Synthetic hydrogels: 4. The permeability of poly(2-hydroxyethyl methacrylate) to cations—an overview of solute–water interactions and transport processes

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The permeability of hydrated poly(2-hydroxyethyl methacrylate) membranes to a series of mono- and divalent cations in the form of their chlorides has been examined. These initial studies indicate that a simple relationship involving some function of the size of the hydrated cation is unable to provide a basis for understanding the transport process. This view is confirmed by the results of studies of the permeation of a single cation (potassium) in the presence of a series of anions. Indeed, anion variation proved to exert an appreciably greater effect than did cation variation. The results are discussed in terms of the structure-making and structure-breaking potential of the ions and the various ways in which such properties have been correlated or measured. The structure-making or structure-breaking properties of an ion appear, to a degree, to be subsumed in the experimentally determined partition coefficient of a salt between solution and membrane. This enables the residual diffusion coefficient to be calculated and provides a reasonable basis for correlation with the hydrodynamic radii of the individual ions.

INTRODUCTION

The permeability of hydrogels in aqueous systems has been a feature of great importance in setting these materials apart from other polymers. The fact that water exists as an intimate and essential part of the polymer matrix implies that it might have the ability to modulate transport behaviour of water-soluble species. Indeed, it is the link between oxygen permeability and water content that enabled contact lenses to be developed that are sufficiently permeable to be worn during sleep. The transport properties of hydrogels are important in reverse osmosis (particularly desalination) processes and controlled drug-delivery systems. More recently, the potential applications of hydrogels as membranes for sensors have been recognized.

In the late 1960s interest in desalination stimulated work on sodium chloride transport through hydrogels[1] but little work on other ionic permeants has been reported. The interest in sodium chloride transport lay primarily in the computation of salt rejection factors for the membrane, these being derived from the relative values of water permeability to that of sodium. A great deal of published work involving neutral molecules such as amides[2], steroids[3], sugars[4] and water itself[5,6] exists, and models for the permeability process through hydrogels have been suggested. Despite this permeability studies involving hydrogels have been far from systematic.

To understand more fully ionic transport processes in hydrogels, it is essential to consider ion–water, ion–polymer and ion–water–polymer interactions. The permeation of anions and cations does not appear to be directly related to any single physical characteristic, but rather to a complex interaction of competing processes. From our reading of the literature it is evident that some of the fundamentals regarding the physicochemical interactions concerning ions in solution are not generally appreciated by polymer scientists interested in the transport phenomena of water-swollen polymer matrices. It is therefore appropriate at this point to highlight various factors relating to water structuring and to such concepts as hydrodynamic radii and the Hofmeister series in relation to ion permeation in water-swollen hydrogels.

A comprehensive study of water has been compiled by Franks[7]. The structure of bulk water can be considered to consist of long-range, tetrahedrally coordinated hydrogen bonds. Electrolytes perturb this steady-state equilibrium giving rise to three essentially different water phases[8]. The primary water phase around the electrolyte can be considered to be strongly associated and ordered by the electrolyte. The secondary water phase is considered to be less ordered than the primary phase, although it is still influenced by the electrolyte. Finally, there is the tertiary phase, which is unperturbed bulk water.

The ratio of primary-phase ordering to secondary-phase disordering is dependent on the nature of the electrolyte. Relatively small ions and multivalent ions such as Li^+, Na^+, H_3O^+, Ca^{2+}, OH^- and F^- are said to be structure-making ions[9]. That is to say, they order and electrostrict near-neighbour water molecules to form a primary water shell and have a tendency to induce order beyond that to form a long-range hydration shell, thus reducing the effect of the secondary disordered phase. Such structuring would increase the relative viscosity of
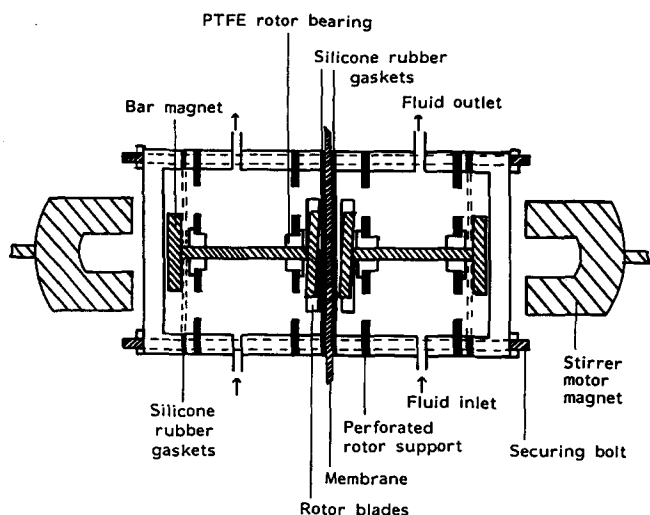
Figure 1 Diagrammatic representation of permeability cell

water (quantitatively expressed as the viscosity β coefficient[10,11]) and decrease the rate of ion permeation compared to that of a non-water-structuring species.

Large, monovalent ions are generally thought of as net structure-breakers. Ions such as K^+, Cl^-, Br^-, I^-, No_3^- and ClO_4^- generate a relatively weak electrostatic field capable of perturbing only near-neighbour water molecules. The secondary disordered phase is extensive and the fluidity of this phase is greater than that of bulk water itself. Therefore, permeation of these structure-breakers appears greater than expected from size predictions alone.

Another important concept in ion permeation is that of the hydrodynamic size of the permeating species. Stokes' law of motion characterizes the movement of a spherical particle through a continuous medium, in terms of the particle's mobility, radius and the solvent viscosity. The Stokes' radius, therefore, describes the effective size of the hydrated ion in water and, as such, has been of interest in the examination of ion permeation through a water-containing membrane[4,12,13]. It has, however, been noted that the application of Stokes' law to simple electrolytes yields inappropriately low values for the radius[10,14]. The Stokes' assumption of continuous viscous flow of the solvent medium is not valid since the water molecule is of comparable size to the hydrated ions[14].

In this paper we present results relating to the transport of a series of cations through, principally, poly(2-hydroxyethyl methacrylate), poly(HEMA), hydrogel. The effects of counterion variation are described and the results used as a basis for a discussion of the available models for transport phenomena in hydrogels.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (optical grade) was supplied with a certificate of analysis by Ubichem Ltd. Laboratory-grade α-azobisisobutyronitrile (AIBN) was supplied by Aldrich Chemical Co. and recrystallized before use as the initiator. Laboratory-grade ethyleneglycol dimethacrylate (EGDM) was purchased from BDH and used without further purification as the crosslinking agent. All salts were of analytical grade and purchased from Fisons or BDH. Salt solutions were

prepared with distilled water of ionic conductivity $1.5 \pm 0.5 \, \mu S \, cm^{-1}$.

Membrane preparation

Membranes were prepared in a polymerization mould consisting of two glass plates covered by two sheets of poly(ethylene terephthalate) and separated by a 0.25 mm thick polyethylene gasket[15]. Nitrogen-degassed monomers were combined with 0.5% by weight of the initiator and 1.0% by weight of the crosslinker. The resulting solution (ca. 4–5 ml) was injected into the glass mould through a G22 syringe needle. Polymerization was carried in an oven for 72 h at 60°C followed by a post-cure period of 2–3 h at 90°C. Membranes were separated from the poly(ethylene terephthalate) film and soaked in distilled water for three weeks. The equilibrium water contents of the membranes were measured at 37°C.

Permeation cell

Permeability studies on hydrated membranes were carried out in a horizontally held Perspex cell, shown diagrammatically in *Figure 1*. The cell was filled from two separating funnels and the solutions were circulated by a Schuco two-channel mini-peristaltic pump (flow rate $30 \pm 1 \, ml \, min^{-1}$) around the circuit described by *Figure 2*. The whole cell assembly was seated in a water bath, which was thermostatically controlled by a Techne TE-8J circulating water heater maintained, normally, at 37°C. Paddles inside the cell ensured that the surface layers of water adjacent to the membranes were stirred and were turned by two large magnets externally mounted and driven by geared linkages to a Citenco motor running at 180 ± 10 rpm. The receptor half of the cell was filled with deionized water and the donor side with the analyte solution (0.25 M) under investigation. The hydrostatic
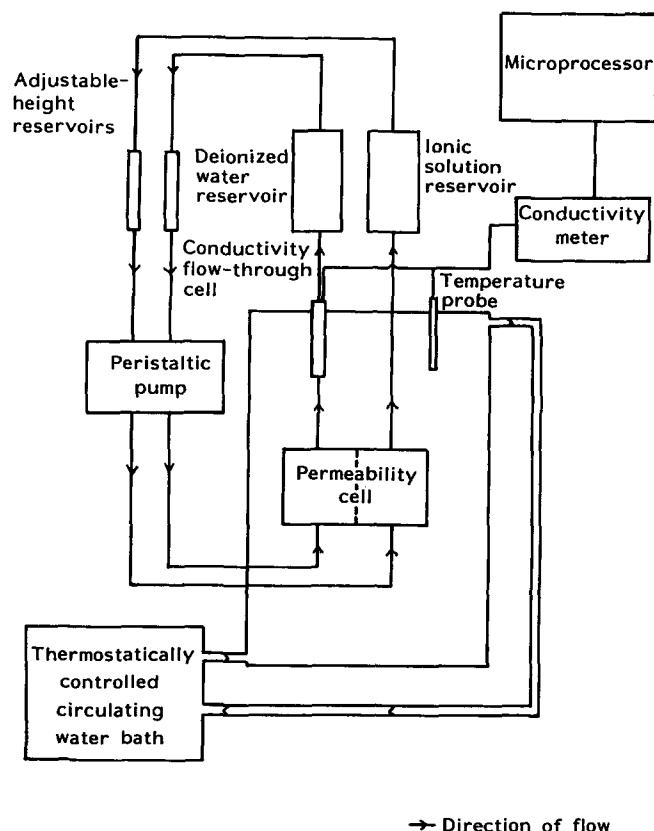

→ Direction of flow

Figure 2 Permeability apparatus: solution flow path

Table 1 Effect of salt solutions on EWC at 37°C

Salt	Conc. (M)	EWC (%)	$EWC_{ss} - EWC$ (%)
LiCl	0.25	33.4	−2.7
NaCl	0.25	33.4	−2.7
KF	0.25	33.0	−3.1
KCl	0.25	33.4	−2.6
KBr	0.25	34.9	−1.2
KI	0.25	39.9	+3.8
KSCN	0.25	44.1	+8.0
KHCO₃ [a]	0.25	34.3	−1.8
K₂SO₄	0.125	31.6	−2.2
CaCl₂	0.25	32.7	−3.4
KNO₃	0.25	35.1	−1.0
K₂CO₃	0.125	33.9	−4.5

[a] EWC of membrane measured after 8 h to minimize poly(HEMA) degradation in presence of salt

pressure either side of the membrane was equalized by adjustments to the heights of two reservoirs. The experimental run was timed from the introduction of the solutions into the cell.

Samples (1.0 ml) were withdrawn from the deionized water reservoir every hour for a period of 7 or 8 h. Analysis was undertaken on an EEL Flame Photometer model A (Evans Electroselenium Ltd) of the transported cation concentration. Alternatively, a glass conductivity flow-through cell (cell constant $k = 1$), linked to an Alpha 800 conductivity meter supplied by CP Instrument Co. Ltd, was inserted between the outlet of the deionized water side of the permeation rig and the filling reservoir. The change in ion concentration was monitored throughout the experimental run and an optional linkage through the A/D port of a Tatung Einstein computer enabled data to be stored and manipulated.

Permeation coefficients

Permeation coefficients are calculated according to equation (1), which is based on previous studies involving gas and drug diffusion through various polymer membranes[16,17] and fully described in the following paper[18]:

$$P = DK_p \qquad (1)$$

where P is the permeation coefficient $(cm^2\,s^{-1})$, K_p is the partition coefficient and D is the diffusion coefficient $(cm^2\,s^{-1})$.

Equilibrium water contents

The equilibrium water content (EWC) of a membrane can be calculated from the weights of a hydrated and dehydrated sample, as shown in equation (2)[15]:

$$EWC\ (\%) = \frac{\text{weight of water in hydrated sample}}{\text{total weight of hydrated sample}} \times 100$$

$$(2)$$

The equilibrium salt solution content (EWC_{ss}) can be similarly determined from the weight of a membrane after being soaked in salt solution. Details of the determination and its statistical significance ($\pm 0.4\%$) have been given in part 1 of this series[19], where a statistical analysis on 100 samples of poly(HEMA) gave a mean EWC of 36.1% with $\Sigma_{n-1} = 0.42$ at 37°C.

Partition coefficients

Water-swollen poly(HEMA) partition coefficients for the various salt solutions were calculated from the results of salt desorption experiments[1,20]. Membrane samples were allowed to equilibrate overnight at 37°C in 0.25 M salt solutions, molarity being based on the cation concentration. After surface water had been removed from the membrane, it was weighed and transferred to a known quantity of deionized water and the salt allowed to leach out of the membrane. The ion concentration was measured by flame photometry and the partition coefficient then calculated (equation (3)):

$$K_p = \frac{\text{moles of salt/gram of membrane}}{\text{moles of salt/gram solution}} \qquad (3)$$

RESULTS AND DISCUSSION

Procedural variables and system calibration

The standard poly(HEMA) membrane when stored in water can be considered to have an EWC of 36.0% at 37°C. Small changes in the thickness and EWC of a membrane were found to accompany changes in the storage solution, and these are listed in *Table 1*.

The effects of experimental parameters upon permeation rates were investigated to eliminate any effects from subsequent studies. Early permeability studies suggested that the stirring rate at the surface of the membrane was not critical at 30 rpm or above[21], and subsequent work has shown, in particular, that it is essential to stir the high-concentration side of the membrane to prevent any surface-layer effects[22,23]. Furthermore, our own studies with the experimental system used in this work showed that there is a decrease in permeation of 3% if the high-concentration side only is stirred and a decrease of $10 \pm 1\%$ if the low-concentration side only or neither side is stirred. Forward and reverse solution flow appear to have no significant effect. Similarly, changes in flow rate between 30 and 90 ml min⁻¹ did not appear to be critical.

Steady-state permeation was observed after 2 h with experimental errors of 2–3% for repeat runs on either the same or different sample membranes. Typical results are shown in *Figure 3*. No dramatic change in permeation rates was observed over the temperature range of 18 to 45°C, as the effects of temperature on membrane properties in conjunction with the activation energy for Fickian-type diffusion processes tend to cancel each other. Variation in sampling time was used to examine the consequence of sample extraction. Samples (1 ml) extracted every 20, 60 and 90 min ultimately led to a 20%, 6% and 4% reduction in the sampled solution volume, respectively. No significant differences were noted in the permeation coefficients provided that concentrations were normalized to account for volume reduction. Analysis by conductivity requires no reduction in solution volume and correlates well with flame photometry analysis.

Permeability of poly(HEMA) membranes

Various experiments were carried out to establish the relative effects of cation and anion on permeation. The permeability of poly(HEMA) membranes to lithium, sodium, potassium and calcium cations was first investigated, at 37°C using 0.25 M cation solutions in the
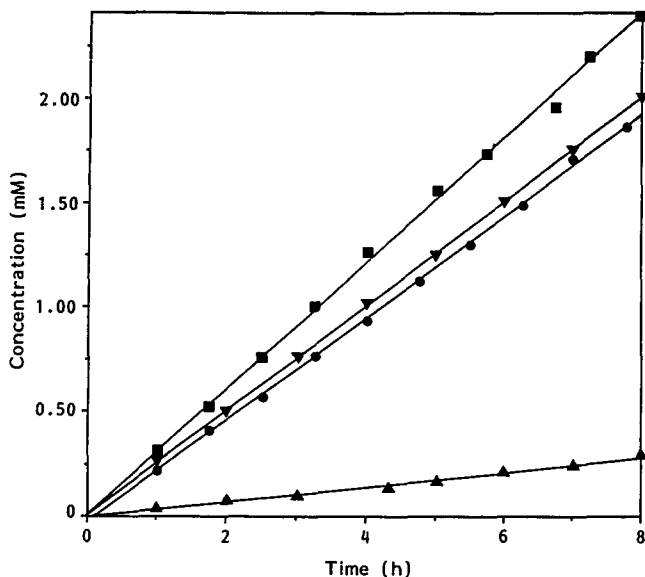
Figure 3 Effect of cation variation on transport through poly(HEMA): ■, KCl; ▼, NaCl; ●, LiCl; ▲, CaCl$_2$

Table 2 Cation permeability and diffusion coefficients of salts at 37°C

Salt	$P \times 10^8$ (cm^2 s^{-1})	$K_p{}^a$	$D_m \times 10^7$ (cm^2 s^{-1})	$D_0 \times 10^{5b}$ (cm^2 s^{-1})	$\ln(P/D_0)$
LiCl	16.7	0.179	9.3	1.267	−4.329
NaCl	17.9	0.157	11.4	1.475	−4.412
KCl	23.9	0.179	16.9	1.838	−4.129
CaCl$_2$	2.9	0.157	18.5	1.107	−5.945

^{a} 0.25 M cation concentration, equation (3)
^{b} Values taken from Stokes[10]

form of the chloride on the donor side of the cell. Primary transport data, of the form shown in *Figure 3*, were used to determine the respective permeation coefficients for the cations, which are listed in *Table 2*. In a subsequent set of experiments the effect of the counterion on potassium ion transport across poly(HEMA) was investigated under similar conditions (37°C, donor solution 0.25 M with respect to cation concentration). Primary transport data are illustrated in *Figure 4*, and the resultant potassium ion permeation coefficients listed in *Table 3*. A significant difference between the permeability coefficients of the various anions investigated was found. Thus, the thiocyanate ion produces permeability coefficients some three times greater than that of the chloride, which in turn is some 15 times faster than that of the sulphate ion.

Permeability correlation with the Stokes' or hydrodynamic radii of the permeating species has been previously inferred[4,12,13,24,25]. Whilst the crystallographic radii increase in the order Na$^+$ <Ca^{2+} <K$^+$, the Stokes' or hydrodynamic radii increase in the order K$^+$ <Na$^+$ <Ca^{2+}, which is the same order as the relative ion permeation through both water and water-swollen poly(HEMA), a point reflected in the results shown in *Table 2*. However, in previous work, the examination of a limited range of permeating species and the extent and quality of the data presented were insufficient for the correctness of the correlation to be assessed. The work was restricted to cation variation in the presence of the chloride ion, which exerts a relatively modest effect on the transport process. Our results presented in *Tables 2–5*

enable various aspects of this correlation to be more precisely evaluated.

Even when a simple correlation of cation permeability with hydrodynamic radii for the metal chlorides is attempted, an obvious anomaly arises in the case of lithium. This is even more evident when the ratio of the diffusion of the ion through the membrane (D_m) to that through water (D_0) is used as the basis of correlation. Treatment of the results in this way is particularly interesting in that it enables comparisons to be made with
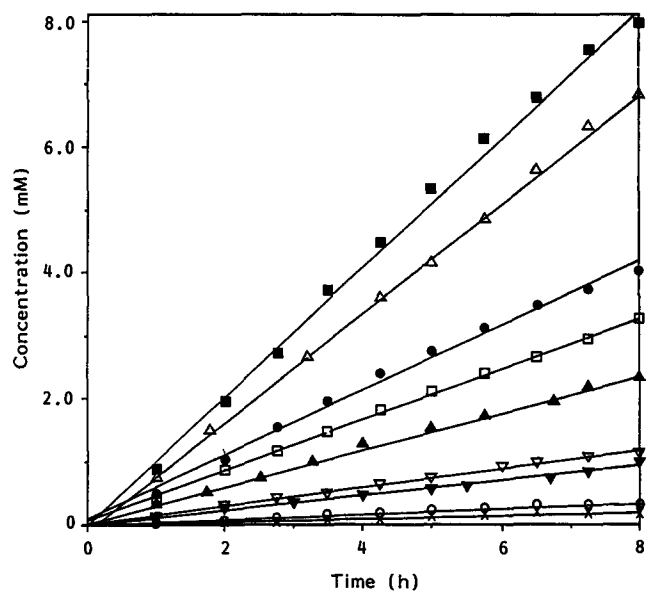

Figure 4 Effect of anion variation on transport through poly(HEMA): ■, KSCN; △, KI; ●, KNO$_3$; □, KBr; ▲, KCl; ▽, KF; ▼, KHCO$_3$; ○, K$_2$CO$_3$; ×, K$_2$SO$_4$

Table 3 Anion permeability and diffusion coefficients of salts at 37°C

Salt	$P \times 10^8$ (cm^2 s^{-1})	$K_p{}^a$	$D_m \times 10^7$ (cm^2 s^{-1})	$D_0 \times 10^{5b}$ (cm^2 s^{-1})	$\ln(P/D_0)$
KF	12.2	0.117	10.4		
KCl	23.9	0.179	13.4	1.838	−4.343
KBr	32.0	0.226	14.2	1.870	−4.068
KI	61.0	0.390	15.6	1.859	−3.417
KSCN	86.8	0.533	16.2		
KHCO$_3$	9.4	0.116	8.1		
K$_2$SO$_4$	1.8	0.044	4.1		
KNO$_3$	41.8	0.278	15.0		
K$_2$CO$_3$	3.6	0.045	8.0		

^{a} 0.25 M cation concentration, equation (3)
^{b} Values taken from Stokes[10]

Table 4 Radii of cations^a

Ion	r_c (Å)	r_s (Å)	r_s^2 (Å)^2	r_n^2 (Å)^2
Li$^+$	0.60	2.12	5.66	14.59
Na$^+$	0.95	1.64	3.39	12.82
K$^+$	1.33	1.12	1.56	10.96
Ca^{2+}	0.99	2.76	9.61	16.97

^{a} Radii are as follows:
r_c = crystallographic radii[26]
r_s = Stokes' hydrodynamic radii[10]
r_n = Nightingale's hydrodynamic radii[14]

Table 5 Radii of anions[a]

Ion	r_c (Å)	r_s (Å)	r_s^2 (Å)^2	r_n^2 (Å)^2
F⁻	1.36	1.49	2.76	12.39
Cl⁻	1.81	1.07	1.44	11.02
Br⁻	1.95	1.05	1.39	10.89
I⁻	2.16	1.07	1.42	10.96
SCN⁻		1.23	1.51	
HCO₃⁻		1.84	3.39	
SO₄²⁻	1.44	2.06	5.29	14.36
NO₃²⁻	2.64	1.29	1.66	11.22
CO₃²⁻	2.66	2.66	7.07	15.92

[a] Radii are as follows:
r_c = crystallographic radii[26]
r_s = Stokes' hydrodymanic radii[10]
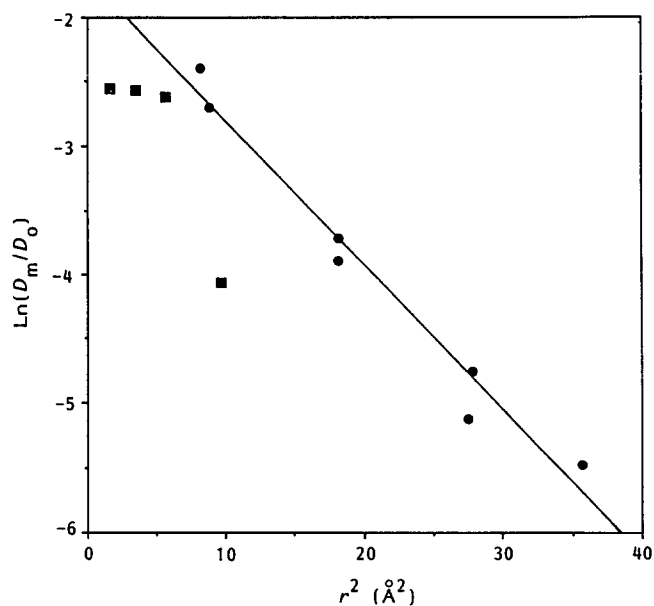r_n = Nightingale's hydrodynamic radii[14]

partition behaviour of anions are collected in *Tables 3* and *5*. Two attempted correlations are shown in *Figures 6* and *7*. *Figure 6* presents the variation in permeability coefficients of potassium as a function of hydrodynamic radius of its coanion. Clearly no correlation exists. *Figure 7*, on the other hand, is more promising and indicates that the diffusion component of the transport process is probably size-dominated.

This still leaves several questions unanswered. Even if diffusion coefficients of a cation can be related to the hydrodynamic radius of the counteranion, on what basis can the important partition or solubility components be structurally correlated? Will the anion always dominate the transport process or will the larger of the two (anion or cation) exert the controlling influence? Does the lack of correlation between D_m/D_0 values for hydrophilic solutes
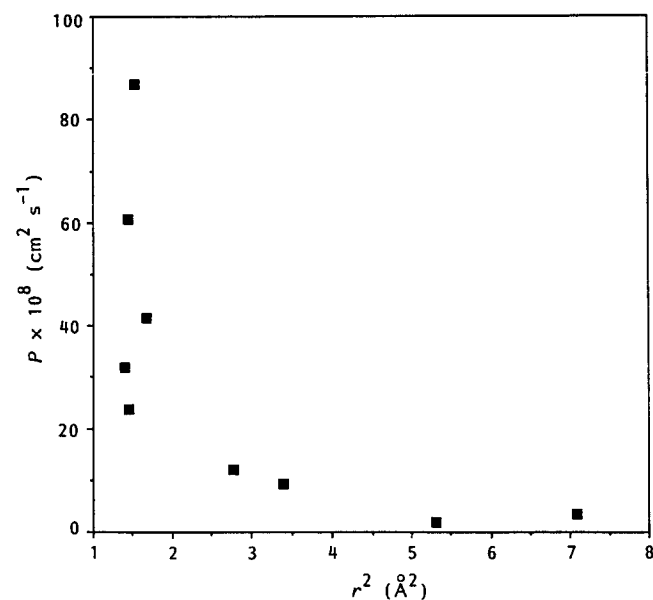

Figure 5 Comparison of cation transport data (■) with that of Kim's for neutral solutes (●)[4]

Figure 6 Variation of permeability of potassium as a function of the hydrodynamic radius of its coanion

the transport of neutral solutes of various sizes across poly(HEMA) membranes to be made. *Figure 5* shows a plot of log(D_m/D_0) against the square of the radius of the diffusing cationic species using data from *Tables 2* and *4*. In addition a solid line showing the position of the diffusion coefficient ratios obtained by Kim[4] for a series of hydrophilic solutes of various sizes is included. It is immediately apparent that, even if the abnormality of the lithium value is ignored, the diffusion rates for the cations are much lower than would be expected from the results on neutral hydrophilic solutes of similar size. The difference may be associated with the validity of the respective values used for the hydrodynamic radii and the size of the non-ionic solutes, a point that must be considered further.

It is apparent from *Figure 4* and *Table 3* that the effect of the anion on cation permeability is dramatic and that any transport model must take this into account. Furthermore, the fact that coanions have relatively small effects on the water diffusion (D_0) values for individual cations indicates that it is the transport process within the membrane that must be addressed. As a basis for discussion, data relating to the size, transport and
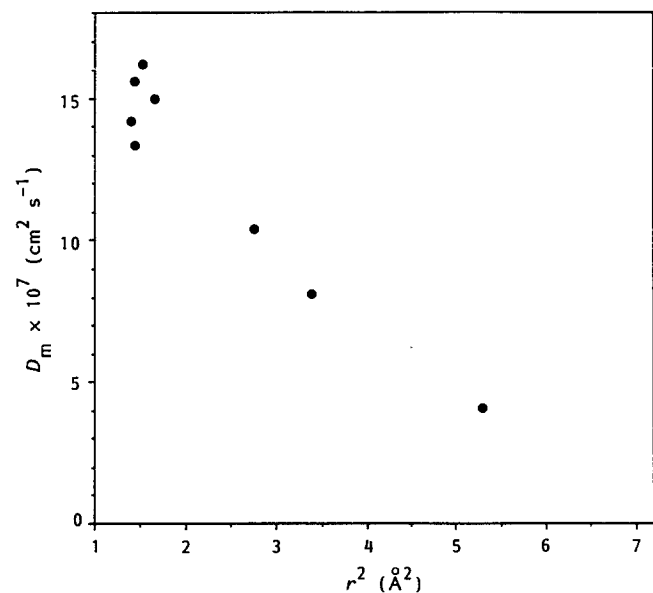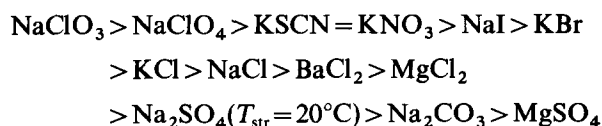

Figure 7 Variation in diffusion of potassium as a function of the hydrodynamic radius of its coanion

and for ionic species reflect fundamentally different behaviour, or merely a failure to recognize the effective dimensional correlation for a pair of transported ions? Clearly some molecular model is needed to enable both the size permeability effects and the structural relationship of the diffusing species and the hydrogel matrix to be established.

Permeation models

Qualitatively, cation permeation is observed to fall into two categories. On the one hand, there are the highly mobile structure-breakers, for example K^+, and on the other, the less mobile structure-makers, such as Li^+, Na^+ and Ca^{2+}. The anions can also be classified as structure makers or breakers, and it is interesting to compare this division of the ions with observed permeation rates. Anion structure-breakers like SCN^-, I^-, Br^- and Cl^- are observed to permeate more rapidly than structure-makers such as F^- and SO_4^{2-}. Polyatomic ions are not easily classified, other than by experimentation, and the hydrogen carbonate anion does not fit into this simple qualitative scheme. From size and valancy HCO_3^- is predicted to be a structure-breaker but in order of ion permeation it is sandwiched between two structure-making ions. However, it is worth remembering that the pH of the water in the hydrogel is slightly acidic, pH 6. Under this condition it is possible that the hydrogen carbonate partially dissociates to give the carbonate anion (CO_3^{2-}), which, owing to its greater charge density, is more likely to structure its aqueous environment. For the purpose of illustration the partition functions of both the CO_3^{2-} and the HCO_3^- anions are included in *Table 3*.

The order of permeability of the salts (*Tables 2* and *3*) is found to be consistent with the changing influence of ionic structure on behaviour found in the lyotropic (Hofmeister) series. It is significant that this series has been interpreted by Luck[27] as one in which water binding changes. Measurements were made of the structure temperature (T_{str}), which is defined by Luck as the temperature to which pure water is raised or lowered in order that it should have the same extinction coefficient, in the region of free or weakly bound OH, as the electrolyte solution. The structure temperature corresponding to 1 M anion concentrations of various salts at 20°C gave a series:

$$NaClO_3 > NaClO_4 > KSCN = KNO_3 > NaI > KBr$$

$$> KCl > NaCl > BaCl_2 > MgCl_2$$

$$> Na_2SO_4(T_{str} = 20°C) > Na_2CO_3 > MgSO_4$$

This spectroscopic series is obviously similar to the Hofmeister series. In commenting upon his experiences with the concept, Luck makes the point that the anions play the dominant, and cations a secondary, ordering role in the series. This point emerged in earlier studies of the swelling of poly(HEMA) hydrogel[28,29]. The dominant effect of the anion over the cation is thought to arise from the fundamental difference between the water–ion interaction. Anions are considered to react strongly with water to form partial covalent bonds with the primary hydration shell, whereas cations interact with water in a less intense and probably electrostatic manner. Furthermore, there is a reasonably good correlation with the structure-making and structure-breaking concepts discussed above.

Despite the obvious general relevance of hydrodynamic radii to transport processes involving hydrated ions, they do not provide an adequate basis for understanding the behaviour of ionic species in water-swollen membranes. This may be illustrated in several ways. On comparing results based on hydrodynamic radii and on Nightingale's 'corrected' radii[14] with Kim's results (*Figure 5*) that relate the diffusion of neutral species with their radii, it is apparent that no satisfactory correlation is obtained. In addition, this approach does not take into account the discontinuous nature of water held within a polymer matrix, nor can it allow for any interaction of the permeating species with the polymer itself. Not even refinements to the Stokes' radii can explain (*Figure 3*) why lithium ions appear to migrate through water-swollen poly(HEMA) much faster than anticipated on the basis of the hydrodynamic radii. It is apparent that any satisfactory permeation model must take additional factors into account.

The simple permeation of a solute that requires a solvent in order to permeate through an otherwise impermeable membrane is well documented[1,24]. In the case of a simple salt such as NaCl it is indisputable that the ions permeate through a membrane such as water-swollen poly(HEMA) in the water phase. This is extended in theoretical models such as the 'free-volume theory'[1], or mathematical models relating permeation to pore size[30], to take into account the size of the hydrated solute. Additionally, some fundamental relationships between solutes and polymer partition coefficients have been investigated. The partition coefficient is defined as the concentration of the solute in the membrane phase. For simple electrolytes, such as the alkyl halides, the partition coefficient in the water-swollen polymer, K_p, should be not more than 1, and K_p will increase with an increase in polymer hydration[1,20]. However, this is not necessarily the case for non-electrolytes. Previous workers have demonstrated that the diffusion of non-electrolytes through water-swollen polymers can be influenced by the interaction of the solute and the polymer chain[4,20]. Kim describes the diffusion of macromolecules through poly(HEMA) membranes, swollen to various degrees, as either hydrophilic or hydrophobic solute diffusion[4]. Hydrophilic macromolecules are described as permeating though the bulk-water phase of the membrane via the 'pore' mechanism. Hydrophobic macromolecules are described as diffusing either by the 'pore' or 'partition' mechanism.

An examination of the effect that the partition coefficient has upon cation transport (for various cations with common coanions) shows little correlation. This implies that the diffusion of these cations does not occur by a partition effect but by transport through the water phase only. A similar conclusion was reached by other authors from studies of diffusion through hydrated membranes of electrolytes, and, in the case of NaCl, from the associated activation energy[12,31]. However, an interesting trend may be observed in the effect of the counterion on cation permeation. The permeation of potassium appears directly related to the partition coefficients of the particular salts involved (*Table 3* and *Figure 7*). This point is highlighted by the structure-breaking halides Cl^-, Br^- and I^-, which have similar diffusion coefficients and whose differences in permeability can be explained in terms of the partition

coefficient alone (*Table 3*). It is recognized that a certain degree of membrane expansion or contraction is observed in different salt solutions (*Table 1*). The relative volume change in the membrane does not, however, absolutely parallel the relative changes in potassium permeation in the presence of different coanions. Some comparison of partition and structuring effects is relevant. The membrane partition coefficients increase in the order $SO_4^{2-} < HCO_3^- < F^- < Cl^-$. These particular anions are all water-structuring ions, Cl^- being a borderline case. These ions are also classed as hard bases. Partition coefficients increase further in the order $Br^- < I^- < SCN^-$. These ions are all classed as structure-breakers in water. They are also classed as soft bases, Br^- being a borderline case.

It is useful to consider the 'interfacial zone' of water between the polymer and the ions. The greater the water-structuring ability and the harder the ion, the greater the requirement of aqueous 'pores' or domains for the ion to permeate through. As the water-structuring ability decreases, however, so the hydration requirement decreases. For the particular anions under investigation, this trend is accompanied by a greater ability for the ion to approach the lipophilic backbone. Thus, as this trend is extrapolated, permeation through the membrane becomes possible, not only through the mobile hydration shell but also, to a lesser extent, via the polymer. Whereas it is accepted that the permeation of KSCN would not be possible in the absence of water, it is arguable that the ease of SCN^- approach to the backbone influences the rate of ion permeation to a secondary extent. This would explain the relatively large values for its partition coefficient (*Table 3*) and permeability through the hydrated membrane (*Figure 4*). It should be noted that, like all studies involving water structuring, the results are concentration-dependent[32]. At infinite dilution it can be expected that the solvent cospheres around an ion are complete. As concentrations increase, then the probability of the cospheres overlapping increases, to a point where contact ion pairs may be formed.

In summary it is apparent that both size and water-structuring effects are important in determining the transport properties of an ion in a hydrated matrix. The effect of the ion on the hydrated matrix itself and the resultant nature of the 'interfacial zone' is more difficult to measure, but an interesting and informative reflection of this behaviour is found in the melting endotherms obtained using differential scanning calorimetry (d.s.c.) The role of this technique in characterizing water-structuring phenomena in hydrogels has been discussed in part 1 of this series[19]. Although a well established technique, d.s.c. has not previously been used in the study of water-structuring effects for different salt solutions in hydrated polymer matrices. *Figure 8* shows the melting endotherms obtained for poly(HEMA) hydrogels hydrated in water and in solutions of potassium iodide, potassium chloride and potassium sulphate. *Table 6* collects, for convenience, the ionic concentrations of the hydrated solutions, the partition coefficients and the expected cryoscopic depression together with equilibrium freezing and non-freezing water contents. It is apparent that both the structure-making ions (Cl^- and SO_4^{2-}) reduce the free or freezing water content and increase the non-freezing (sometimes called 'bound') water content relative to hydration in deionized water. Similarly the structure-breaking ion (I^-) has the opposite effect in that it increases the freezing and decreases the non-freezing water contents. The fine structure of the endotherm and in

a KI
EWC = 38.3%
FWC = 17.6%
NFWC = 20.7%

b K₂SO₄
EWC = 31.4%
FWC = 5.2%
NFWC = 26.2%

c KCl
EWC = 33.5%
FWC = 6.8%
NFWC = 27.6%

d H₂O
EWC = 36.1%
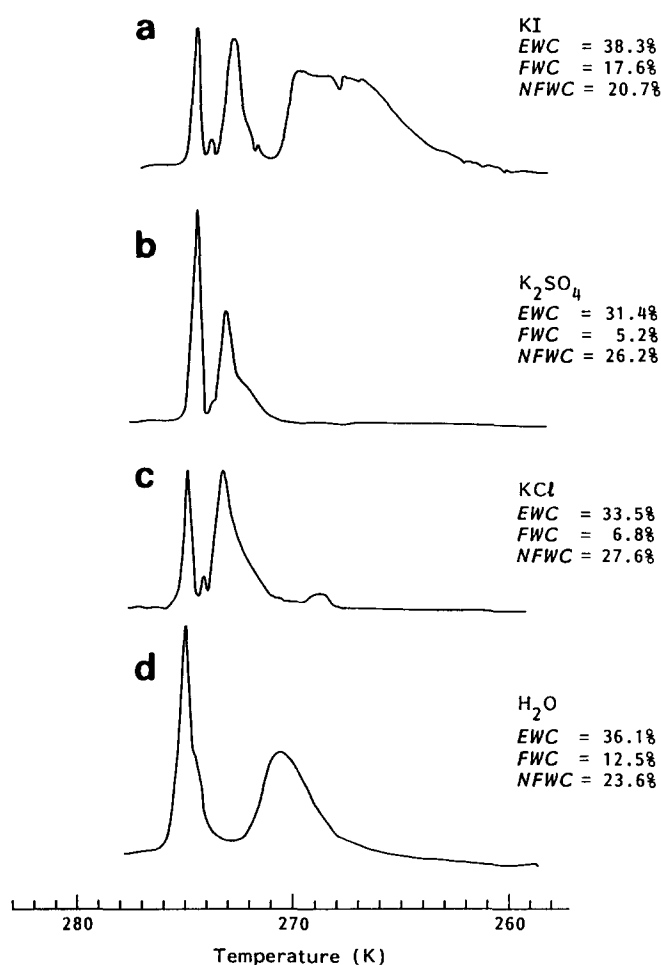FWC = 12.5%
NFWC = 23.6%

Temperature (K)

Figure 8 Melting endotherms obtained for poly(HEMA) hydrogels hydrated in solutions of: (a) KI (250 mM); (b) K₂SO₄ (125 mM); (c) KCl (250 mM); and (d) pure water (*EWC* = equilibrium water content, *FWC* = freezing water content, *NFWC* = non-freezing water content)

Table 6 Collected data relating to membranes and respective hydrating solutions of *Figure 8* and determined at 37°C

Hydration solution	Solution concentration (M)	Partition coefficient	Expected cryoscopic depression (°C)	*EWC* of membrane (%)	Freezing water (%)	Non-freezing water (%)
K₂SO₄	0.12	0.017	0.9	31.4	5.2	26.2
KCl	0.25	0.133	<0.1	33.5	6.8	27.6
KI	0.25	0.244	0.5	38.3	17.6	20.7
Water	–	–	–	36.1	12.5	23.6

particular the position of the depressed water peak is also characteristically different with the two classes of ions.

In this paper, a single polymer composition was used to examine the effect that the nature of the permeant has on water structuring and transport in hydrated membranes. Such work provides an essential basis for the study of ion transport and water structuring in various hydrated membranes, in which the modulation of the water binding properties of the polymer itself, and its consequent influence on ion transport is examined. This involves keeping the anion constant and producing variations in water binding by changing polymer structures. The results of these studies are presented in the next paper of this series[18].

ACKNOWLEDGEMENT

REFERENCES

1 Yasuda, H., Lamaze, C. E. and Ikenberry, L. D. *Makromol. Chem.* 1968, **118**, 19
2 Koo, H. S. and Jhon, M. S. *Bull. Korean Chem. Soc.* 1980, 1(4), 138
3 Zenter, G. M., Cardinal, J. R., Feijen, J. and Song, S.-Z. *J. Pharm. Sci.* 1979, **68**, 970
4 Kim, S. W., Cardinal, J. R., Wisniewski, S. and Zentner, G. M. in 'Water in Polymers', (Ed. S. P. Rowland), ACS Symp. Ser. 127, American Chemical Society, Washington DC, 1980, p. 347
5 Yasuda, H., Olf, H. G., Crist, B., Lamaze, C. E. and Peterlin, A. in 'Water Structure and Water–Polymer Interface', (Ed. H. H. G. Jellinke), Plenum Press, New York, 1972, p. 39
6 Wisniewski, S. and Kim, S. W. *J. Membr. Sci.* 1980, 6(3), 309
7 'Water, A Comprehensive Treatise: The Physics and Physical Chemistry of Water', (Ed. F. Franks), Plenum Press, New York and London, 1972, Vol. 1
8 Frank, H. S. and Wen, W. Y. *Disc. Faraday Soc.* 1957, **24**, 133
9 'Water and Solute–Water Interactions', (Ed. J. L. Kauanau), Holden-Day, San Francisco, 1964, pp. 52–88
10 Robinson, R. A. and Stokes, R. H. 'Electrolyte Solutions', 2nd Edn., Academic Press, New York, 1968
11 Cox, W. M. and Wolfenden, J. H. *Proc. R. Soc. (A)* 1934, **145**, 475
12 Kimura, Y., Lim, H. J. and Iijma, T. *J. Membr. Sci.* 1984, **18**, 285
13 Peppas, N. A. and Moynihan, H. J. *J. Appl. Polym. Sci.* 1985, **30**, 2589
14 Nightingale, E. R., Jr *J. Phys. Chem.* 1959, **63**, 1381
15 Pedley, D. G. and Tighe, B. J. *Br. Polym. J.* 1979, **11**, 130
16 Garret, E. R. and Chemburker, P. B. *J. Pharm. Sci.* 1968, **57**(6), 949
17 Daynes, H. A. *Proc. R. Soc. (A)* 1920, **97**, 286
18 Murphy, S. M., Hamilton, C. J. and Tighe, B. J. *Polymer* 1988, **29**, 1891
19 Corkhill, P. H., Jolly, A. M., Ng, C. O. and Tighe, B. J. *Polymer* 1987, **28**, 1758
20 Kojima, Y. H., Furuhata, K. and Miyasaka, K. *J. Appl. Polym. Sci.* 1984, **29**, 533
21 Flynn, G. L. and Smith, E. W. *J. Pharm. Sci.* 1971, **60**, 1713
22 Kumanoto, E. *J. Membr. Sci.* 1981, **9**, 43
23 Atherton, N. D. PhD Thesis, Department of Chemistry, The University of Aston, Birmingham, 1982
24 Yasuda, H. and Lamaze, C. E. in 'Permselective Membranes', (Ed. C. E. Rogers), Marcel Dekker, New York, 1971, p. 111
25 Refojo, M. F. *J. Appl. Polym. Sci.* 1965, **9**, 3417
26 Pauling, L. 'The Nature of the Chemical Bond', 3rd Edn., Cornell University Press, Ithaca, New York, 1960
27 Luck, W. A. in 'Water in Polymers', (Ed. S. P. Rowland), ACS Symp. Ser. 127, American Chemical Society, Washington DC, 1980, Ch. 3
28 Refojo, M. F. *J. Polym. Sci. (A-1)* 1967, **5**, 3103
29 Dusek, K., Bohdanecky, M. and Vosicky, V. *Coll. Czech. Chem. Commun.* 1977, **42**, 1599
30 Ratner, B. D. and Miller, I. F. *J. Biomed. Mater. Res.* 1973, **7**, 353
31 Higuchi, A. and Iijima, T. *J. Appl. Polym. Sci.* 1986, **32**, 3229
32 Choppin, G. R. and Buijs, K. *J. Chem. Phys.* 1963, **39**, 2042