

Synthetic hydrogels (10): anomalous transport behaviour in crown ether-containing hydrogel membranes

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Received 15 June 1999; received in revised form 30 July 1999; accepted 5 August 1999

Abstract

The physical immobilisation of a range of crown ethers within hydrogel membranes of a range of water contents has been examined. The efficiency of the immobilisation process increases with increasing size of the crown and decreasing water content (and thus mean pore radius) of the hydrogels. Successful occlusion was achieved with dicyclohexano-18-crown-6 in a poly(2-hydroxyethyl methacrylate) membrane containing 10% ethyleneglycol dimethacrylate crosslinking agent. Of various ions examined with this modified membrane, K^+ was subject to the greatest modulation of its transport behaviour; this being characterised by a substantial initial induction period followed by a steady state rate that never attained the value achieved with unmodified membranes of a similar water content. This behaviour is quite novel in comparison with ionophore modulated transport in hydrophobic membranes but bears some resemblance to that of gas permeation in glassy polymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogel; Membrane; Ion transport

1. Introduction

The past two decades have seen a growing interest in the use of neutral chelating agents to achieve ion permselectivity in membranes [1–9]. These ionophores bind specifically to particular ions, usually alkali and alkaline earth metal cations, and thus affect the relative flux of these species through the membrane. Up till now, virtually the only way that ionophores have been used in permselective membranes is as mobile sites (ion-selective carrier ligands) incorporated into a lipophilic liquid membrane or solvent impregnated poly(vinyl chloride) [3,5]. This “ferry” mechanism, known as facilitated transport, has been the subject of much study since the early 1970s [8–13]. Membranes containing these neutral ion selective ligands can be exploited in separation processes or as the sensing component in ion-selective electrodes [4,8,14] where extremely high selectivities can be achieved [5].

The first multidentate synthetic macrocyclic compounds with a proven ability to form stable complexes with the alkali and alkaline earth metal cations, were the crown

ethers [15,16]. These are macrocyclic polyethers which contain repeating $(-OCH_2-CH_2-)_n$ units. From the early work by Pederson on crown ethers, there has been a continuous growth in both the number of new ionophores and in their applications in various scientific disciplines [14,17–23]. The ability of ionophores to chelate selectively to a specific species, coupled with the ability to modify structural parameters, such as cavity diameter, with the consequent effect on selectivity, means that these compounds possess a clear potential as possible modulators of the permeability characteristics of both liquid and polymeric membranes. In the case of the latter type, this has involved incorporating them into the polymer backbone [1,24] or as pendant side groups [2,25–29].

Such work has, however, almost exclusively involved the use of ionophores in relatively hydrophobic membranes. Early transport studies with crown ethers involved their use in hydrophobic liquid membranes such as chloroform [5,6]. The transport of electrolytes such as KCl and NaCl through such membranes occur via the complexation of the cation with the crown ether at the membrane surface followed by diffusion of the complex ion pair across to the other side where dissociation can occur. In these systems, the diffusion of free ions and uncomplexed ion pairs through the membrane does not contribute significantly to the total amount of electrolyte transported [5].

There seems to have been little work carried out on the

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effect of ionophores on the transport of salts through a water swollen polymer matrix. In such systems, the electrolytes are readily soluble in the polymer matrix and can be transported by the conventional solution diffusion mechanism, in contrast to the liquid membranes described above. In earlier papers of this series [30,31] the importance of the nature of the solute and the chemical composition of the polymer on water binding and consequently permeation behaviour of solutes through unmodified water swollen (hydrogel) polymers was discussed.

Although a few papers relate to ionophores in membranes containing small amounts of water [1,2] the influence of the ionophore has not been considered against with the background knowledge of water binding and other phenomena that are so important in controlling transport through water-swollen polymer systems. It appears therefore, that the selective chelating ability of ionophores in water-swollen polymers has not been studied, although it is a potentially useful way of influencing the transport characteristics of a hydrophilic polymer. It is with this aspect of membrane behaviour of hydrogel polymers that this paper is concerned.

2. Experimental

2.1. Membrane materials

Optical grade 2-hydroxyethyl methacrylate (HEMA) was supplied with a certificate of analysis by Ubichem Ltd. The crown ethers used were of laboratory grade and supplied by Lancaster Synthesis Ltd. The initiator α -azobisisobutyronitrile (AIBN) was supplied by Aldrich Chemical Co. and recrystallised before use. Both the crosslinking agent, ethyleneglycol dimethacrylate (EGDM) and the monomer, methyl methacrylate (MMA) were supplied by BDH. The methyl methacrylate was washed, dried and then purified by reduced pressure distillation. EGDM was used as supplied without further purification.

2.2. Membrane preparation

All membrane compositions are reported in terms of weight percent. Membranes were prepared in a polymerisation mould consisting of two glass plates covered by two sheets of poly(ethylene terephthalate) and separated by a 0.4 mm thick polyethylene gasket [32]. The crown was dissolved in the monomer mixture and combined with 0.5% by weight of the initiator. The resulting solution was purged with nitrogen and 4–5 ml injected into the glass mould through a G22 syringe needle. Polymerisation 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. Membranes were separated from the poly(ethylene terephthalate) film and stored dry. Films were soaked overnight in distilled water before use.

2.3. Permeability studies

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 $1.5 \pm 0.5 \text{ mS cm}^{-1}$. Discs of 5 cm diameter of the hydrated membrane were cut out and clamped between the two cell halves of a horizontally held perspex permeability cell, described in a previous paper [30].

The cell assembly was seated in a water bath which was thermostatically controlled and maintained at 37°C. The receptor cell was filled with deionised water and the donor side with the analyte solution under investigation: typically 250 mM unless otherwise stated. The experimental run was timed from the introduction of the solution into the cell. The change in ion concentration was monitored throughout the experimental run by means of a glass conductivity flow through cell (cell constant $k = 1$), linked to an Alpha 800 conductivity meter (supplied by CP Instrument Company Limited) which was inserted between the outlet of the deionised water side of the permeation rig and the filling reservoir.

Measurements of the membrane thickness were made at the end of each run when the membrane was at the experimental temperature and was equilibrated with the salt solution (both factors that might affect swelling). Thickness was typically 0.038 cm.

The steady state permeability coefficients were calculated as described in paper 5 of this series [32]. It was an artefact of this technique that there was a non-zero concentration on the receptor side at zero time. The trace amount of salt initially present was too small to affect sink conditions or steady state transport, but was taken into account in the determination of the associated time lags. The time lag was obtained using the time course curve of the salt concentration in the receptor cell. It was calculated using the intersection of the final steady state portion of the curve with the zero time concentration.

2.4. Equilibrium water contents

The equilibrium water contents (EWC) of the membranes were measured at 37°C. These were calculated from the weights of a hydrated and dehydrated sample, as shown below:

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

3. Results and discussion

3.1. Immobilisation studies

The concept of physical immobilisation of a species in hydrogel matrices is well known. It was anticipated, therefore, that physical immobilisation of crown ethers would be

doubly dependent on the size and hydrophobicity of the ionophore and on the water content of the membrane. Hydrogels are sometimes regarded as having an associated mean pore but fluctuating size with concomitant cut-off point for diffusion of any species larger than this [33]. Initial experiments were carried out using, sequentially, 12-crown-4, 15-crown-5 and 18-crown-6 as the selective chelating agent. A range of water contents corresponding to a range of decreasing pore sizes were synthesised to investigate the extent of physical immobilisation of these simple ionophores. All the crowns studied at this stage were found to be readily soluble in the reaction (i.e. monomer) mixture. The membranes produced were clear, indicating that no phase separation had occurred between the polymer and ionophore during the polymerisation process. On hydration, the membranes remained transparent, which is consistent with the membranes retaining their homogeneity in the water-swollen state. However, no significant changes were found in the properties of such initially ionophore-containing membranes, either in terms of EWC or transport behaviour, in comparison with the unmodified membranes.

Since it was suspected that these ionophores were leaching out of the polymer matrix during hydration, ionophore loss was monitored. These studies demonstrated that all three crowns (12-crown-4, 15-crown-5 and 18-crown-6) had substantially leached out of the hydrogel copolymer membranes of water content between 20 and 30% within 24 h. As a result, it was impossible to perform any realistic ion transport studies on these fully hydrated systems. The classic concept of Refojo's mean pore size assumes that permeants are soluble only in the water phase [33]. The failure of these crowns (which are relatively large in relation to the predicted pore size of hydrogels in this water content range) to become immobilised in the polymer matrix suggests that, in this case, the ionophore may also interact with the polymer phase.

In order to improve retention, dicyclohexano-18-crown-6 was examined, since this is larger and relatively hydrophobic in nature due to its cyclohexyl substituents. This ionophore has been used in plasticised PVC membranes [23] as the electroactive component in ion-selective electrodes and was expected to leach out of the hydrogels less than the unsubstituted crowns, due to its sterically hindering side-rings and the greater hydrophobicity of the hydrogel membranes relative to the bulk aqueous phase. The supporting polymer matrix for the ionophore was required to achieve a compromise between having sufficient permeability for transport measurements to be easily made (a property that increases with increasing EWC) and high enough hydrophobicity (a property that increases with decreasing EWC) relative to the aqueous surroundings. In addition, since water acts as a plasticising agent in such systems, lowering the EWC decreases the rotational freedom of the polymer chain segments (quantitatively determined as an increase in the glass transition temperature, T_g , of the system [34]). The mobility of the ionophore, and consequent rate of

loss from the membrane, should decrease with the increasing polymer chain stiffness. In summary, then, a membrane was required with easily observable transport properties, reasonable hydrophobicity and low ionophore mobility.

The hydrogel matrix originally chosen was a HEMA:MMA(80:20) copolymer with a nominal crosslink density of 1% (ethyleneglycol dimethacrylate). Leaching studies on such a hydrogel, containing 20% by weight dicyclohexano-18-crown-6, showed a weight loss of 11.1% after one week and 19.1% after two weeks. Although retention in this membrane of the substituted ionophore was considerably better than that of unsubstituted 18-crown-6, further modification of the system was felt to be necessary. After preliminary experiments, the polymer composition HEMA:EGDM(90:10) was selected. That is, a polyHEMA membrane containing 10% by weight of crosslinker, which possesses a similar equilibrium water content to HEMA:MMA(80:20) membranes (24.3 and 23.5%, respectively). In addition, it possesses a high degree of crosslinking, which should decrease chain mobility and increase steric hindrance to ionophore mobility within the matrix, thus reducing the diffusion of the ionophore out of the membrane.

Ionophore-containing membranes discussed in the rest of this paper have a base composition of HEMA:EGDM(90:10) modified by addition of 5 wt.% dicyclohexano-18-crown-6, at the polymerisation stage.

3.2. Dicyclohexano-18-crown-6 modified membranes: transport studies

In order to minimise the loss of ionophore through leaching, the membranes were stored in their dry state and soaked in water overnight before use. The need for sufficient time for the membranes to fully hydrate was an important consideration. A time course study on water content was performed to enable this point to be resolved. The amount of water absorbed by the hydrogel was observed to reach equilibrium within 2 hours.

The presence of ionophore in the membrane led to no significant deviation in the value of the EWC relative to that of the unmodified polymer, 24.6 and 24.3% being the water content of the membranes with, and without, 5 wt.% of dicyclohexano-18-crown-6. In addition, the established ability of dicyclohexano-18-crown-6 to chelate to cations, especially K^+ , does not seem to have any noticeable impact on the overall hydration of the water swollen polymer matrix in 250 mM solutions of the test salts.

The first point to be established was whether the presence of the ionophore in the hydrogel matrix altered the transport characteristics of the membrane. Figs. 1 and 2 compare results for the transport of potassium chloride and ammonium chloride through an unmodified HEMA:EGDM(90:10) membrane with one containing 5 wt.% of dicyclohexano-18-crown-6. Although this ionophore caused little change in the EWC of the host membrane, its effect on

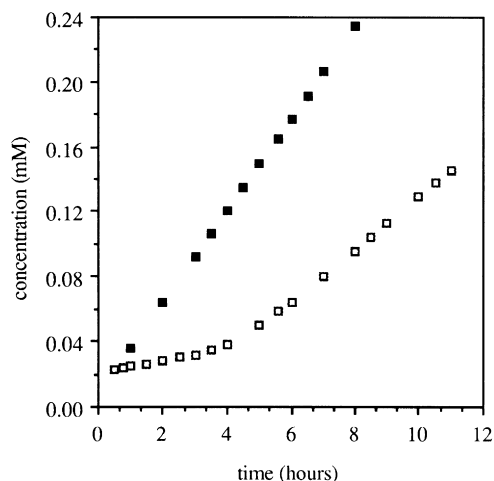


Fig. 1. Transport of KCl through HEMA:EGDM(90:10) with (□) and without (■) 5% dicyclohexano-18-crown-6.

permeability was significant and clearly visible. The calculated steady state permeability coefficients for the two cations through modified and unmodified membranes are presented in Table 1.

It is a general aspect of steady state transport processes through membranes that they have a time lag associated with the dissolution of the penetrant to a constant level, before steady state is achieved. The ionophore-containing membranes possess an increased induction period, or time lag, relative to the crown-free analogues. The extended time lag seems to be greater in the case of potassium chloride than ammonium chloride; this correlates with the free energy of the complexation of the crown and cation in water being greater for K^+ than for NH_4^+ [17]. The ionophore, dicyclohexano-18-crown-6, possesses a central cavity diameter in the range of 0.26–0.32 nm [35]. From the range of chloride salts which was examined, the K^+ cation with an ionic diameter of 0.266 nm would generally

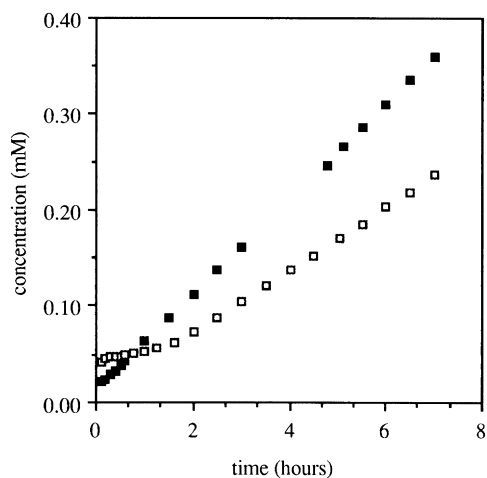


Fig. 2. Transport of NH_4Cl through HEMA:EGDM(90:10) with (□) and without (■) 5% dicyclohexano-18-crown-6.

Table 1

The effect of dicyclohexano-18-crown-6 on the permeability of KCl and NH_4Cl through a hydrogen membrane of composition [HEMA:EGDM(90:10)]

Salt (250 mM)	Permeability (no crown ether) ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)	Permeability (5 wt.% crown ether) ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)
KCl	2.36	1.36
NH_4	4.14	3.06

be expected to form the most stable complex with this crown ether [17,35].

It is clear from Figs. 1 and 2, and from Table 1, that in the comparison of permeation through ionophore-containing and ionophore-free membranes, not only is the time lag extended by the presence of the ionophore but the final steady state permeation is also affected. The greatest impact is found for KCl permeability which falls by 42% when the ionophore is present, this is in contrast to a fall of 26% in the case of NH_4Cl . It is interesting to compare these observations of suppressed permeation, with membranes that display facilitated transport, where the presence of the selective chelating agent greatly enhances the flux of the permeant [5,36]. Both reductions seen here, however, are significant and it should be repeated that this fall cannot be accounted for by a drop in EWC of the membrane on the addition of dicyclohexano-18-crown-6, since no measurable fall in the water content occurs. The final steady state permeation may, therefore, be indicative of interaction between the transported solute and the ionophore within the membrane matrix.

Permeability experiments were carried out with the chlorides of potassium, sodium, ammonium and lithium. A common anion was used because the nature of the anion has an effect on transport behaviour [6,11]. Their primary

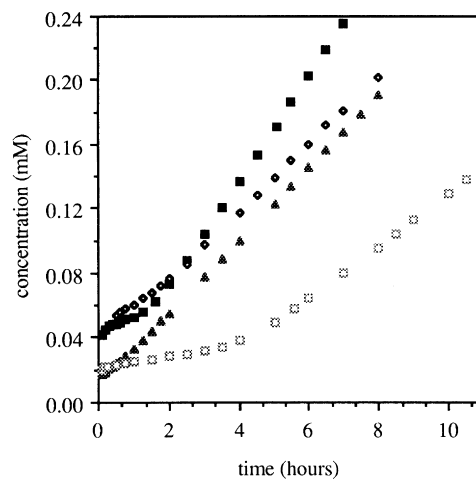


Fig. 3. Transport of various salts through HEMA:EGDM(90:10) + 5% dicyclohexano-18-crown-6: (NH_4Cl (■), NaCl (◇), LiCl (▲) and KCl (□)).

Table 2

Permeability data for a series of chloride salts through a hydrogel membrane of composition [HEMA:EGDM(90:10) + 5 wt.% dicyclohexano-18-crown-6]

Salt (250 mM)	Permeability P (10^{-8} cm ² s ⁻¹)	Time lag, J^a (h)	Calculated P^b (10^{-8} cm ² s ⁻¹)
LiCl	1.84	0.27	1.9
NaCl	1.67	0.68	2.0
KCl	1.36	3.35	2.2
NH ₄ Cl	3.06	1.16	–

^a Time at intersection of associated curves of P and the zero-time concentration.^b Theoretical value of P , calculated from EWC of test membrane.

concentration versus time curves are compared in Fig. 3. There are a number of initial observations that can be made from the primary data. The most significant is the fact that the final steady state permeability rates, P , for the salts change lies in the order NH₄Cl > LiCl > NaCl > KCl. This order is different from what might be predicted from the permeability studies discussed in previous papers in this series [30,31]. For unmodified hydrogel membranes it was found that the order of permeability for salts with a common anion is dictated by the size of the hydrated cation [30]. The order for transport across a simple polyHEMA membrane, for example, is NH₄Cl > KCl ~ NaCl > LiCl. The time lags observed in Fig. 3, associated with the crown-modified membrane range from 3.35 h for KCl to 0.27 h for LiCl. The former seems significantly extended in comparison to transport behaviour found in conventional membranes whereas the LiCl value falls within the pre-steady state induction period observed in conventional hydrogels. This indicates that although there is clearly an ionophore effect on the transport of KCl, the behaviour of LiCl is relatively unperturbed by the presence of the crown ether.

The importance of water structuring within a hydrogel membrane has been discussed elsewhere in this series [30,31,37]. In essence, water exists in a continuum of states between bulk like (or “free”) and water strongly associated with the polymer matrix (“bound”). An informative reflection of this behaviour is found in the melting endotherms obtained using differential scanning calorimetry. The role of this technique in characterising water structure phenomena in hydrogels in terms of freezing (or “free”) and non-freezing (“bound”) water has been discussed in part 1 of this series [37]. It has further been established that the nature of the water within the hydrogel matrix markedly affects the transport of salts through the membrane [30,31]. If the presence of the crown ether was significantly influencing water structuring, (the ratio of freezing/non-freezing water) then all salts studied would be equally affected by its presence. It is observed however, that although KCl is greatly influenced by the presence of the crown ether, LiCl is relatively unperturbed. This is, therefore, consistent with a selective chelation effect by the ionophore rather than a water structuring effect, being the main cause of perturbation of transport behaviour.

It has been shown elsewhere that in a series of copolymer membranes, that share the same hydrophilic centre [31], the

EWC was the major parameter for determining the permeability coefficient of a given salt. The “free-volume” plot of $\ln P$ versus $1/H$ was shown to be linear, where P is the steady state permeability and H the degree of hydration ($H = \text{EWC}/100$). Where HEMA is the hydrophilic component, it is therefore possible to predict the permeability coefficient of a salt through a membrane of known EWC (and therefore $1/H$ value) by interpolating the corresponding $\ln P$ value on a free-volume plot. Using the data from paper 5 of this series [31], in conjunction with the HEMA:EGDM(90:10) + 5% dicyclohexano-18-crown-6 membrane, which has an EWC of 24.6%, it is possible to predict transport behaviour with measured values (Table 2). The predicted permeabilities for KCl, NaCl and LiCl of 2.2×10^{-8} , 2.0×10^{-8} and 1.9×10^{-8} cm² s⁻¹ respectively, compare with the corresponding measured values: 1.36×10^{-8} , 1.67×10^{-8} and 1.84×10^{-8} cm² s⁻¹. It is clear that the measured KCl permeability is considerably less than the predicted value, again indicating that the presence of ionophore has a strong influence on KCl transport. The measured permeability coefficient of KCl through the HEMA:EGDM(90:10) membrane with no ionophore at 2.36×10^{-8} cm² s⁻¹, does however correlate well with the predicted value (2.2×10^{-8} cm² s⁻¹). This shows the validity of using the $\ln P$ versus $1/H$ plot to predict permeabilities in cases where the EWC is the only significant parameter, and confirms the reality of the effect demonstrated here. In contrast, in the case of LiCl, the closeness in measured and predicted permeability values seems to show that this salt is relatively uninfluenced by the presence of ionophore in the membrane.

The comparison of predicted and measured permeability coefficients for NaCl indicates that Na⁺ is a marginal case showing some interaction with the ionophore. This effect clearly requires investigation with other crowns since it may indicate that the size specificities of crowns with ions in non-aqueous systems are somewhat affected by the presence of water as a competitive solvating agent. This point is considered in detail in subsequent studies of the behaviour of covalent bond 15-crown-6 on the transport properties of hydrophilic membranes [38].

Further studies were carried out on the dicyclohexano-18-crown-6 modified membrane to examine the effect of KCl concentration on the transport behaviour. Primary transport data for three initial concentrations are compared in Fig. 4.

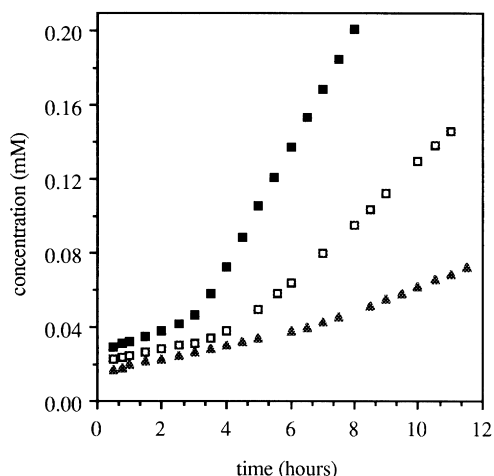


Fig. 4. Transport of KCl solutions of different concentration through HEMA:EGDM(90:10) + 5% dicyclohexano-18-crown-6: (500 mM (■), 250 mM (□), and 125 mM (▲)).

It is clear from this data that the transport curve associated with the pre-steady state induction period, is itself nearly linear. This allows apparent pre-steady state permeabilities, P' , to be calculated. For the sake of completeness, in addition to the conventional time lag, the induction period will also be described in terms of the intersection between the final steady state and the apparent initial pre-steady state permeabilities. The values are listed in Table 3.

An examination of both the time lags and final steady state permeabilities, show no clear trends, but the time lag for the 500 mM KCl solution is markedly less than that for the lower concentration solutions. The final steady state permeabilities, however, remained relatively constant over the range of concentrations studied, although the calculated permeability of the 125 mM solution is somewhat less than the others.

In contrast, however, the apparent permeabilities associated with the induction period and the redefined induction periods described above, both show a marked decrease with increasing concentration. The various conventional interpretations and diffusion models discussed previously in relation to hydrogel membranes [30,31] are clearly insufficient on their own to understand the phenomena in this study. It is necessary, therefore, to draw together the observations made on the transport through this ionophore-containing

membrane and rationalise them in terms of what is already known about membrane transport phenomena in both the liquid and gaseous phase.

4. Concluding discussion

Although various polar polymers have been examined in conjunction with ionophores by other authors [1,2,24–29], none were as hydrophilic as the system studied here. Although permeability work was carried out on such membranes [1,2] it must be emphasised that the role of water was relatively unimportant compared to that in hydrogel membranes. This was largely because they were being considered for such applications as reverse osmosis [1]. As a consequence, the permeabilities observed in the HEMA:EGDM(90:10) + 5% dicyclohexano-18-crown-6 membrane were in the order of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$: a value considerably higher than the 10^{-11} and $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ permeabilities observed with the ionophoric polymers studied by Shchori [1] and Kimura [2] for example. There are problems in making direct comparisons between the work described here, and that of earlier workers. These are principally related to differences in techniques and non-compatibility of measurement conditions. Shchori and Jagur-Grodzickshi, for example, use a desorption technique to obtain their values. On the other hand, Kimura et al. do not discuss pre-steady state phenomena in their work, nor do they say if their linear concentration versus time plot corresponds to the point of salt introduction, or to a procedural zero selected during the final steady state period. Despite superficial resemblance in the systems studied, therefore, there is no literature base corresponding to either materials or experimental procedures with which the results here can be compared.

Perhaps surprisingly, it is from studies in the field of gas transport through polymer membranes that some of the best analogies to this work may be found. It has been observed that with elastomeric polymers, as with conventional non-ionophore containing hydrogels, the partitioning of gas into the polymer matrix may be adequately described in terms of Henry's Law. With many glassy polymers, however, a non-linear sorption isotherm is observed for a number of gases: this led to the "dual sorption" model being proposed which considers that the penetrant exists in two populations within

Table 3

The effect of concentration on the permeability behaviour of KCl through a hydrogel membrane of composition [HEMA:EGDM(90:10) + 5 wt.% dicyclohexano-18-crown-6]

KCl concentration (mM)	Time lag (h)	Permeability, P ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)	Apparent pre-steady state permeability P' ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)	Induction time ^a (h)
125	3.17	1.13	0.06	6.75
250	3.35	1.36	0.30	4.45
500	2.52	1.37	0.13	3.15

^a Time at intersection of associated curves of P' and P .

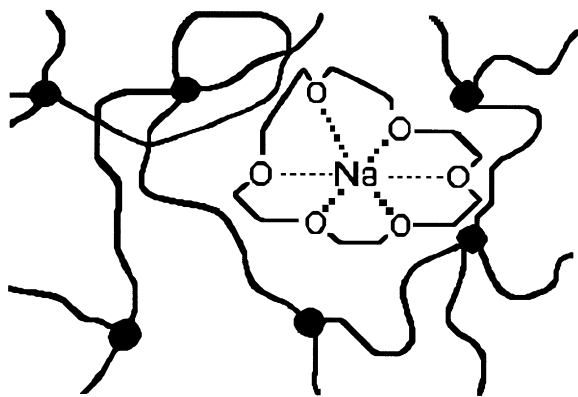


Fig. 5. Schematic representation of ion-ionophore complex entrapped within crosslinked polymer matrix.

the polymer matrix; namely, a population with a Henry's Law isotherm and the other with a Langmuir isotherm [39–42]. This behaviour of glassy polymers may be mirrored in the ionophoric hydrogel, where salts partitioning in the water phase of the polymer matrix can be described by Henry's Law, while the ionophore provides sorption sites that follow Langmuir type behaviour.

In the study of gas transport through glassy polymers, where the dual sorption model is seen to apply, both the time lag and permeabilities are observed to decrease with increasing feed concentration [43,44]. In the study of concentration effects in this work both the induction time and, less clearly, the classical time lag, for KCl through the HEMA:EGDM(90:10) + 5% dicyclohexano-18-crown-6 was found to decrease with increasing feed concentration—a result consistent with a dual-sorption mechanism. This is not so clearly reflected in the final permeability rate, P . The latter remains relatively unaffected by initial salt concentration. Although the dual-sorption model predicts a decrease in permeability with increasing feed concentration, this is a diminishing effect with the permeabilities tending to a constant value. The feed concentrations used here may have been too high for a change in the final permeabilities to be detected.

The Langmuir type sorption sites associated with glassy polymers have been said to originate from frozen microvoids that occur because of the non-equilibrium nature of glassy polymers [45]. Although in the case of such amorphous glassy polymers it is reasonable to describe the dual sorption model as a theoretical curve fit, it should be highlighted that in the case of the ionophore-containing hydrogels described here, the model may be a very unprecise description. A more recent, and perhaps closer analogy to this work, involved the development of an oxygen selective membrane using 2.5–4.5 wt.% of a porphyrin complex as a fixed carrier in a poly (butyl methacrylate) matrix [36], the studies being performed above the glass transition temperature of the polymer. The complex more closely approximates to the concept of a Langmuir sorption site, than to the free-volume heterogeneities of glassy polymers.

Reduction in both permeabilities and induction period with increasing upstream gas pressure was reported: an observation consistent with the dual-sorption model. In the light of these comparisons with gas transport studies, it seems reasonable to conclude that an analogous dual-sorption mechanism may also be in operation in the ionophore-containing membrane.

Some parallels to the present study are found in a study by Noble, who investigated the effect on gas permeability of the presence of a fixed site complexing agent [46]. Although at low complex loadings (0.6–8 wt.%), there was an enhancement in the permeabilities of O_2 ; at a relatively high loading of 12 wt.%, the measured permeability was below that of the complex free polymer. This was explained in terms of a “tightening” of the polymer film. Although the morphological change caused by high loadings of complex may explain a comprehensive decrease in the permeability coefficient of permeant in such membranes, an analogous situation is unlikely to be occurring in the hydrogels studied here, since the effect is selective; LiCl, for example, is unaffected by the presence of the crown ether.

Despite these superficial similarities it is clear that the transport phenomena associated with ionophore-modified hydrogels are quite different from those reported for other systems. The exact nature and scope of the phenomena needs to be further explored and clarified but underlying differences from conventional ionophore-related membrane transport are apparent. The observed behaviour is not a conventional facilitated transport mechanism, since the permeability of salts such as KCl and NH_4Cl are suppressed when the ionophore is present. This suppression is unlikely to be due to a significant change in the membrane morphology or water structuring, induced by the ionophore, since LiCl transport is unperturbed by the crown ether. The role of ionophores in hydrogel membranes is, then, quite different from that in organic membranes where they essentially act by selectively solubilising a species, allowing it to partition in the membrane, and in the case of liquid membranes, transporting the species via a ferry mechanism. Perhaps the nearest analogy is to be found in the field of reverse osmosis membrane. In such systems the passage of a hydrated ion through a partially hydrated membrane is inhibited. This rejection of the ion by the membrane is frequently thought of in terms of both the size of the ion and its inability to readily exchange its hydration shell with the water within, and strangely associated with, the membrane. Using this analogy the phenomena reported here may be thought of as an extension of the behaviour of a partially hydrated membrane by entrapment of more specific ion complexation sites and is represented schematically in Fig. 5.

The influence of ionophores in hydrogel membranes produces a type of behaviour that has not been clearly identified in the literature and does not seem to have an analogy in nature. These phenomena seems significant and may be potentially important for applications requiring

permselective membranes especially where time dependent or concentration dependent behaviour is important, such as sensor devices. It is clearly necessary to investigate this behaviour further by exploring the size–specificity relationships for ionophores in aqueous polymer systems. The results obtained with sodium here suggest that the cavity matching behaviour is slightly different from that encountered in organic solvents. Similarly, the effect on transport behaviour of covalently binding crown ethers to the polymer backbone of these water-swollen systems must be explored.

Acknowledgements

We are grateful to the EPSRC for financial support.

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