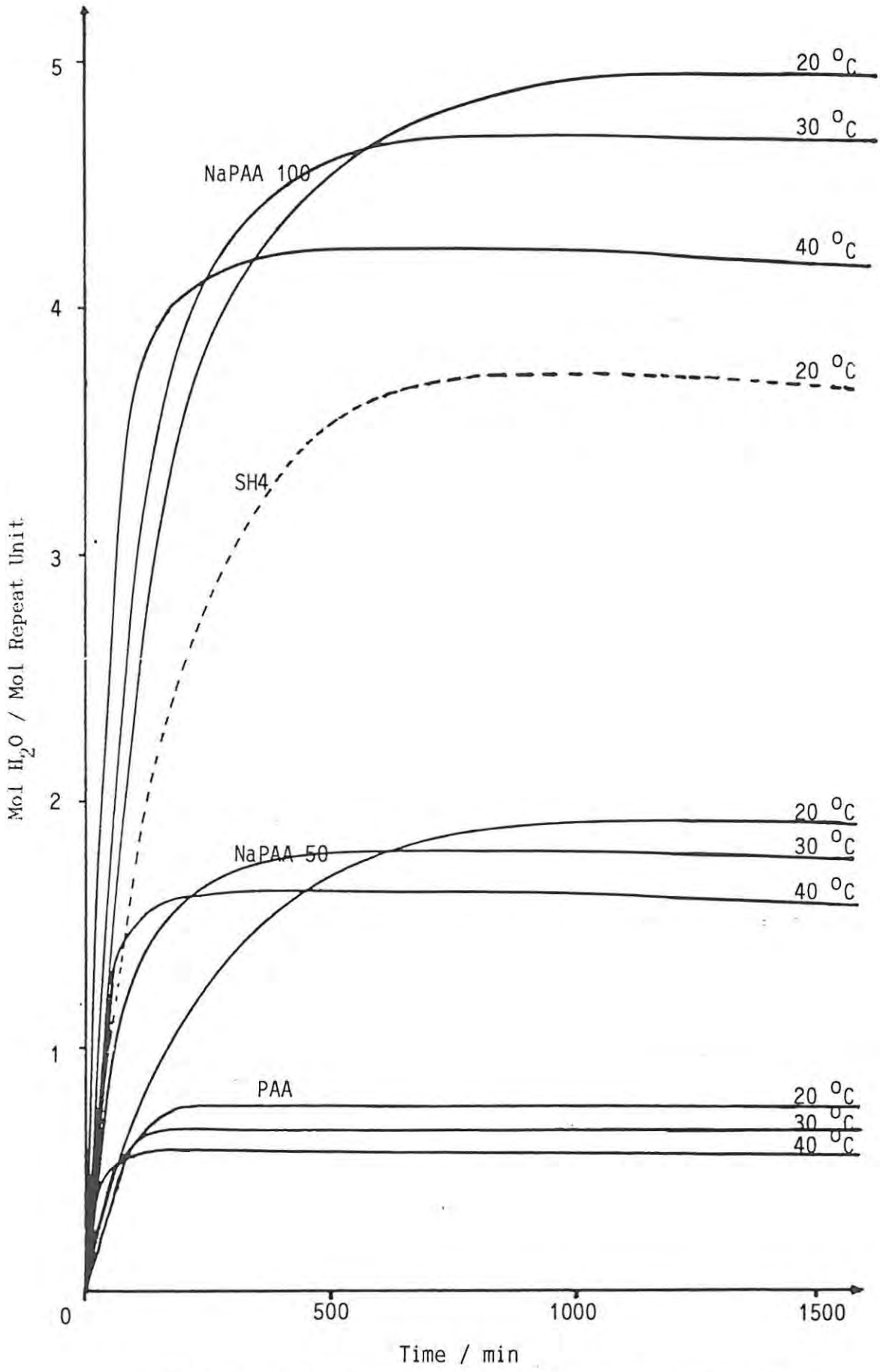

Fig. 9: Rate of water uptake of linear polyacrylates at 75% relative humidity and 25 °C.

From optical microscopy and screening, particle size appeared to increase with increasing neutralisation. Despite the fact that NaPAA 100 had the largest particle size, it showed the highest rate and equilibrium water uptake values. For a stricter comparison, attempts were made to crush and screen the samples to within similar particle-size limits. However, this was unsuccessful due to the sorption of moisture during crushing and screening. This obstacle has ruled out any meaningful quantitative comparison of isothermal rates of hydration of polymers of varying degrees of neutralisation.

For a particular polymer sample, the rate of sorption increased slightly with temperature, indicating a small activation energy for the overall sorption process. However, meaningful quantitative analysis is not possible due to particle size effects.

The decreasing equilibrium water content of each sample with increasing temperature indicates that the sorption process is mildly exothermic. This is to be expected, as sorption incurs an obvious decrease in entropy of the system therefore requiring a negative enthalpy change (exothermic) for the sorption process to be spontaneous.

The relative sorption rate and equilibrium water content of Aquakeep SH4 at 20 ^{o}C indicate a degree of neutralisation in the range obtained by titration. However, unknown variables such as particle size effects, degree of crosslinking, tacticity etc. precluded unambiguous conclusions from comparison with other samples.

3.4.2 Equilibrium Water Uptake

3.4.2.1 Relative Humidity Studies

Equilibrium water uptake for various samples, as a function of relative humidity at 25,0 °C is shown in fig. 10. (See Appendix 2) Absolute humidity values may be inferred directly from the isothermal relative humidity values, 100% relative humidity at 25,0 °C corresponding to a partial pressure of water vapour of 23,756 mm Hg.[100]

The equilibrium water content values at 75% relative humidity were in good agreement with those obtained in the rate studies after equilibrium had been reached. (See section 3.4.1).

Attempts were made to fit the experimental data to several adsorption isotherms (BET, Bradley).[34] Although a satisfactory fit could be obtained for a range of humidity values, none of the theories proposed could successfully account for the observed water uptake over the entire humidity range studied.

Water content values at 25,0 °C and 73% relative humidity obtained by interpolation, are plotted against degree of neutralisation in fig. 11a. These values are shown to be in good agreement with those obtaind by other workers under similar conditions by comparison with Fig 11b.[79]

The sharp break in the curve at $\alpha = 0,33$ led to the formulation of an octahedral coordination structure model for the sodium ion, with the coordination sites occupied by polymeric carboxyl oxygen

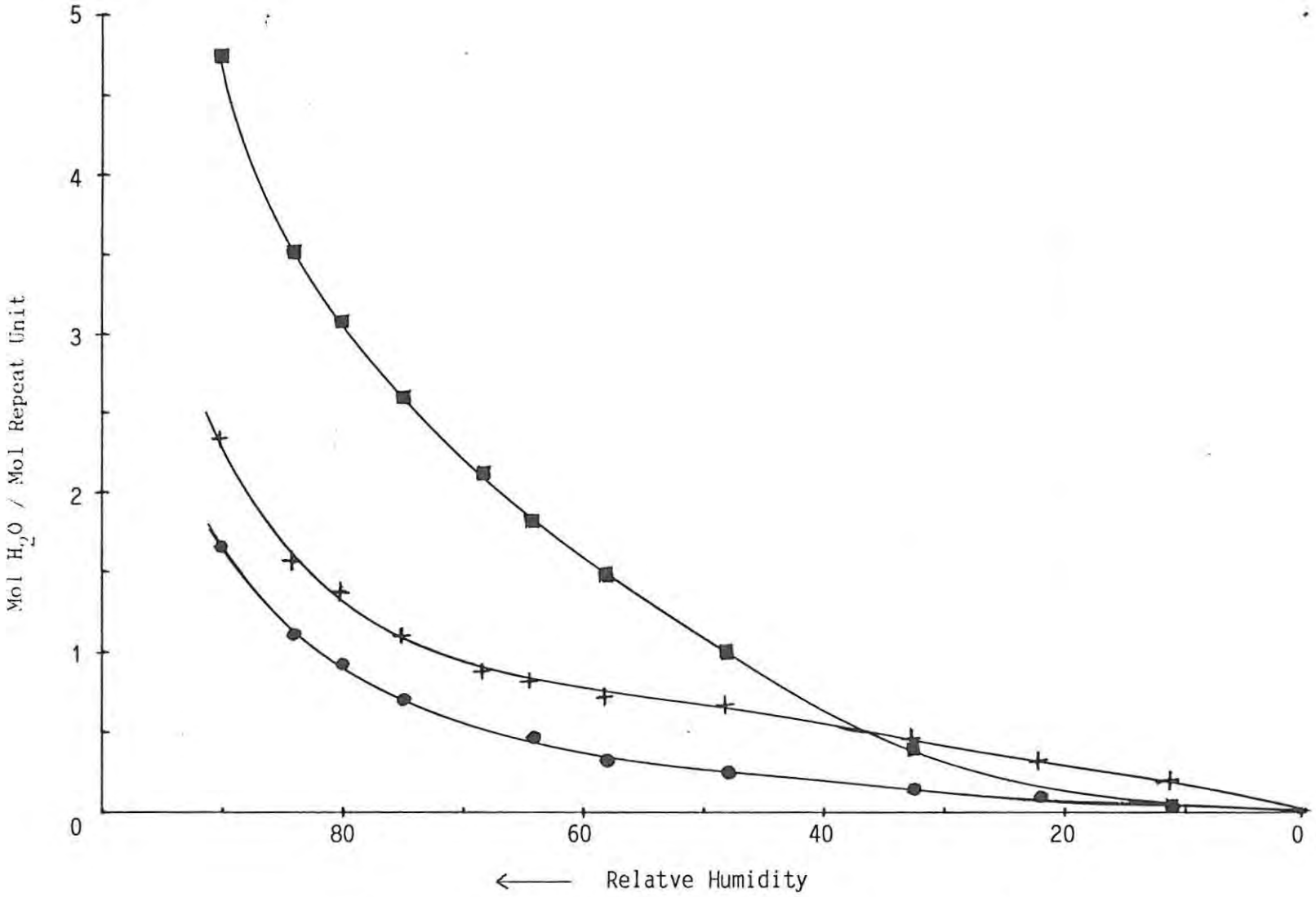

Fig. 10 a: Equilibrium molar water content as a function of relative humidity at 25 °C. ● = PAA ; + = NaPAA 32 and ■ = NaPAA 67.

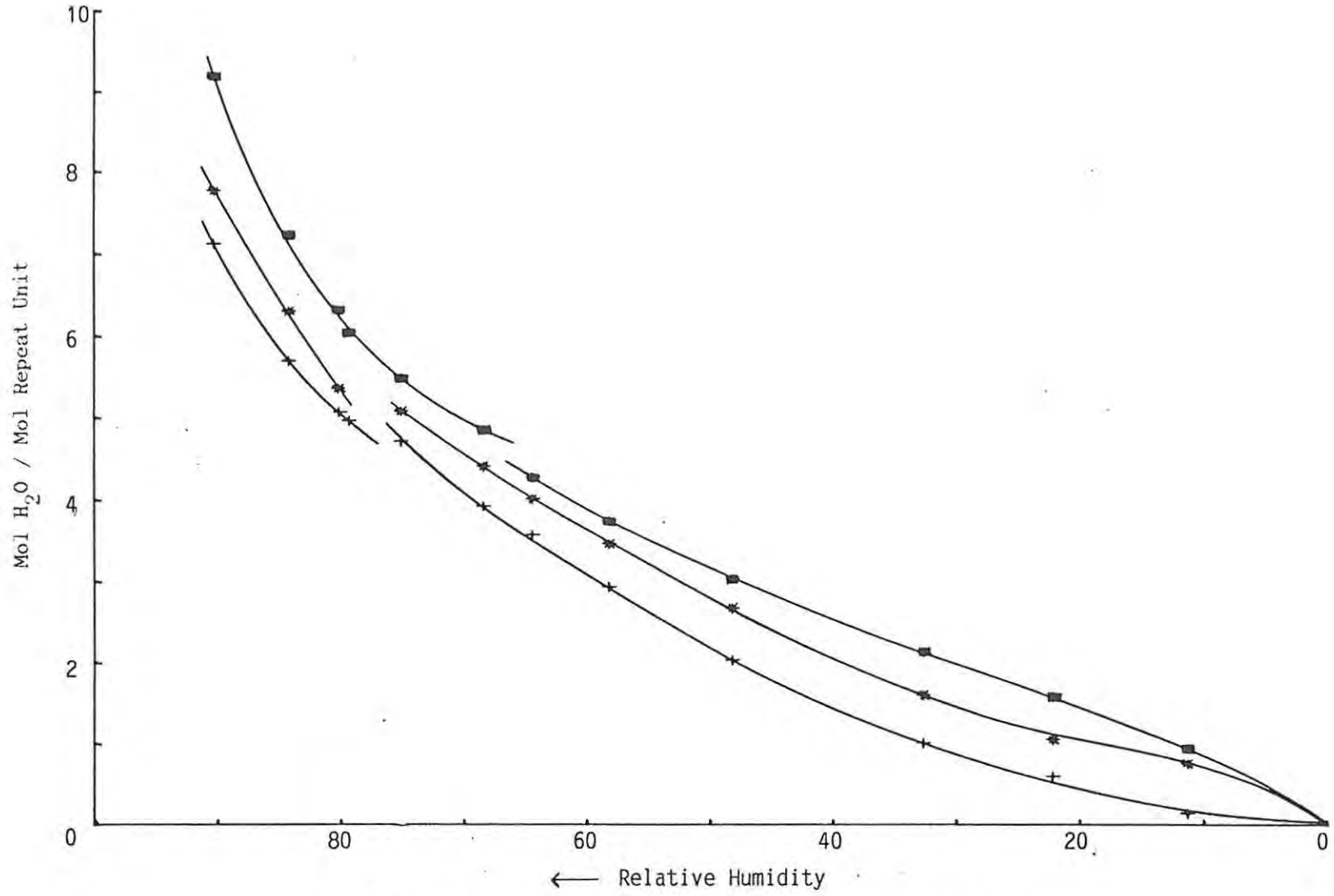

Fig. 10 b: Equilibrium molar water content as a function of relative humidity at 25 °C. + = NaPAA 100 ; ● = KPAA 100 and ■ = CsPAA 100.

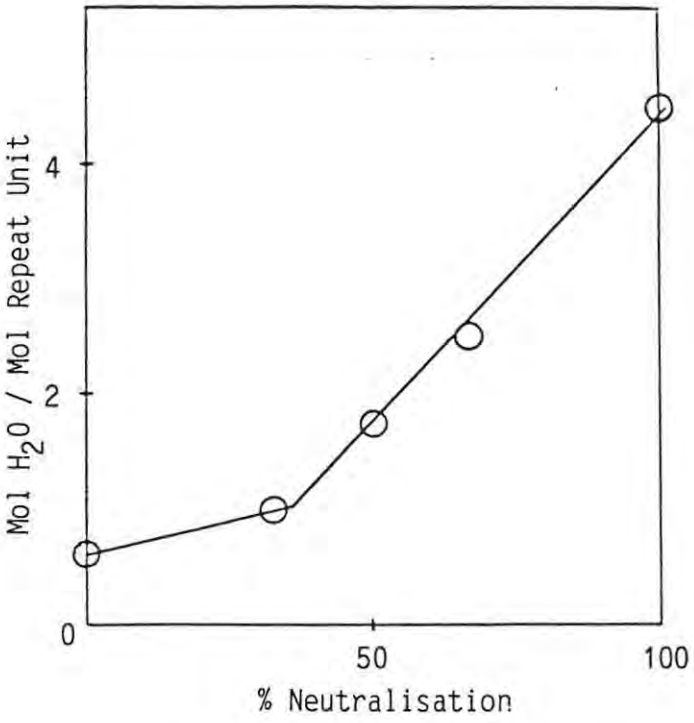

Fig. 11 a: Equilibrium molar water content of poly(acrylic acid) sodium salts with different degrees of neutralisationa at 25 °C and 75% relative humidity as determined in this study

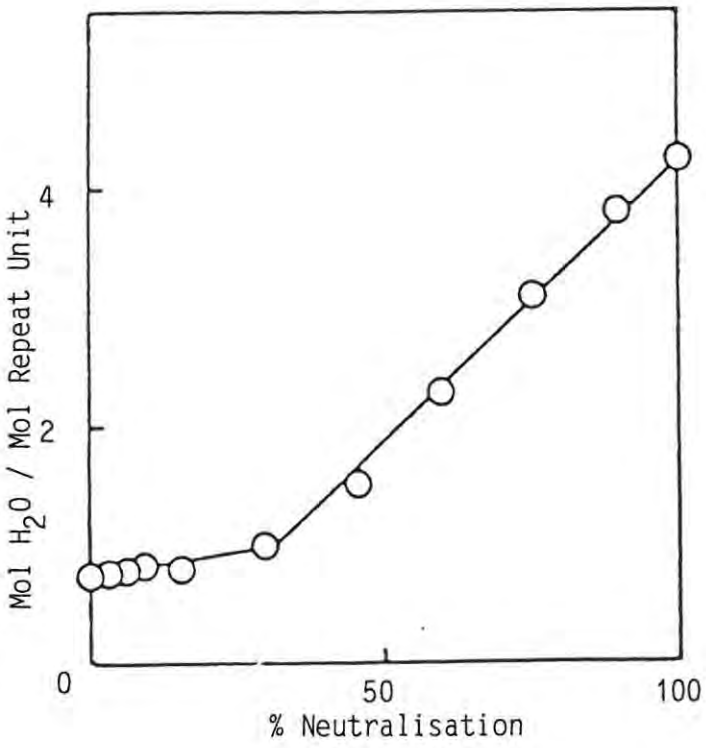

Fig. 11 b: Equilibrium molar water content of poly(acrylic acid) sodium salts with different degrees of neutralisationa at 25 °C and 75% relative humidity Reproduced from ref. 79.

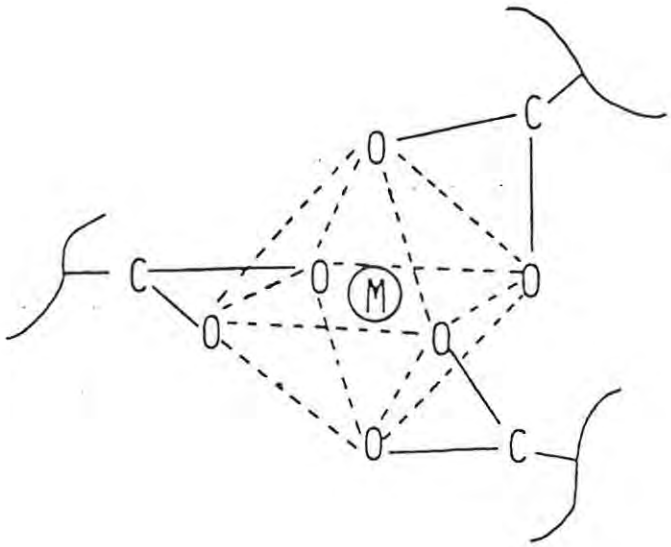

Fig. 12 a: A model for the octahedral coordination structure of the sodium ion in a 33% neutralised polyacrylate system. Reproduced from ref. 79.

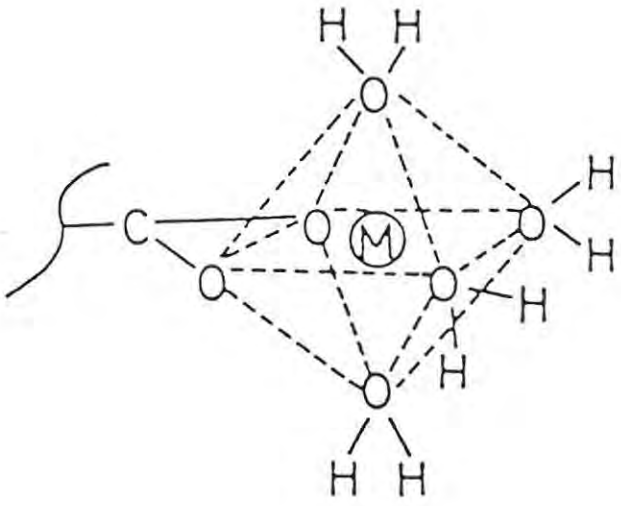

Fig. 12 b: A model for the octahedral coordination structure of the sodium ion in a fully neutralised hydrated poly(sodium acrylate) system. Reproduced from ref. 81

atoms at degrees of neutralisation less than 33%, and by oxygen atoms of water molecules at greater than 33% neutralisation.[79] (See fig 12). Partial molar volume studies of the water in the polyacrylate system appeared to support this model[80] despite the fact that x-ray diffraction and neutron scattering studies indicated that the sodium ion has a tetrahedral primary hydration structure with a coordination number of 4 in concentrated aqueous solution.[80]

The proposed octahedral model does not account for the observed water uptake of the polymer system below 33% neutralisation and no attempt is made to explain how charge neutrality is preserved in the dehydrated gel at 33% neutralisation. For the break in the water content vs. neutralisation curve to occur at α =0,33 , all of the sodium ions and carboxyl groups present in the system would have to be coordinated simultaneously in this manner for the model to be valid. This is clearly not the case, as such a system would be 100% crystalline and could have no absorbed water present. Furthermore, the octahedral structure model is based on hydration studies at 73% relative humidity at 25 ^{o}C which indicate a primary hydration number of four water molecules per repeat unit for fully neutralised poly(sodium acrylate). The present studies show a marked dependence of the equilibrium water uptake of the polymer on temperature and relative humidity. (See figs 9 and 10). Hence it appears that the primary hydration number of four was obtained fortuitously due to the experimental conditions.

For all fully neutralised samples in the present study, a small

but reproducible break in the equilibrium molar water content vs. relative humidity curve was observed at a water content value of approximately five water molecules per repeat unit of polymer. The anomaly appears to be independent of the nature of the alkali metal counterion present in the polymeric salt, and occurs at a different relative humidity value in each case. This suggests that the five water molecules per repeat unit adsorbed initially are not directly associated with the metal cation, as the Na^+, K^+, and Cs^+ ions are known to have different primary hydration numbers.[84,85] However, the metal ion does influence the initial adsorption process, as samples that were not completely neutralised did not attain adsorption values of five water molecules per repeat unit in the relative humidity range studied.

A predicted primary hydration number of 5 for each repeat unit is in good agreement with values of 4,9 to 5,4 obtained from diffusion studies on polyacrylates by other workers.[37,101] Partial molar volume studies cited in support of the octahedral structure model for the Na^+ ion in polyacrylate systems,[80] do not appear to be sufficiently precise to distinguish between primary hydration numbers of 4 and 5.

In the dehydrated state, site binding of Na^+ ions must occur (counterions in direct contact with one or more charged groups on the polyion with no intervening water molecules have been defined as site bound.).[54] It appears feasible that the apparent primary hydration number of 5 could be the number of water molecules per repeat unit required to hydrate the polyion and/or

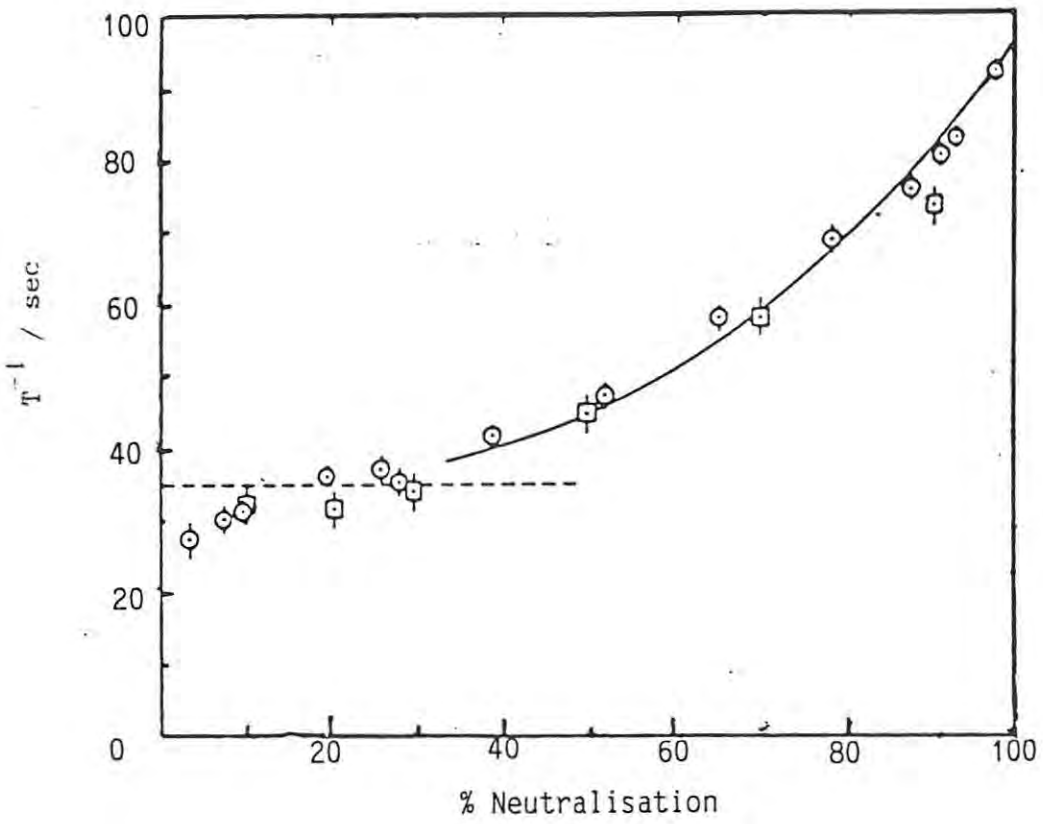

Fig. 13: Spin-lattice relaxation of sodium nuclei in poly(acrylic acid) solutions as a function of the degree of neutralisation. Reproduced from ref. 61.

counterion to the extent that the counterion is no longer site bound.

At low degrees of neutralisation very little binding of any sort is evident in the presence of sufficient water. As the degree of neutralisation is increased above $\alpha = 0,35$, which corresponds to the critical charge density for PAA,[61] hydrated counterions condense onto the macroion[54] thus increasing the effective amount of water associated with the polymer and affecting the electrostatic forces in the neighbourhood of the polymer chain. (See section 1.3.1.2). This successfully explains the observed break in the equilibrium molar water content vs. neutralisation curve at approximately $\alpha = 0,33$ without recourse to a rigid structure model.

A graph of spin-lattice relaxation of sodium nuclei in polyacrylate solutions as a function of degree of neutralisation of the polymer [55,61,102] shows remarkable similarities to the equilibrium molar uptake vs. neutralisation graph.[79] (See fig. 13) This lends further support to the hypothesis that the observed break in the equilibrium molar water content vs. curve at $\alpha = 0,33$ is due to counterion condensation.

3.4.2.2 Saturated water uptake

Neutralisation of acid groups within extracted gel samples subsequent to crosslinking yielded saturated equilibrium molar water uptake values as a function of neutralisation for each gel system. (See section 2.4.2.2). These data are presented in fig. 14.

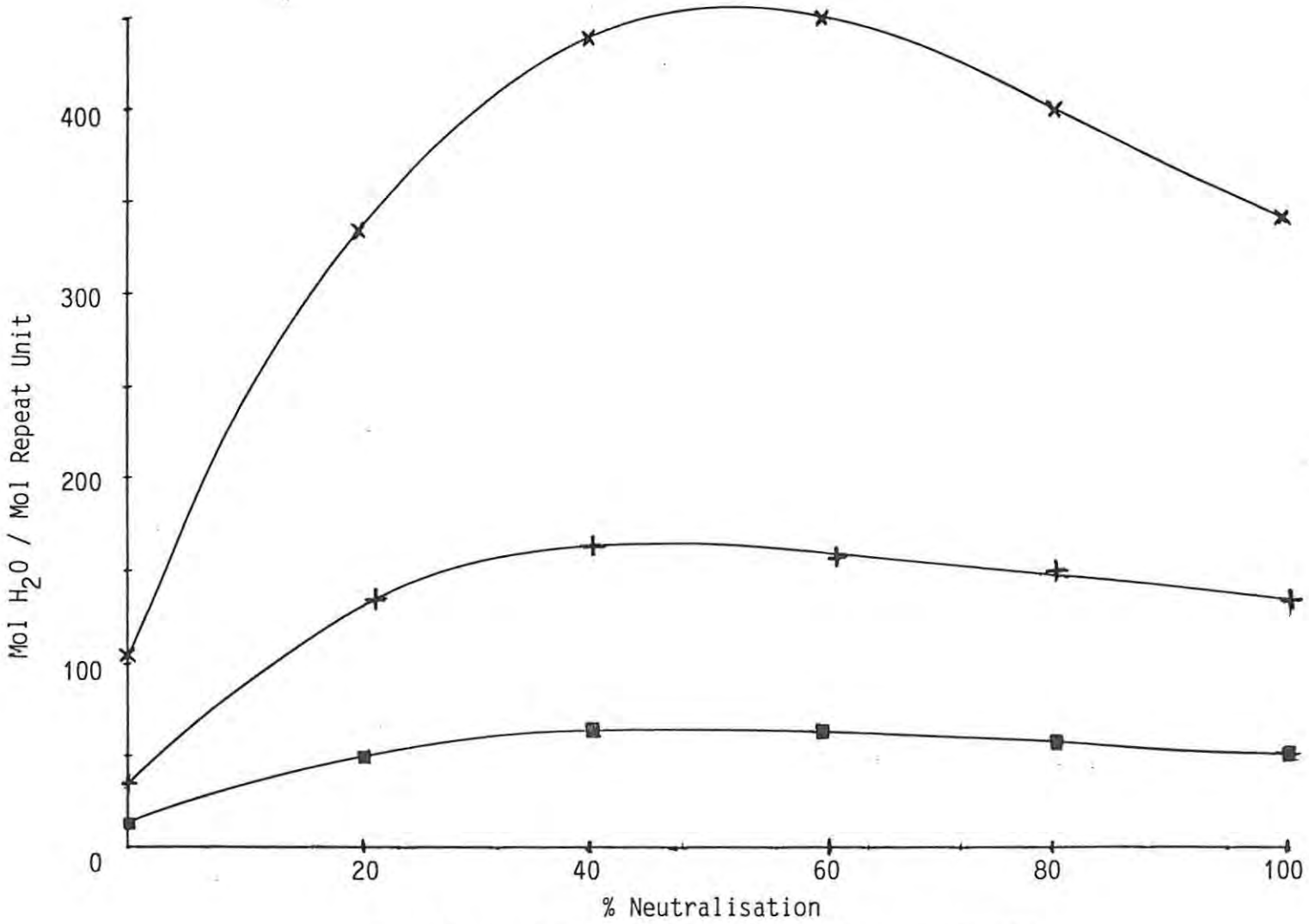

Fig. 14 a: Molar water uptake vs. % neutralisation for gels obtained from irradiated 2% PAA solutions. × = 10 KGy ; + = 25 KGy and ■ = 50 KGy total dose.

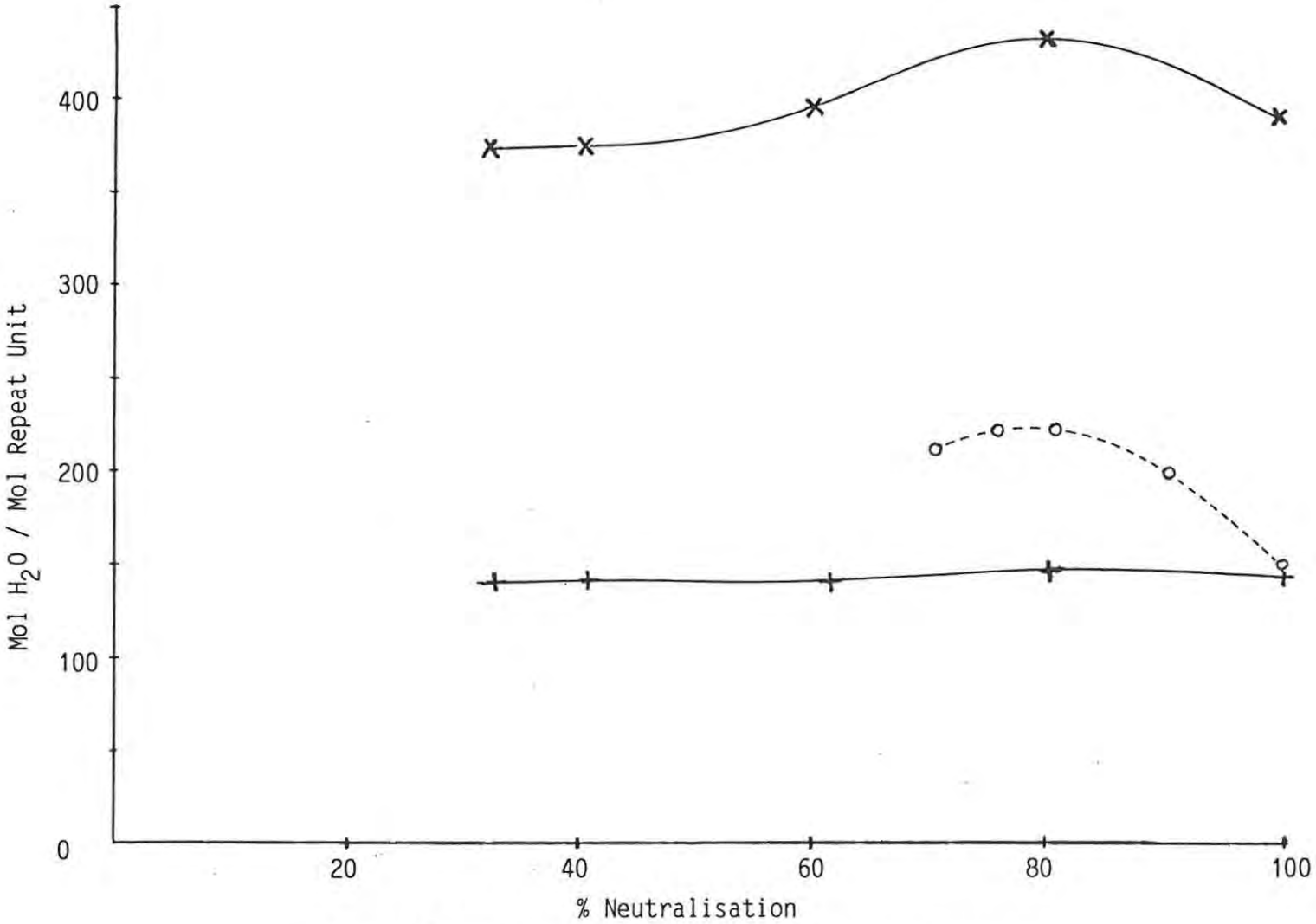

Fig. 14 b: Molar water uptake vs. % neutralisation for gels obtained from irradiated 5% NaPAA 32 solutions. x = 25 KGy and + = 50 KGy . o = Aquakeep SH4.

Gels obtained from 2% samples of PAA and 5% samples of NaPAA 32 irradiated to 10, 25 and 50 KGy showed decreasing water uptake with increasing dose for all degrees of neutralisation as expected from previous experiments. (See section 3.3)

Maxima were observed in the saturated molar water uptake vs. neutralisation curves for the crosslinked gels at low levels of crosslinking (low dose), whereas linear material appeared to exhibit increased water uptake with neutralisation throughout the neutralisation range. (See section 3.4.2.1) Similar maxima have been reported for lightly crosslinked poly(methacrylate) hydrogels.[71]

Differences between absolute water uptake values for gels obtained from PAA and NaPAA 32 solutions can be attributed to different ratios of crosslinking to main-chain scission events occurring in each system on irradiation. However, reasons for the observed maxima at low levels of crosslinking are not as obvious.

It has been shown that in the absence of added salt, a linear polyion in solution expands with increasing degree of neutralisation.[103,104] As the long-range forces exerted by the polyion stem from a cooperative effect of the charges attached to the polymer backbone, it seems feasible that the macromolecule could expand beyond the dimensions required for these long-range forces to be a maximum, while the short-range forces exerted by each individual functional group would remain unimpaired.

It is reasonable to assume that the higher the level of crosslinking, the more constrained the polyion. Hence, the polymer chains in a lightly crosslinked gel may expand beyond the dimensions for which long-range ordering forces are optimum thus giving rise to reduced water uptake at high degrees of neutralisation. In more highly crosslinked systems, this phenomenon is not observed as the polyion dimensions associated with optimum long-range forces are not exceeded.

Decreased water uptake at high levels of neutralisation in the absence of crosslinking is not observed, as hydration experiments on linear material involve only relatively small amounts of adsorbed water. As this water is held by short-range binding forces, a reduction in the strength of long-range forces would not affect the equilibrium water content of the system. Polymer-polymer interactions may be important under such conditions as the system effectively constitutes a very concentrated polyelectrolyte solution with the polyion molecules in close proximity to each other.[70]

3.5 Effect of Salt on Gel Deswelling

In order to ensure sample uniformity, dried Aquakeep SH4 was used in all gel deswelling experiments. (See section 2.5). This material was readily available in relatively large quantities and was also selected partly because of it's commercial importance. The dependence of saturated equilbrium water uptake of the gel as a function of concentration of added salt is shown in fig. 15.

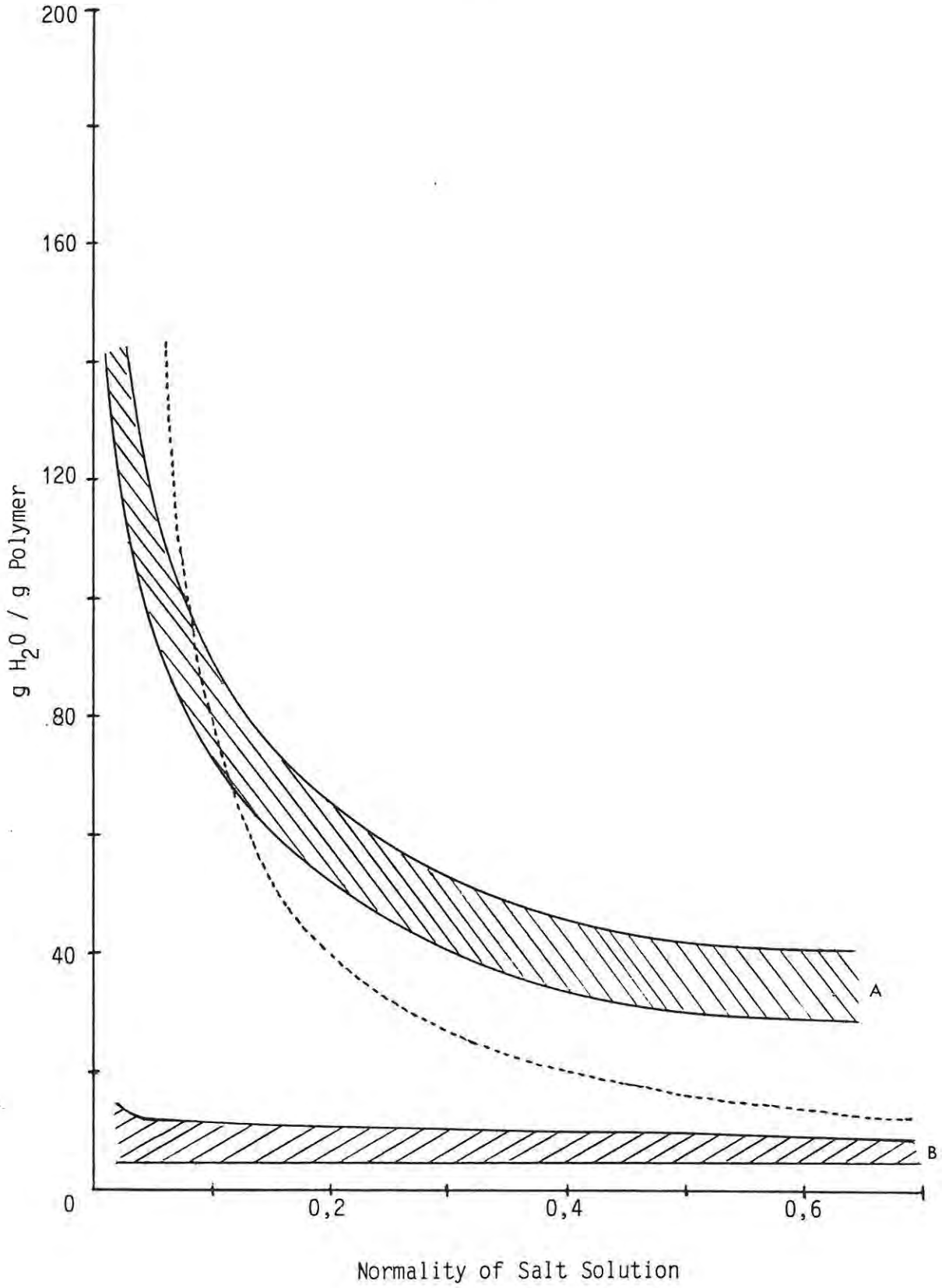

Fig. 15: Saturated water uptake as a function of ionic strength of solution. A = monovalent cationic salts : B = polyvalent cationic salts. the dotted line indicates the concentration of polyions within the gel.

The data presented in fig. 15 indicate that the effect of the added salt is dependent only on the concentration of the salt in the system and the valence of the cation. All univalent cationic species of the same concentration had a similar effect on the water uptake of the gel independent of the radius of the cation or the nature of the anion. Similarly, all multivalent cations of the same charge concentration (normality) influenced the swelling of the gel to approximately the same extent, having a far greater deleterious effect than univalent cations.

This is in keeping with the findings of other workers that univalent ions have similar effects on gel swelling [71] and that highly charged ions are generally more completely sequestered by polymers than are ions of low charge. [50,105] In a purely univalent system, little or no site binding of the counterion occurs (See section 1.3.1.1.2). Ions such as copper (II) cations form complexes with PAA, thus showing that PAA has a much stronger preference for ring formation than its monomeric analogue, and is closer in its chelation behaviour to substances such as oxalic acid. [52,106] Titration data indicate that two carboxylates of the polyanion are involved in chelate formation with the divalent cation. [107] At low polymer and/or polyvalent counterion concentrations, once the cation is bound to a polyanion, its further interaction with a ligand group involves, with an overwhelming probability, a group carried by the same flexible polymer chain. [2] At high concentrations, chelation may involve carboxylates from different polymer chains thus giving

rise to ionic crosslining. This is evidenced by the appearance of a gel phase under such conditions.[64]

For trivalent cations in the presence of a polyanion of relatively low charge density, binding to fewer than three carboxylate groups has been shown to persist even when sufficient triads are available to accommodate all the trivalent cations in the system.[65] This indicates that counterion binding is dependent only on the overall charge density of the polyion, in agreement with the counterion condensation theory.

4 CONCLUSION

The aim of this study was to obtain a qualitative picture of the interactions of water molecules with crosslinked polyacrylate macromolecules in a hydrogel and to gain some insight into the structure of the gel. From experimental results obtained in this study and those of other workers, the following conclusions could be drawn.

The formation of a firm gel with high water absorbance properties by irradiation crosslinking of a weak polyacid such as PAA in solution (in the absence of added salt) is a complex function of the original molecular mass of the polymer, the extent of neutralisation of acid groups on the polymer, the concentration of solution and the total irradiation dose. Firm gels with water retention capacities in the region of 1000 g of water per gram of polymer were synthesised.

4.1 Forces Responsible for Gel Swelling

4.1.1 Osmotic Forces

Although osmotic effects have been shown to be responsible for only part of the swelling in hydrogels [77], it has recently been suggested that swollen gels owe their rigidity to osmotic pressure from imbibed water, similar to an inflated balloon which

is only rigid due to the internal pressure.[1] However, this would imply that the higher the internal pressure, the more rigid the gel would be. This is clearly not the case, the rigidity of a swollen hydrogel decreasing with increasing water content.

Osmotic pressure shows a linear dependence on salt concentration under normal membrane conditions. However, the graph of saturated equilibrium water uptake vs. concentration of simple monovalent salt is clearly non-linear, very small amounts of added electrolyte causing a drastic reduction in swelling properties. (See fig. 15). This can be attributed to the screening of long-range electrostatic forces exerted by the polyions [38], rather than a reduction in osmotic pressure.

4.1.2 Electrostatic Forces

Local short-range electrostatic forces are evidently responsible for the primary hydration of each polymeric charge. Cooperative long-range electrostatic forces capable of structuring water beyond the primary hydration region to a certain extent are thought to hold most of the water in a swollen hydrogel. (See section 1.4.2)

The importance of electrostatic effects in gel swelling can be demonstrated by applying a potential difference across a swollen gel sample. Above a particular potential, the gel collapses, the volume of the collapsed gel being up to several hundred times smaller than that of the swollen gel.[78] (See section 1.4.1.2)

4.2 Structure of the Gel

Hydration experiments in this study indicate a primary hydration number per repeat unit of 5 for polyacrylate alkali-metal salts, independent of the size of the monovalent cationic counterion. This finding is in conflict with models proposed for these systems under similar conditions[79,80] but is in good agreement with values obtained from diffusion studies.[37] Reduced partial molar volume studies of water in polyelectrolyte systems [80] indicate that close packing of the water molecules occurs in the neighbourhood of a macroion. From studies of dissociation constants [37] and polymer configurations,[39] it appears that the local ionic strength of the polymer charges and the distance between adjacent polyion charges can be altered by neutralisation of the polyacid, thus allowing efficient structuring of the water by direct short-range interaction with the dipole of the water molecules. The existence of an optimum degree of neutralisation for water uptake by lightly crosslinked gels implies a maximum in the long-range forces associated with a particular degree of expansion of the flexible polymer chains.

There is good evidence that water close to a hydrophilic macromolecule exists in polarized multilayers with the rotational freedom of the water molecules becoming progressively greater further away from the polyion.[33,34] The counterion condensation theory proposes that as the degree of neutralisation of poly(acrylic acid) is increased above $\alpha = 0,35$, hydrated counterions condense onto the macroion.[54] Enthalpy and entropy studies on protein systems suggest that water molecules in the

hydration shell of the counterion merge with water molecules in the polarized layers surrounding the macromolecule, mutually reinforcing the hydration structures of both the polyion and the counterion.[81] Structuring effects may thus exist at substantial distances from a polyion in a swollen hydrogel.

A proposed critical charge density for poly(acrylic acid) at α =0,35 also accounts for the observed increased water uptake of the polymer above this level of neutralisation. (See section 3.4.2)

Beyond the highly structured region surrounding each polyion, long-range forces may perturb the equilibrium between ice-like clusters and free water molecules thus enhancing the structural properties of the water. Capillary effects have also been proposed to play a role in the structuring of the water furthest from the polyions in a hydrogel.[28,35] However, these so-called capillary effects may be nothing more than a manifestation of cooperative effects of ionic species on the surface of the hydrophilic 'capillary' wall exerting long-range electrostatic structuring forces on water molecules in the bulk liquid.

Although the presence of univalent simple electrolyte ions does not affect the extent of counterion binding to the polyelectrolyte matrix within a swollen hydrogel,[10,11] the long-range forces exerted by the macroions are sheilded by the ionic atmosphere surrounding each polyion chain.[71] As most of the water in a swollen hydrogel is held by long-range electrostatic

forces, the screening of these forces by simple electrolyte ions greatly impairs the water retaining properties of the gel. Reduced osmotic pressure due to added simple electrolyte also contributes to the reduction in water retention. Ionic crosslinking and chelate formation by polyvalent cations further reduce the water retaining capacity of a polyacrylate hydrogel.

From the above considerations it is obvious that a complex set of forces is responsible for the swelling of a hydrogel in the presence of water. Any model proposed to simulate such a system must take into account factors such as the charge density of the polymer chains, crosslink density, osmotic effects, concentration and valence of simple electrolyte ions..

5 APPENDIXES

APPENDIX 1: Saturated Water Uptake of Polyacrylate Gels Formed by Irradiation of Polymer Solutions / grams water per gram of polymer

Sample	Soln. Conc.	Dose /KGy 75	50	25	10	5	3
PAA	15%	-	-	80	230	-	-
PAA	10%	-	-	110	220	330	-
PAA	5%	-	60	60	250	-	0
PAA	2%	-	30	60	270	1400	-
PAA	1%	-	90	130	310	900	-
NaPAA 32	15%	-	-	1080	0	-	-
NaPAA 32	10%	-	300	1000	380	0	-
NaPAA 32	5%	-	310	790	96	0	-
NaPAA 32	2%	-	300	410	29	-	-
NaPAA 32	1%	-	0	0	0	-	-
NaPAA 50	15%	-	500	80	-	-	-
NaPAA 50	10%	260	650	1250	0	-	-
NaPAA 50	5%	370	420	590	0	-	0
NaPAA 50	2%	0	0	0	0	-	-
NaPAA 50	1%	0	0	0	-	-	-

(0 indicates complete dissolution of the sample)

APPENDIX 2: Equilibrim Molar Water Uptake of Linear Polyacrylates at Various Relative Humidities

Saturated Salt Soln.	Relative Humidity	PAA	NaPAA 32	NaPAA 67	NaPAA 100	KPAA 100	CsPAA 100
LiCl	11,3	0,02	0,20	0,05	0,14	0,76	0,95
CH_3COOK	22,2	0,09	0,35	-	0,60	1,06	1,59
$MgCl_2$	32,7	0,14	0,46	0,39	1,02	1,61	2,14
KNO_2	48,2	0,25	0,67	1,00	2,04	2,68	3,04
NaBr	58,2	0,32	0,72	1,48	2,49	3,47	3,75
$NaNO_2$	64,4	0,46	0,82	1,82	3,58	4,02	4,28
$CuCl_2$	68,4	-	0,88	2,12	3,93	4,41	4,85
NaCl	75,1	0,70	1,10	2,60	4,72	5,09	5,50
NH_4Cl	79,3	-	-	-	4,97	-	6,06
$(NH_4)_2SO_4$	80,2	0,92	1,37	3,08	5,08	5,37	6,32
KCl	84,2	1,11	1,57	3,52	5,71	6,31	7,42
$BaCl_2$	90,3	1,66	2,33	4,74	7,13	7,78	9,19

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