# Synthetic hydrogels: 5. Transport processes in 2-hydroxyethyl methacrylate copolymers

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The permeability, to lithium, potassium, sodium and calcium chlorides, of a series of hydrogel membranes based principally on copolymers of 2-hydroxyethyl methacrylate has been studied. These copolymers yield homogeneous hydrogels whose water-binding properties vary regularly between those of the relevant comonomers. Changes of this type, which are most readily characterized by the ratio of freezing to non-freezing water determined by differential scanning calorimetry, reflect in some ways the water structure-making and structure-breaking properties of the transported anions and cations themselves. The role of these and related size exclusion phenomena in governing membrane permeability is discussed in comparison with transport models that depend simply upon the volume fraction of water within the system.

## INTRODUCTION

In the preceding paper in this series[1] we have discussed the effect of solute–water interactions on the transport of ions through poly(2-hydroxyethyl methacrylate), poly-(HEMA), hydrogel. It is apparent that the relative permeation rates of mono- and divalent cations in the presence of a common (chloride) anion are not directly related to a simple function of the size of the hydrated cation. Furthermore, the effect of anion variation on permeability is far greater than that observed for cation variation and, again, unrelated to a simple function of anion size.

The important underlying function that was observed to unify results for both cation and anion variation is the water-structuring ability of the ion. These structure-making and structure-breaking properties were broadly related to the partition coefficient of the salt between membrane and solution. When the relative solubilities of the transported species in the hydrated matrix were thus taken into account, and the residual diffusion coefficient calculated, this parameter was found to correlate reasonably well with the hydrodynamic radii of the individual ions.

Water-structuring phenomena are thus obviously of fundamental importance in transport processes through hydrogel membranes. In seeking a more complete understanding of these phenomena, and the development of an acceptable model, it is logical to study variations in water structuring that may be produced by variations in polymer, and thus membrane, structure. In addition to the importance of this underlying understanding of the molecular aspects of transport processes, great interest centres around the ability to design permselective membranes by achieving a degree of discrimination against the transport of specific individual ions. In this paper we describe the results of ion permeation studies (various cations in the presence of a common anion)

through a series of hydrogel membranes in which both the gross water content and the water binding (or structuring) processes are varied. The results are discussed in terms of models that seek to relate the transport process to the quantity and nature of water in the membrane.

## EXPERIMENTAL

### Membrane materials

2-Hydroxyethyl methacrylate (optical grade) was supplied with a certificate of analysis by Ubichem Ltd and was used without further purification. Other reagents used in the preparation of membranes were of laboratory grade and supplied by BDH unless otherwise stated. Methyl methacrylate (MMA) was treated with sodium hydroxide solution (0.1 M), washed with distilled water, dried with magnesium sulphate and vacuum distilled at *ca.* 54°C and 35 mmHg. Styrene (Sty), 2-hydroxypropyl acrylate (HPA) and 2-hydroxypropyl methacrylate (HPMA) were purchased from Polysciences Inc. and were purified by vacuum distillation prior to use.

The initiator α-azobisisobutyronitrile (AIBN) was supplied by Aldrich Chemical Co. and recrystallized before use. The crosslinking agent, ethyleneglycol dimethacrylate (EGDM), was used without further purification.

### Membrane preparation

Membranes were prepared by the method described in part 4 of this series[1]. Nitrogen-degassed monomers were mixed with 0.5% by weight of the initiator and, unless otherwise stated, 1.0% by weight of the crosslinking agent. The resulting solution (*ca.* 4–5 ml) was injected into the glass mould through a G22 syringe needle. Polymerization was carried out in an oven for 72 h at 60°C followed by a post-cure period of 2–3 h at 90°C, leading to a conversion of substantially 100% (ref. 2). Membranes were soaked in distilled water for three
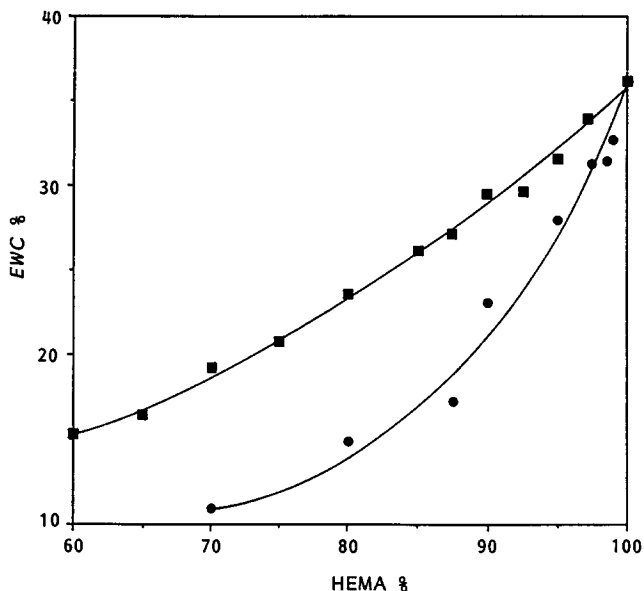
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**Figure 1** *EWC* as a function of the weight per cent of HEMA in HEMA–MMA (■) and HEMA–Sty (●) copolymers

weeks. The equilibrium water contents of the membranes were measured at 37°C.

### Salt solutions

All salts were of analytical grade, were purchased from Fisons or BDH and were used without further purification. Salt solutions were prepared with distilled water of ionic conductivity $1.5 \pm 0.5 \, \mu S \, cm^{-1}$.

### Permeation studies

Permeability studies on hydrated membranes were undertaken by the method described in part 4 of this series[1]. Circular membranes (diameter 5 cm) were placed at the centre of a two-compartment cell. Two paddles stirred the surface water of the membrane, set at an optimum speed to prevent any build-up of charged species. The cell was jacketed in a constant-temperature water bath, normally maintained at 37°C. One side of the cell was filled with deionized water and the other side with an alkali-metal chloride or alkaline-earth-metal chloride solution (0.25 M). The permeation studies were timed from the introduction of the solutions into the cell. The solutions were circulated through the cell by a Schuco mini-peristaltic pump into two reservoirs. The height of these reservoirs could be adjusted in order to equalize the hydrostatic pressure on either side of the membrane and they were fitted with Suba-Seals to allow samples of the solutions to be extracted.

The concentration of the permeant species was analysed either by flame photometry or by conductivity. In the case of flame photometry, 1.0 ml samples were withdrawn from the deionized water reservoir every hour, for a period of 7 or 8 h, and were analysed on an EEL Flame Photometer model A (Evans Electroselenium Ltd). Alternatively, a conductivity flow-through cell (cell constant $k = 1$) on the deionized water side of the permeation rig was used to monitor the change in ion concentration throughout the experimental run. Conductivity readings were recorded every 30 min by an Alpha 800 conductivity meter made by CP Instrument Co. Ltd. Calibration curves for both flame photometry

and conductivity were constructed for the individual metal chlorides between the range $1.0 \times 10^{-6}$ and 0.125 M.

Permeation coefficients are calculated according to the equations:

$$Q_t = A_p V / t \tag{1}$$

$$P = Q_t h / A C_0 \tag{2}$$

and

$$P = D K_p \tag{3}$$

where $Q_t$ = quantity of ions permeating ($mg \, s^{-1}$), $A_p$ = the amount of ions permeated (mg), $V$ = volume of the permeating ion per litre, $t$ = time (s), $P$ = permeation coefficient ($cm^2 \, s^{-1}$), $h$ = thickness of hydrated membrane (cm), $A$ = area available for permeation ($cm^2$), $C_0$ = initial concentration of permeating species ($mg \, ml^{-1}$), $K_p$ = partition coefficient and $D$ = diffusion coefficient ($cm^2 \, s^{-1}$).

The equilibrium water content (*EWC*) of a membrane can be calculated from the weights of a hydrated and dehydrated sample, as shown in equation (4):

$$EWC \ (\%) = \frac{\text{weight of water in hydrated sample}}{\text{total weight of hydrated sample}} \times 100 \tag{4}$$

Details of the determination and its statistical significance ($\pm 0.4 \%$) have been given in part 1 of this series[2].

Partition coefficients for the various water-swollen membranes in metal chloride solutions (0.25 M) were calculated from the results of salt desorption experiments at 37°C, see equation (5):

$$K_p = \frac{\text{moles of salt/gram of membrane}}{\text{moles of salt/gram of solution}} \tag{5}$$

## RESULTS AND DISCUSSION

### Membrane characterization

A series of hydrogel membranes based on copolymers of 2-hydroxyethyl methacrylate (HEMA) with styrene and with methyl methacrylate was prepared. Membrane thicknesses were chosen to enable a reasonable compromise of strength (and thus ease of handling) and transport properties (minimum equilibration, lag time and duration of experiments) to be achieved. Styrene and methyl methacrylate were known, from previous experiments[2], to yield homogeneous hydrogels whose water-binding properties vary regularly between those of the respective comonomers. In the present study it was necessary to achieve, by change in membrane structure, variations in the membrane that in some way reflect the water structure-making and structure-breaking properties previously observed[1]. The analogous behaviour in hydrogel membranes is frequently characterized by the terms freezing and non-freezing water. These are obtained by analysis of the melting endotherms obtained with differential scanning calorimetry[2-4]. Briefly, water that is strongly associated with polar groups in the polymer matrix is unable to freeze and does not, therefore, contribute to the melting endotherm. In this way the relative proportions of freezing and non-freezing water in the polymer can be determined.

*Figure 1* shows the relative effect of styrene (Sty) and of methyl methacrylate (MMA) comonomers on the
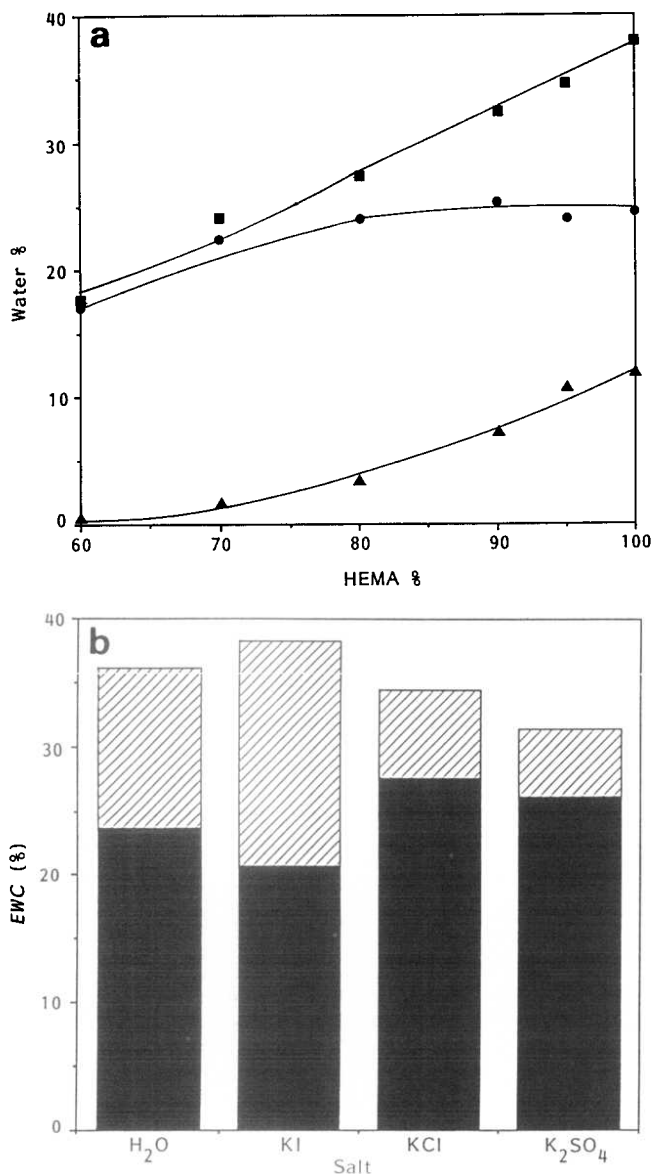
**Figure 2** (a) The *EWC* (■) and the percentage of freezing (▲) and non-freezing (●) water as a function of the weight per cent of HEMA in HEMA–MMA copolymers. (b) The percentage of freezing (hatched blocks) and non-freezing (filled blocks) water for poly(HEMA) in a series of potassium salt solutions

equilibrium water content (*EWC*) of 2-hydroxyethyl methacrylate copolymers. Perhaps more significant, in the present context, are the relative proportions of freezing and non-freezing water that make up the *EWC* values. These proportions are shown in *Figure 2a* for MMA–HEMA and in *Figure 2b*, in the form of a histogram, for Sty–HEMA. The effects of three salts (whose transport behaviour was studied in the previous paper[1]) on the water-binding properties of poly(HEMA) are included in *Figure 2b* for comparison. From these figures it can be seen that an interesting parallel exists between the effect of ions and of monomer structure on water-binding processes in polymer membranes.

*Permeation studies*

The permeability of these membranes to a range of cations in the presence of a fixed anion (chloride) was studied at 37°C. The experimental conditions were identical to those previously described[1] and involved the use of 0.25 M cation solutions, in the form of their

chlorides, on the donor side of the cell. Examples of the changes in ion concentration in the receptor compartment as a function of time are shown in *Figure 3*. This illustrates both the form of the primary data and the transport properties of a poly(HEMA:MMA) (80:20 w/w) copolymer relative to those of poly(HEMA). The conversion of primary results, obtained in this form, to permeability coefficients is straightforward (see 'Experimental' section) and enables experimental changes arising in membranes (e.g. membrane thickness) to be eliminated. The permeability coefficients thus obtained provide the first basis upon which variations in membrane structure can usefully be correlated. *Figure 4* summarizes the results for HEMA–MMA copolymers. Here, the permeability coefficients for potassium, sodium, lithium and calcium (in the form of their chlorides) are
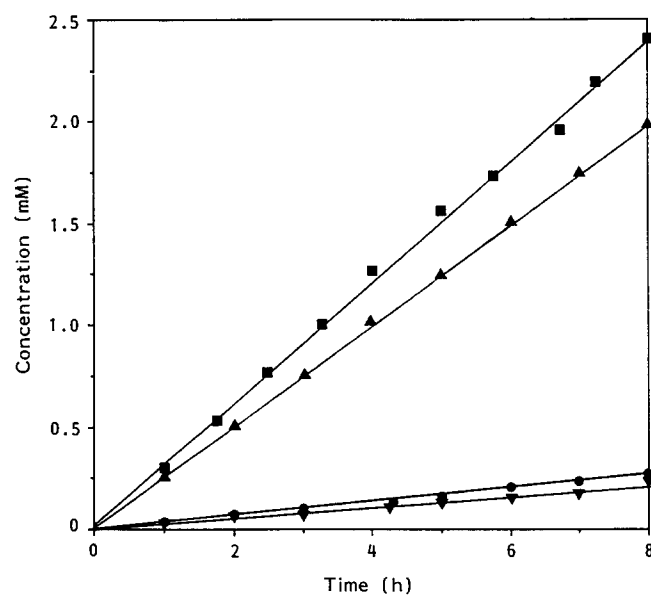


**Figure 3** Typical primary results for the transport of KCl (■), NaCl (▲) and $CaCl_2$ (●) through poly(HEMA) and KCl (▼) through a HEMA–MMA (80:20 w/w) copolymer
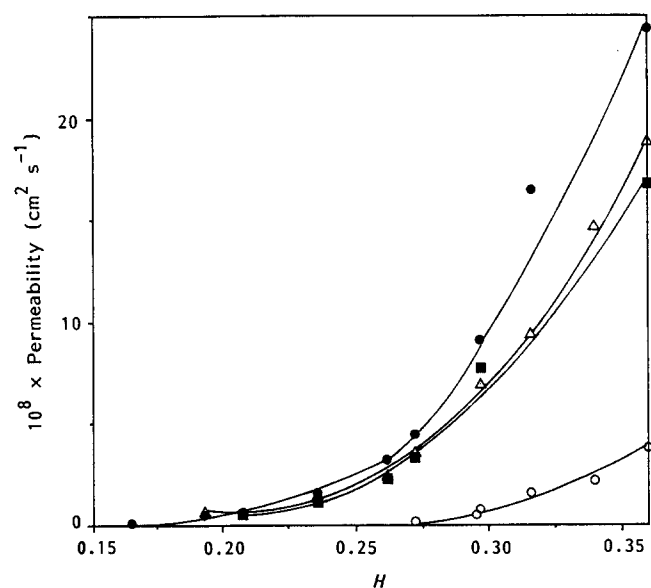


**Figure 4** Effect of the degree of hydration, *H*, on permeability, *P*, for KCl (●), NaCl (△), LiCl (■) and $CaCl_2$ (○) in a series of HEMA–MMA copolymers
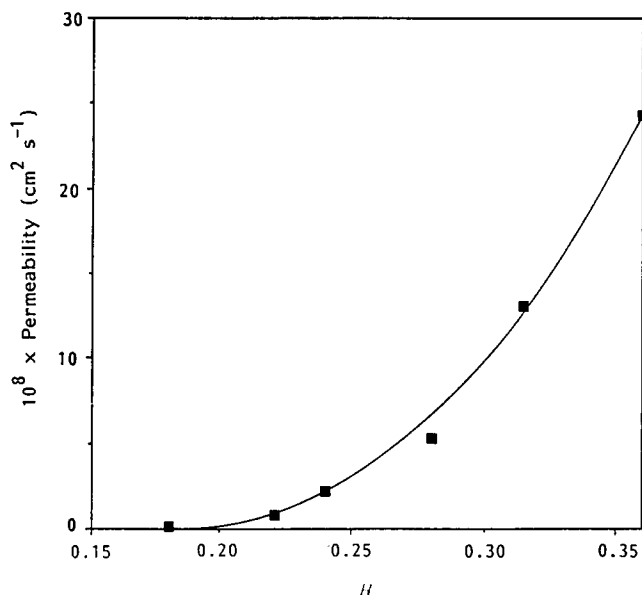
**Figure 5** Effect of the degree of hydration, $H$, on the permeability, $P$, for KCl (■) in a series of HEMA–Sty copolymers

shown as a function of the fractional hydration ($H = EWC/100$) of the membranes.

The proposition that permeation is linked to the water content rather than the polymeric structure of the membrane is well known in the literature and is based on studies with ions[5,6] and with neutral molecules[7,8]. Such studies have, however, been carried out on a limited range of membranes and permeants in each case. It is both necessary and appropriate to examine the validity of the proposition as a basis for interpreting the rather wider range of variations that are achievable. In broad terms the use of fractional hydration does seem to provide a reasonable basis for correlating results. Thus *Figure 5* shows the variation in permeability coefficients of potassium (chloride) as a function of fractional hydration for the HEMA–Sty copolymers. The results are strikingly similar to those obtained with HEMA–MMA copolymers of corresponding water contents. Changes in equilibrium water contents may similarly be achieved, without modification of the backbone structure, by use of variations in the crosslink density. *Table 1* presents results for a series of HEMA membranes in which the proportion of ethyleneglycol dimethacrylate crosslinking agent has been varied. Changes in $EWC$, freezing water content ($FWC$) and non-freezing water content ($NWFC$) are shown together with their effect on calcium, sodium and potassium permeability coefficients. It is apparent that the same broad dependence of transport on the state of hydration of the membrane is exhibited here.

It is relevant at this point to compare techniques for handling permeation data through membranes of varying water contents. There are two major aspects to this point. The first relates to those correlations that assume that all water within the membrane is equivalent and differ in form of mathematical presentation[5-7]; the second relates to differences of behaviour that might be attributed to the two (or more) water-binding states in the polymer[9,10]. The latter point is more closely related to the detail of a transport model for hydrated membranes and will be discussed in that context.

There are two major types of relationship between

hydration and permeation coefficient. The first of these has been most usually associated with the name of Yasuda[5,7] but is in fact based on much earlier work of Cohen and Turnbull[11]. It is based on the concept that the major role of water is to provide a 'free volume' from which the permeant is to be transported, and involves a plot of log(permeability coefficient) (log $P$) against the reciprocal of fractional hydration($1/H$). The second, proposed by Kojima and Furuhata[6], is based on Ogston's theoretical diffusion model[12]. This relates permeability to polymer fraction as does Refojo's treatment[13], which relates log $P$ to $1/(H - 1)$, and is based on Poiseuille-type flow through the membrane. These methods of presentation of our results are compared with a direct plot of log $P$ vs. $H$ in *Figures 6a*, *6b* and *6c*. It should be noted that the values of $EWC$ and thus $H$ upon which these plots are based are determined in deionized water. The effect of individual salt solutions is reserved for later discussion.

The simple plot of log $P$ against $H$ (*Figure 6a*) is, perhaps surprisingly, reasonably linear. This empirical relationship has been found to give the best fit for results of oxygen transport measurements through hydrogel membranes[14]. Although this is obviously not the case here, given that the plot does not take into account any effect of transported ions on water content, it does provide a yardstick against which to judge the other approaches. Such a comparison has the advantage that it engenders caution in the acceptance of the transport models that such approaches imply. A fairly marked change in slope (or onset of curvature) is found in *Figure 6a* at an equilibrium water content of around 25%. A similar phenomenon is observed in the more complex presentation (*Figure 6b*) of log $P$ versus $1/(H - 1)$. This latter function has been found, in water flux experiments, to correlate directly with the effective mean pore radius of the gel[15]. Here again considerable doubt must centre on the meaning and validity of the model, but it does provide a conceptual basis for discussion.

In the absence of other information it would be reasonable to suggest that the significance of departure from linearity in *Figures 6a* and *6b* is found in the change in water-binding behaviour reflected in *Figures 2a* and *2b*. Thus, the more marked decrease in permeability might be supposed to correspond with the point at which 'freezing' water (as determined by d.s.c.) disappears from the hydrogel. Such a view would certainly not conflict with the important part that water structuring plays in these transport processes—a point discussed and demonstrated in previous papers[1-3]. The pore radius to which this change in behaviour corresponds (2.4 Å) is obviously too large to provide the basis for a size exclusion model.

**Table 1** Effect of crosslinking agent on the freezing and non-freezing water contents and permeation coefficients of HEMA hydrogels at 21°C

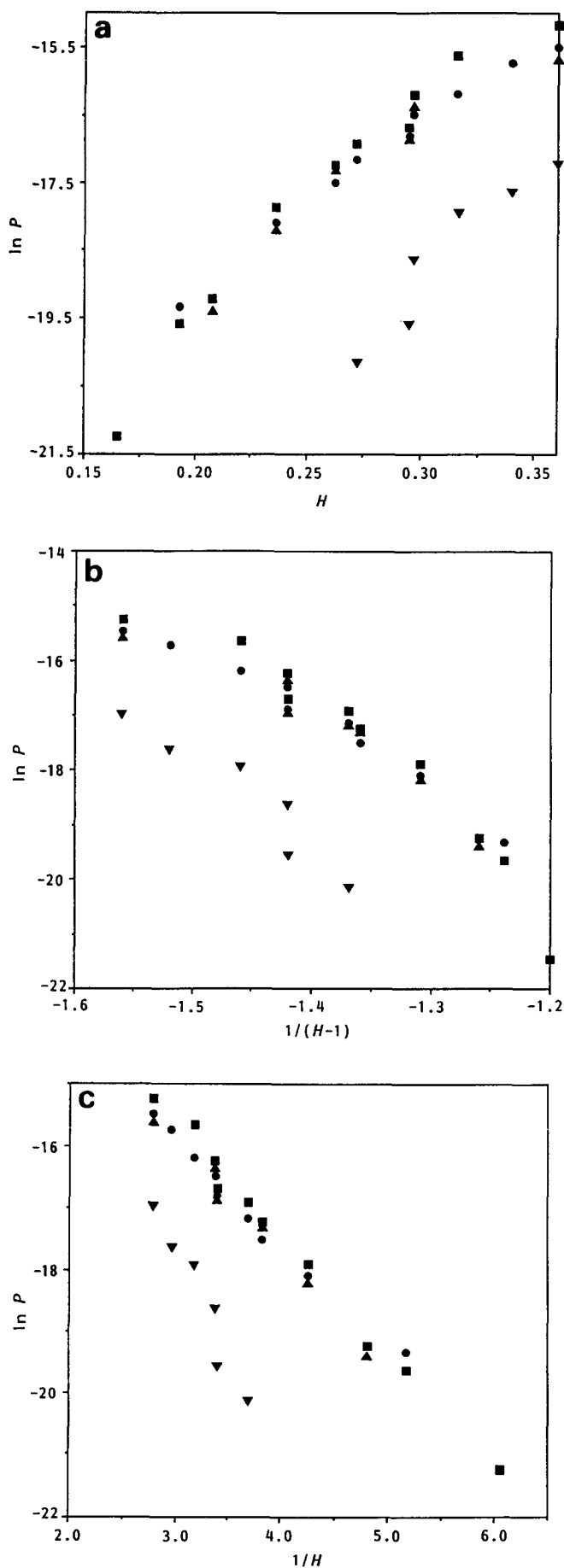| EGDM (wt%) | EWC (wt%) | FWC (wt%) | NFWC (wt%) | Permeability × $10^8$ (cm² s⁻¹) | | |
|---|---|---|---|---|---|---|
| | | | | KCl | NaCl | CaCl₂ |
| 0.50 | 38.5 | 14.4 | 24.1 | | | |
| 1.00 | 37.6 | 13.2 | 24.4 | 29.6 | 17.9 | 2.9 |
| 2.0 | 36.0 | 11.2 | 24.8 | | | |
| 4.60 | 31.5 | 7.6 | 23.9 | 9.1 | 7.4 | 0.8 |
| 7.60 | 28.2 | 4.9 | 23.3 | 4.4 | 3.5 | 0.1 |

**Figure 6** Plots of (a) ln $P$ vs. $H$, (b) ln $P$ vs. $1/(H - 1)$ and (c) ln $P$ vs. $1/H$ for the chloride salts of K$^+$ (■), Na$^+$ (●), Li$^+$ (▲) and Ca$^{2+}$ (▼) through the series of HEMA–MMA copolymers, as shown in *Figure 1*

Because this value is derived from water flux measurements on higher-water-content gels, however, it does not take into account any role that water strongly associated with the polymer might play in reducing available pore size for hydrated ion transport. Even when some notional account is made, it is clear that no specific size exclusion effect can be operating at this point. On the other hand, the results (*Figures 6a* and *6b*) could be taken to sustain a model that would interpret the observed effect in terms of a progressive decrease in effective pore volume combined with a more marked change in water-binding properties.

Against this must be offset the information derived from *Figure 6c*. Here, the relatively undisturbed linearity of log $P$ versus $1/H$ suggests that the permeation process is governed solely by the free volume associated with the aqueous polymer. Before accepting this view, however, it is essential to address some important questions. These relate to the apparent absence in *Figure 6c* of any effect relating to water-binding processes, size exclusion phenomena or changing glass transition temperature in the membrane. The first point that must be made is that it is a consequence of extrapolating log $P$ and $1/H$ to low values of both $P$ and $H$ that errors and deviations in the values of $P$ and $H$ are progressively more difficult to detect in the plot. To this must be added the effect, already alluded to but not included in the $H$ values used, that the salt solutions have on values of equilibrium water contents. It is relevant to point out here that there will be a salt concentration gradient across the membrane (from donor cell to receptor cell) and that the only unambiguously measured value of $EWC$ is that obtained under standard hydration (distilled water, controlled pH) conditions. The effect of salt solution on $EWC$ is likely to increase progressively as $EWC$, and thus $H$, increases. For this reason it may be anticipated that a superimposed correction should be overlaid on *Figures 6a*, *6b* and *6c*, which makes any assesssment of their linearity in their present form suspect.

The question of water binding as it relates to the conditions used in the permeation experiments is complex. It was a deliberate decision to minimize structural variations in the polymers studied by using 2-hydroxyethyl methacrylate as the hydrophilic monomer. Additional experiments with hydroxypropyl acrylate and hydroxypropyl methacrylate were also carried out, the results corresponding with those of hydroxyethyl methacrylate copolymers of corresponding water contents. Thus, we observe that despite variations in non-hydrophilic monomers, despite modifications to the network structure (by use of a non-hydrophilic comonomer as a crosslinking agent rather than a backbone component, *Table 1*) and despite the use of hydrophilic centres in different local environments (hydroxypropyl acrylate and methacrylate), the water content, rather than the polymer structure, is the dominating feature in transport control. The important consequence of the way in which all these structural variations have been made, however, is that the same hydrophilic centre is at work. This in turn produces a uniform variation of 'freezing:non-freezing' water content ratio with equilibrium water content. A further, and most important, consequence of this is that the plot of log $FWC$ versus $1/H$ using data presented here is linear, with no more scatter than that found in *Figure 6c*. These
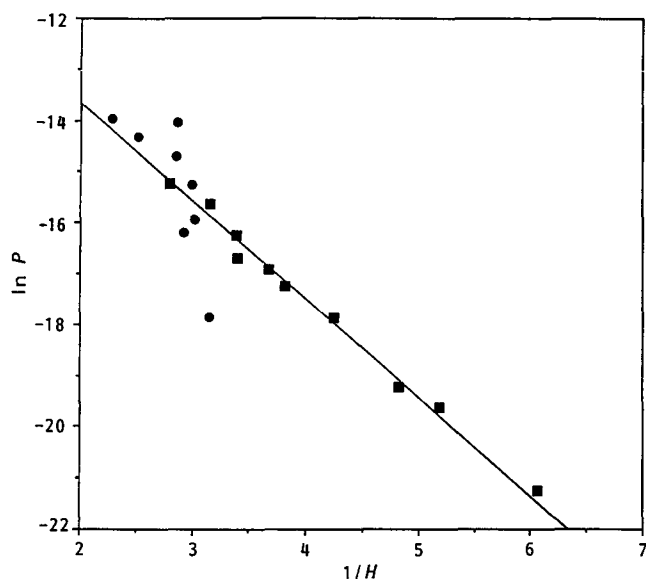
**Figure 7** Use of free-volume treatment to compare the influence on the degree of hydration, $H$, by variation in anion (●) and in polymer backbone (■) and the effect of these variations on permeability (see text)

comments, taken together, offer some explanation of the uniformity of transport variation with equilibrium water content in the polymers studied, but also demand caution in interpreting the uniformity of particular forms of data presentation in terms of a universally applied transport model.

The central point in the use of *Figure 6c* to derive a universal model centres around the proposition that *EWC* alone (and thus free or non-polymer volume) is the determining factor in the transport process. This must be set against the possibility that one or more other factors will induce a discontinuity in this relationship. Such factors might be expected to include water structuring (e.g. the ratio of 'freezing' to 'non-freezing' water); effective mean pore size of the matrix; the partitioning of the ion between different available environments (which in turn will depend upon water-binding behaviour in the matrix); and rate of diffusion of the ion (which may be related to size exclusion effects in the polymer). Some support for the expectation that discontinuities will occur is found in the data for calcium in *Figure 6c* in which no detectable transport is observed at values of $1/H$ above 3.8. Whatever value is taken for the hydrodynamic radius of calcium, a point discussed in a previous paper of this series[1], its value must be regarded as something in excess of twice that of potassium. Since there is little reason to expect the nature of the requirements of the hydrated calcium ion (in terms of water structuring of the matrix) to be greatly different from those of potassium, it is a reasonable assumption that the difference in behaviour is related to size exclusion phenomena.

A similar danger exists in the assumption that the linearity of *Figure 6a* demonstrates that the equilibrium water content and thus free volume is more important than water-structuring phenomena in controlling permeability. The correspondence of decline in freezing water content with decline in equilibrium water content on a regular basis in the polymers studied here has been previously commented on. Results with different polymer structures of similar water contents to those used here demonstrate that *EWC* alone does not control water flux

and salt rejection in membranes[16,17]. Although we find differential scanning calorimetry to be the most convenient method for water-structuring studies, the nature of water in membranes at 37°C (the temperature used here for transport measurements) will not be identical with that existing at or near the melting point of water. Thus d.s.c. provides a useful technique for the study of variations within a series but is not necessarily a good predictor of water-structuring behaviour under different environmental conditions. It would be expected, in general, that under the conditions used for permeation studies, polymers will contain somewhat more 'freezable' water than under the conditions of d.s.c. measurements. As a result, predicted permeation discontinuities resulting from water-structuring phenomena would be expected to occur at slightly lower water contents than those predicted directly by d.s.c. measurements. A secondary effect that may be expected to affect pore-size mobility within membranes is the glass transition temperature of the hydrated polymer. Here again, within the series studied, changes in glass transition temperature are progressive and none of the polymers studied is substantially below its glass transition temperature at the temperature used for transport measurements[2].

One general principle that emerges from results presented in this and the preceding paper is the effect of the counteranion on the transport of potassium salts through poly(HEMA)[1]. Both the size and the water-structuring effect of the anion were found to be important in influencing the overall permeability of the salt. It was found that the anion had a marked influence on the equilibrium water content of the hydrogel membrane. By interchanging data for (a) variations in water content obtained by changes in copolymer composition and relating to hydration in the presence of chloride anion with (b) variations in water content of poly(HEMA) obtained by hydration in the presence of differing anions, the results shown in *Figure 7* are obtained. This shows that permeability data for the potassium salts and their respective water contents can be superimposed on the data for KCl through different HEMA:MMA copolymer membranes. It is observed that those salts that produced a greater *EWC* for poly(HEMA) than does KCl fit the slope of ln $P$ versus $1/H$, while those with comparatively lower *EWC*s are seen to deviate substantially from the straight-line relationship. Like the chloride ion, the anions that fit the slope all have hydrodynamic or Stokes' radii smaller than that of potassium. In these cases the cation will exhibit the size-controlling influence on the permeability. On the other hand, those salts that deviate from the slope have anions with larger effective radii than their potassium counterion.

## CONCLUSIONS

Both size and water-structuring phenomena contribute to the transport process and situations exist where either can play the dominant role.

The free-volume model accounts reasonably well for cation permeation controlled by diffusional size effects.

In systems studied here and elsewhere, however, the similarity of the hydrophilic centres produces changes in water structuring (i.e. non-freezing:freezing ratio) that parallel changes in equilibrium water content.

The free-volume theory cannot, however, account for

water-structuring effects that lead to permselectivity in low-water-content membranes.

Water-structuring phenomena within the membrane are controlled by the combined effects of dissolved cation, dissolved anion and the structure of the polymer itself. Therefore, variations in hydration exert a controlling influence on transport behaviour.

For membranes of a given structure, anion permeation rates follow the Hofmeister series in effect with the 'large, soft' ions permeating fastest.

Thus, in the potassium-dominated cases described here, the overall degree of hydration is observed to have the controlling influence on permeability, irrespective of whether the water content is modulated by the anion or the polymer backbone.

## ACKNOWLEDGEMENT

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