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The lack of selectivity in the transport of transition metal ions exhibited by pyridyl- and 2,2′-bipyridyl-based hydrogel membranes

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A range of hydrogel copolymer membranes of poly(2-hydroxyethyl methacrylate) with 4-vinylpyridine or 4-vinyl-4′-methyl-2,2′-bipyridine have been made and their permeabilities to a series of transition metal salts determined. Ion transport is characterized by an initial induction period prior to the onset of steady-state permeation. This period varies depending on the ion under study and can be related to the relative stabilities of the complexes formed within the membrane. The lag time is attributed to the saturation of coordination sites within the membrane, which also affects the rate of permeation of the metal ion relative to that through unmodified membranes. The potential of these systems for selective transition metal ion transport is assessed by competitive studies using binary salt solutions. The membranes do not exhibit any selectivity; in fact, their behaviour can even be described as being antiselective. In pairs, different cations display similar lag times and permeabilities, characteristic of the more strongly coordinating ion. Membrane ligand density has little influence on the final permeability of the salt, which precludes a site to site mechanism as the main mode of transport. However, complexation to the membrane coordination sites is implicated as the cause of modifications to the permeation properties of the membranes.

(Keywords: 2,2′-bipyridyl; complexation; hydrogel)

INTRODUCTION

In recent years there has been a growing interest in the use of membrane processes for the preconcentration and/or the selective separation of metal ions in solution. This has led to the development of a host of polymeric membranes, particularly for use in Donnan-type separation processes[1–3]. Ideally, membranes of this type should possess high ion exchange capacities to permit site to site diffusion and have enough polymer backbone flexibility to allow a continuous polyelectrolyte network throughout the structure, both of which usually entail crosslinking below 15%[4]. Anion exchange membranes of 4-vinylpyridine with low density polyethylene have produced useful systems of this nature. Further modification of this material by quaternization of the pyridyl nitrogens and subsequent reaction with 'thoron' results in one of the few reported chelating membranes[5].

Here we describe studies of transport across membranes of a hydrogel copolymer. Hydrogels can be simply described as hydrophilic polymers that swell in but are not dissolved by water. The chemical constituents of the polymer confer the ability to interact with water by hydrogen bonding through polar functions such as hydroxy groups; the water thus forms an intimate part of the polymer matrix into which solutes may dissolve and diffuse[6]. The effects of solute–water interactions on the transport of alkali and alkaline earth metal ions through poly(2-hydroxyethyl methacrylate), herein represented as poly(HEMA), and copolymer membranes thereof have been discussed in great detail[7,8]. One fundamental observation made is that the water-structuring ability of an ion, rather than its hydrated size, is paramount in influencing its transport properties across the membranes. Anions have a dominant influence over simple cations on permeability behaviour. The best description of this phenomenon compares the observed permeability order of the salts with the Hofmeister (or lyotropic) series, which arranges ions according to their influence on reactions in colloidal solution and their powers of coagulation, giving the order $ClO_4^- > SCN^- \approx NO_3^- > Cl^- > SO_4^{2-}$. The ionic structures of the various anions influence the surrounding water to different degrees. Small or multivalent ions cause the electrostriction of water molecules beyond their primary hydration shell, induce long range ordering and effectively increase the viscosity of the solution. Thus, ions such as SO_4^{2-} are classed as 'structure makers' and consequently permeate more slowly. When the hydrogel is analysed by differential scanning calorimetry (d.s.c.) it is possible to observe melting endotherms that show the proportion of the water that is 'structured' or non-freezing in nature. By contrast, large monovalent ions such as ClO_4^- are 'structure breakers' because they generate weaker electrostatic fields, leaving much of the bulk water unperturbed and 'fluid' and allowing faster permeation

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rates than for the similarly shaped and sized sulfate ion. The d.s.c. endotherm shows this type of water to be freezing in nature[7,8].

Great effort has been applied to the design of a permselective copolymer membrane which will achieve a degree of discrimination between the transport of particular cations. Hydrogel materials might provide such systems, as their physical properties can be finely controlled by altering the degree of hydrophilicity and crosslink density[7–10]. In previous papers we have outlined the synthesis and transition metal ion complexation behaviour of a range of pyridyl- and 2,2'-bipyridyl-based poly(HEMA) copolymer membranes[11–13]. The interstitial water of the polymer matrix provides a medium for the diffusion of transition metal salts, and subsequent coordination with the immobilized ligands then occurs in what is still essentially an aqueous environment. Here, we describe a study of the transport of transition metal salts, both singly and in mixtures, through these complexing systems.

The literature already contains accounts by various workers of the theoretical treatment of systems related to those described here. For example, Noble[14–16] has reported the development of models for the description of facilitated transport through fixed-site carrier membranes. These models are not directly applicable here as they deal with the passage of gases or neutral solutes through membranes which are treated as rigid polymeric structures, while we are investigating the transport of ionic solutes through a more mobile copolymer. Nevertheless, Noble's work offers some interesting insights. Thus, even at low concentration levels of the complexing agent attached to the polymer chain, transport can be facilitated; in addition, the morphology of the complexing sites and the concentration terms are very important[17].

EXPERIMENTAL

Materials

Optical grade 2-hydroxyethyl methacrylate (HEMA) was used as supplied by Ubichem. 4-Vinylpyridine (VPy) was obtained from Aldrich and purified by distillation under reduced pressure (62–64°C, 15 mmHg); the monomer was stored at 5°C under a nitrogen atmosphere. 4-Vinyl-4'-methyl-2,2'-bipyridine (VBpy) was synthesized and purified as described previously[11–13]. Ethylene glycol dimethacrylate (EGDM) crosslinking agent was obtained from BDH and used without further purification. The free radical initiator α-azobisisobutyronitrile (AZBN) was obtained from Aldrich and recrystallized before use.

Membrane fabrication

Membranes of 0.4 mm unhydrated thickness were prepared by a previously described method[18]. The mixture of monomers, also containing 0.5% w/w AZBN and 1% w/w EGDM, was purged with nitrogen, injected into a glass mould and heated at 60°C for 72 h followed by a 2–3 h postcure at 90°C. Membranes were separated from the mould and left to hydrate in distilled water for at least one week, with frequent changes of water.

Transition metal salt solutions

$Co(PF_6)_2$ was prepared from a slight stoichiometric excess of KPF_6 (23.01 g) dissolved in water (100 ml) at 50°C and added to $Co(ClO_4)_2$ solution (22.87 g in 150 ml) to give a 0.25 M concentration with respect to cobalt(II). This solution was kept overnight at 5°C before the $KClO_4$ precipitate was filtered off. The weight of precipitate obtained indicated that the removal of perchlorate was complete. A sample of the filtrate was evaporated down and the solid subjected to infra-red analysis. This showed a symmetrical stretch ν_1 around 740 cm^{-1}, as expected for hexafluorophosphate, and no sign of the sharp ν_1 symmetrical stretch and ν_4 scissoring absorption seen at 935 cm^{-1} and 630 cm^{-1}, respectively, for perchlorate. This 0.25 M solution was then used directly in equilibrium water content (*EWC*) and permeability experiments. All other transition metal salt solutions were prepared from analytical grade reagents, obtained from BDH, which were dissolved in distilled water of ionic conductivity 1.5 ± 0.5 μS cm^{-1}.

Equilibrium water contents

The equilibrium water contents (*EWC*s) of the membranes were determined from the weights of the hydrated and dehydrated samples, and are discussed more fully in a preceding paper[12].

The total metal contents of treated membranes

Separate samples of prehydrated poly(HEMA), 2% w/w VPy and 2% w/w VBpy copolymer membranes were weighed and immersed in a variety of 0.25 M transition metal salt solutions for a number of days until equilibrium had been attained. The membranes were then carefully rinsed, their surfaces were dried and they were then digested in a 10:3 mixture of concentrated sulfuric and nitric acids. The resultant solutions were carefully evaporated to dryness, roasted, and finally the residues were redissolved in dilute mineral acid. The metal ion contents of these solutions were determined by atomic absorption spectroscopy (AAS).

Permeation apparatus

Two types of permeability cell were employed in this investigation. One was used for the study of solutions containing a single metal ion, and the other for binary metal ion solutions. Both cells were constructed mainly of Perspex to enable the condition of the fragile membranes to be observed. The cell used in the single-ion system was based on the design of Misra *et al.*[19], the operation of which has been described in detail elsewhere[7]. Ion transport across the membrane was monitored by automatically measuring the conductivity of the low concentration side using an interfaced Alpha 800 conductivity meter and a BBC microcomputer. Appropriate software was written by us.

The cell used for the study of the binary system was similar in design to that described by Uragami *et al.*[20] consisting of two chambers (8 cm high × 7 cm long × 5 cm deep). One side of each chamber was a backing plate (15 × 14 cm) with a 4 cm diameter hole in it. The test membrane was placed between two silicone rubber sheets of the same dimensions as the backing plates, and the 'membrane sandwich' was completed by bolting the plates together with the membrane in the middle. The solution chambers were surrounded by a thermostatically controlled water jacket and the top of each chamber was left open to permit solution sampling. The perpendicular placement of the membrane overcame the problems of hydrostatic pressure build-up and air bubble collection on the underside associated with the use of horizontal membranes. Stirring close to the membrane was still essential to the prevention of concentration polarization.

On assembly of the unit, distilled water and the mixed salt solution of interest were poured simultaneously into the respective chambers of the cell, and stirring and timing were started immediately. At regular intervals, 1 ml aliquots were removed from both chambers of the cell. The sample from the low concentration side was then diluted to 10 ml and retained for analysis, whereas that removed from the high concentration side to maintain equal hydrostatic pressure on the membrane was discarded. Samples were analysed within 48 h by atomic absorption spectroscopy on a Perkin–Elmer 360 double-beam spectrophotometer.

Permeation studies

The permeability coefficient P_c can be calculated from the gradient of the concentration *versus* time plot using an equation based on Fick's first law of diffusion in solution

$$P_c = (\mathrm{d}m/\mathrm{d}t)L/AC \qquad (1)$$

where L is the membrane thickness, A is the cross-sectional area, C is the concentration of the source solution and $\mathrm{d}m/\mathrm{d}t$ is the rate at which moles of permeant pass across the membrane aperture. Plots of the concentration of transported salt in the receiving compartment against time approximate to straight lines with non-zero intercepts on the time axis. Only close to that intercept is the plot non-linear. We applied the method of least squares to the linear data to obtain the value of $\mathrm{d}m/\mathrm{d}t$, while we defined the computed intercept as the lag time (T_L).

Reproducibility

Both experimental rigs yielded results with a reproducibility between runs of ±2.5%. Permeation of 0.25 M $CaCl_2$ through purely poly(HEMA) membranes, as determined by the conductimetric technique, yielded a P_c of $2.83 \times 10^{-6}\,\mathrm{cm}^{-2}\,\mathrm{min}^{-1}$. This is in excellent agreement with the value of $2.75 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{min}^{-1}$ produced by the AAS method. Thus, data from the two rigs agree to ±3%.

RESULTS

Transition metal ion permeation through poly(HEMA) membranes

A series of experiments were performed to investigate the permeability effects of various transition metal salts through crosslinked but otherwise pure poly(HEMA) membranes. A range of 0.25 M salts were used at 25°C, and the observed primary transport data, shown for the chlorides in *Figure 1*, were used to calculate P_c for each of the cations (*Table 1*). For these chlorides P_c varies in the order $Ca^{2+} > Cu^{2+} > Ni^{2+} > Mn^{2+} \geqslant Co^{2+}$. Similarly, the influence of anions of cobalt(II) salts on the transport properties of the membrane is shown in *Figure 2* (and in *Table 1*). The permeabilities are in the order $PF_6^- > ClO_4^- > SCN^- > NO_3^- > Cl^- \gg SO_4^{2-}$. It is clear that there is a correlation between the permeability of the ions in these two series and their influence on the equilibrium water content of the treated membrane. For the salts with singly charged anions a good straight line can be drawn through a plot of the square root of the permeability coefficient *versus* the equilibrium water content (see *Figure 3*). When all the 2:1 electrolytes are considered, a least-squares fit gives an intercept at ca. 29% water content. There is some scatter as the monovalent anions are varied, but it is slight compared to the effect when sulfate is the anion. This is attributable to the structure-making properties of sulfate[7,8].

When a cation is present within the membrane it will be surrounded by its own solvation shells and also by solvated counterions. The incorporation of this sphere into the membrane may either force the structure to open out with the consequent uptake of more imbibed water, or it may tighten the structure leading to a lower equilibrium water content. That is, it will alter both the quantity of water within the swollen membrane and the fraction of that water that can be described as being fluid, or 'freezing', and available for permeation. This will in turn affect the partitioning S_m of the salt between the two aqueous phases, which is related to its permeability coefficient and diffusivity by

$$P_c = S_m D \qquad (2)$$

The observation of some relationship between P_c and the equilibrium water content is obviously reasonable, and we choose to present it as

$$P_c = c(EWC - 29)^2 \qquad (3)$$

where EWC is the equilibrium water content expressed as a percentage and c is a constant. This can be rationalized by saying that, for divalent transition metal salts of monovalent anions passing through a hydrogel membrane, approximately 29% of the mass of the hydrogel consists of non-fluid, or non-freezing, water.

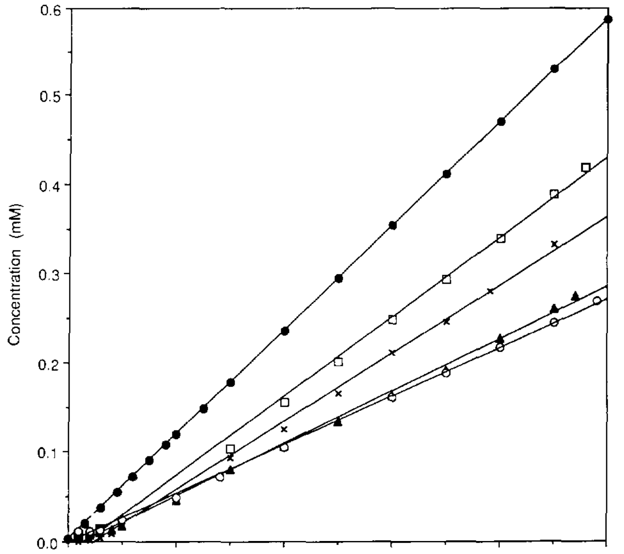

Figure 1 Effect of transition metal ion variation on the transport of a range of chloride salts through poly(HEMA) membranes: (●) Ca^{2+}; (□) Cu^{2+}; (×) Ni^{2+}; (▲) Mn^{2+}; (○) Co^{2+}

Table 1 Permeability data for selected metal salts through poly(HEMA) membranes

Salt	Concentration (M)	*EWC*[a] (%)	Thickness[a] (cm)	d*m*/d*t* (mol min^{-1})	T_L (min)	P_c (cm^2 min^{-1})
$CaCl_2$	0.25	35.8	0.041	1.87×10^{-7}	5	2.83×10^{-6}
$MnCl_2$	0.25	33.4	0.039	9.77×10^{-8}	23	1.50×10^{-6}
$CoSO_4$	0.25	29.5	0.038	2.63×10^{-9}	~60	3.92×10^{-8}
$CoCl_2$	0.25	30.7	0.04	8.92×10^{-8}	23	1.38×10^{-6}
$Co(NO_3)_2$	0.25	36.9	0.04	2.40×10^{-7}	30	3.76×10^{-6}
$Co(NCS)_2$	0.25	41.1	0.0425	8.81×10^{-7}	15	1.49×10^{-5}
$Co(ClO_4)_2$	0.25	43.4	0.043	9.93×10^{-7}	10	1.64×10^{-5}
$Co(PF_6)_2$	0.25	46.1	0.045	1.31×10^{-6}	<5	2.32×10^{-5}
$NiSO_4$	0.25	32.3	0.038	3.67×10^{-9}	>50	5.47×10^{-8}
$NiCl_2$	0.25	33.7	0.039	1.26×10^{-7}	37	1.93×10^{-6}
$Ni(NO_3)_2$	0.25	38.0	0.041	3.04×10^{-7}	28	4.90×10^{-6}
$Ni(ClO_4)_2$	0.25	44.2	0.042	1.14×10^{-6}	7	1.87×10^{-5}
$Ni(PF_6)_2$	0.25	49.6	0.0485	2.42×10^{-6}	4	4.29×10^{-5}
$CuSO_4$	0.25	32.6	0.037	4.42×10^{-9}	>50	6.42×10^{-8}
$CuCl_2$	0.25	34.1	0.041	1.49×10^{-7}	32	2.40×10^{-6}
$Cu(NO_3)_2$	0.25	38.0	0.0395	3.68×10^{-7}	25	5.71×10^{-6}
$Cu(ClO_4)_2$	0.25	45.2	0.042	5.51×10^{-6}	~5	9.08×10^{-5}

[a] With transition metal salt present

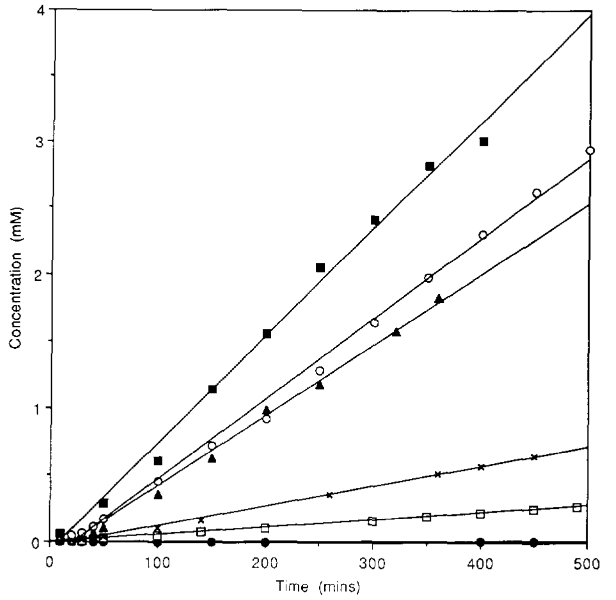

Figure 2 Effect of counterion variation on the transport of a range of cobalt(II) salts through poly(HEMA) membranes: (■) PF_6^-; (○) ClO_4^-; (▲) SCN^-; (×) NO_3^-; (□) Cl^-; (●) SO_4^{2-}

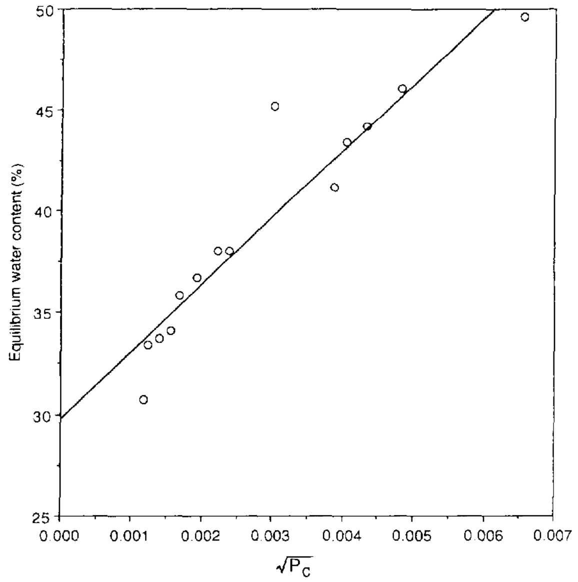

Figure 3 Linear correlation between the square root of the permeability coefficient of the salt and the *EWC* imposed on the membrane

In every experiment there is also a time lag before the passage of the permeant through the membrane is detected. These time lags match those predicted from a consideration of the solubilities and steady-state permeation rates of the permeants[21].

Transition metal ion interactions with ligand-modified hydrogel membranes

In order to assess the extent of transition metal ion interaction within our copolymeric hydrogel systems, we determined the total metal ion contents resulting from the immersion of a range of membrane samples in various salt solutions. The metal ion content within a ligand-modified membrane consists of two components: that partitioned into the interstitial water of the gel matrix, and that coordinated to the appended ligand sites. The former quantity can be separately estimated by determining the metal ion content for poly(HEMA) membranes which do not contain ligand groups. Hence the amount of coordinated metal can be determined. In *Table 2* we list the important determinations, expressed in terms of the ratio $[M^{2+}]/[\text{ligand}]$, along with the known stability constants for the equivalent free complexes in aqueous solution[22,23].

For the pyridyl copolymer, the order for the extent of cation–ligand interactions follows that of the stepwise

Table 2 Metal–ligand interactions and stability constant[a] data for the free complexes[20]

M^{2+}	$[M^{2+}]/[VBpy]$ observed	Stability constants $(M(VBpy)_x)$			$[M^{2+}]/[VPy]$ observed	Stability constants $(M(VPy)_x)$		
		$\log K_1$	$\log K_2$	$\log K_3$		$\log K_1$	$\log K_2$	$\log K_3$
Ca^{2+}	0.05				0.01			
Mn^{2+}	0.14	2.6	2.0	1.0	0.16	0.14		
Fe^{2+}	0.35	4.3	3.7	9.5	0.1	0.71		
Co^{2+}	0.45	5.7	5.6	4.8	0.18	1.14	0.4	
Ni^{2+}	0.2	7.1	6.8	6.2	1.78	1.05	0.31	
Cu^{2+}	0.8	8.1	5.5	3.5	0.56	2.52	1.56	1.31
Zn^{2+}	0.02	5.4	4.4	3.5	0.01	0.95	0.5	

[a] The stability constants quoted are those for the stepwise addition of the free ligand to the metal ion in solution, as given by the expressions

$$K_1=\frac{[M^{2+}(L)]}{[M^{2+}][L]},\ K_2=\frac{[M^{2+}(L)_2]}{[M^{2+}(L)][L]},\ K_3=\frac{[M^{2+}(L)_3]}{[M^{2+}(L)_2][L]},\ \text{etc.}$$

Table 3 Permeability data for selected metal salts through vinylpyridine-based membranes

VPy content (% w/w)	Salt	Concentration (M)	*EWC*[a] (%)	Thickness[a] (cm)	d*m*/d*t* (mol min^{-1})	T_L (min)	P_c ($cm^2\ min^{-1}$)	$[M^{2+}]/[VPy]$ retained
2	$CaCl_2$	0.25	35.7	0.041	1.37×10^{-7}	50	3.04×10^{-6}	0.10
2	$MnCl_2$	0.25	33.9	0.039	1.25×10^{-7}	48	1.91×10^{-6}	0.05
2	$CoCl_2$	0.25	36.9	0.04	1.07×10^{-7}	176	1.68×10^{-6}	0.27
2	$NiCl_2$	0.25	37.4	0.039	2.13×10^{-7}	216	3.26×10^{-6}	0.62
2	$CuCl_2$	0.25	38.0	0.041	3.01×10^{-7}	252	4.85×10^{-6}	1.08
0	$CuCl_2$	0.25	34.1	0.041	1.49×10^{-7}	32	2.40×10^{-6}	
0.5	$CuCl_2$	0.25	36.0	0.041	2.77×10^{-7}	102	4.46×10^{-6}	1.27
1	$CuCl_2$	0.25	36.1	0.04	2.82×10^{-7}	158	4.43×10^{-6}	1.16
4	$CuCl_2$	0.25	39.9	0.041	2.46×10^{-7}	354	3.97×10^{-6}	0.65
0.5	$CuCl_2$	0.05		0.0395	1.78×10^{-8}	250	1.38×10^{-6}	0.25
0.5	$CuCl_2$	0.10		0.04	5.01×10^{-8}	190	1.97×10^{-6}	0.52
0.5	$CuCl_2$	0.175		0.04	1.43×10^{-8}	120	3.21×10^{-6}	0.82

[a] With transition metal salt present

stability constants for the addition of the *n*th ligand to the metal, i.e. $\log K_n$ (the Irving–Williams series): $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. For the bipyridyl system, the order of interaction no longer follows the known order for $\log K_n$. Unless the stability constants for hydrogel membranes are several orders of magnitude smaller than those for aqueous solutions, when 0.25 M salt solutions pass through the membranes the quantity of non-coordinated ligand will be negligible (that is also true for the case of Cu^{2+} with the unidentate pyridine group). However, it is known that Fe^{2+} and Co^{2+} can form tris(bipyridyl) complexes within bipyridyl-containing copolymer membranes, while Cu^{2+} coordinates to a maximum of two bipyridyl groups[11–13,24]. Therefore different types and mixes of complex will occur and so a simple series cannot be expected in this case. The observed $[M^{2+}]/[VBpy]$ ratios quoted in *Table 2* are those for membranes in which the complex centres present are at equilibrium with 0.25 M aqueous solutions of M^{2+}. Only in the case of Fe^{2+} does the ratio show that one complex form is predominant.

Comparisons with known stability constants for the homogeneous aqueous solutions do appear to be helpful in the explanation of the behaviour of our hydrogel systems. We make use of them below in explaining the lag times in the ligand-modified systems.

Transition metal ion permeation through ligand-modified hydrogel membranes

A number of permeability experiments for the copolymer membranes were carried out as before at 25°C, using 0.25 M metal chlorides in the high concentration compartment. The membranes initially used were in the range 0.5–2% w/w for copolymers of HEMA/VPy and HEMA/VBpy. In this composition range the hydrophilicity of the hydrogel does not alter, but a change in the permeability characteristics compared to those of poly(HEMA) itself is seen.

Tables 3 and *4* and *Figures 4* and *5* summarize the transport data obtained for the two membrane systems. The permeability coefficient varies with the cation and is proportional to its concentration, but is independent of the ligand loading in the membrane over our experimental range (*Figure 6*). The most striking difference between these data and those for poly(HEMA)-only membranes is the presence of a significant lag time for the ligand-based systems. The lag times for chloride salts passing through poly(HEMA)-only membranes are

Table 4 Permeability data for selected metal salts through vinylbipyridine-based membranes

VBpy content (% w/w)	Salt	Concentration (M)	*EWC*[a] (%)	Thickness[a] (cm)	d*m*/d*t* (mol min^{-1})	T_L (min)	P_c (cm^2 min^{-1})	[M^{2+}]/[VBpy] retained
2	$MnCl_2$	0.25	32.4	0.039	1.11×10^{-7}	246	1.70×10^{-6}	0.75
2	$CoCl_2$	0.25	34.6	0.0395	5.56×10^{-8}	257	8.62×10^{-6}	0.40
2	$NiCl_2$	0.25	33.8	0.040	7.51×10^{-8}	275	1.18×10^{-6}	0.54
2	$CuCl_2$	0.25	34.2	0.041	1.67×10^{-7}	220	2.68×10^{-6}	0.75
0	$CuCl_2$	0.25	34.1	0.041	1.49×10^{-7}	32	2.40×10^{-6}	
0.5	$CuCl_2$	0.25	34.4	0.04	1.92×10^{-7}	78	3.02×10^{-6}	1.07
1	$CuCl_2$	0.25	34.4	0.04	1.66×10^{-7}	125	2.62×10^{-6}	0.96
4	$CuCl_2$	0.25	35.9	0.041				

[a] With transition metal salt present

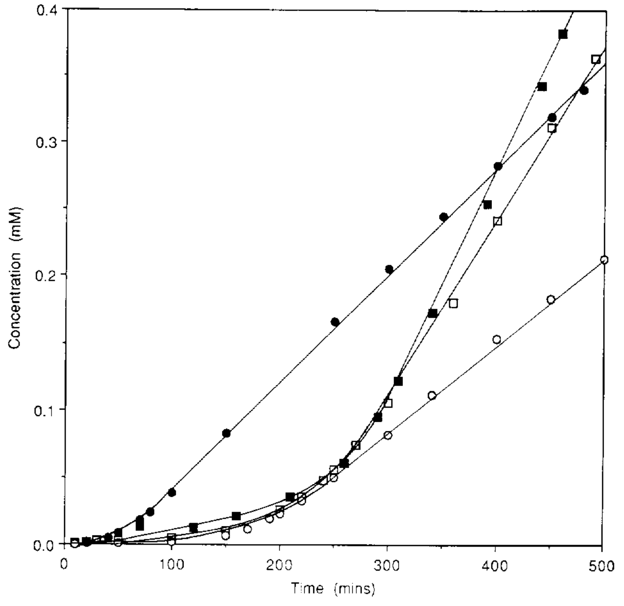

Figure 4 Primary transport data for a range of metal chlorides through 2% w/w HEMA/VPy copolymer membranes: (●) Mn^{2+}; (■) Cu^{2+}; (□) Ni^{2+}; (○) Co^{2+}

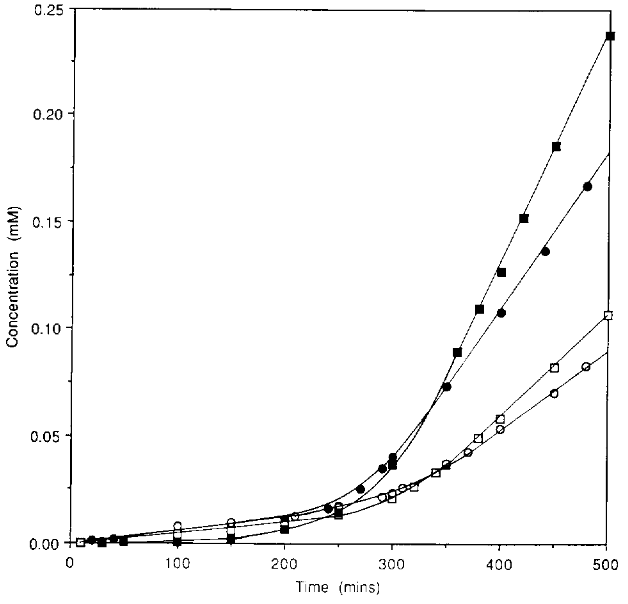

Figure 5 Primary transport data for a range of metal chlorides through 2% w/w HEMA/VBpy copolymer membranes: (■) Cu^{2+}; (●) Mn^{2+}; (□) Ni^{2+}; (○) Co^{2+}

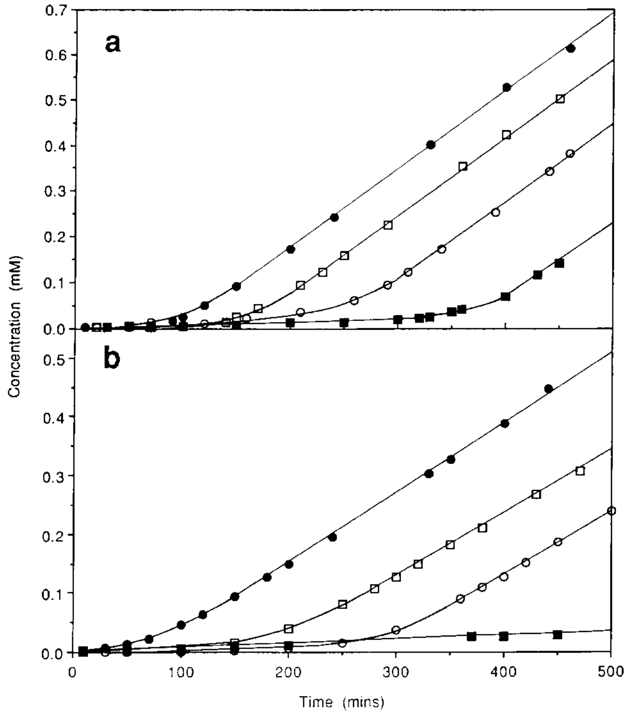

Figure 6 Transport data for 0.25 M $CuCl_2$ with 0.5% w/w (●), 1% w/w (□), 2% w/w (○) and 4% w/w (■) ligand loading in (a) HEMA/VPy and (b) HEMA/VBpy copolymer membranes

short, but those observed with ligand groups in the copolymer membranes are much more pronounced. Now they depend both on the rate of salt permeation and on the interaction between the metal ions and the immobilized ligand groups. Also, unlike the permeability coefficients, the lag times are dependent on ligand concentration (*Figure 6*).

Permeation through vinylpyridine-containing copolymer membranes

The behaviour of the two distinct types of copolymer membranes is very different. We consider the vinylpyridine-containing copolymer first. The permeability coefficients for the passage of 0.25 M chloride salts through the 2% w/w copolymers are still dependent on the concentration of the salt in the source compartment. They can be modelled using equation (4) in which *z* is a constant, and the subscript *x* denotes the vinylpyridine content of the copolymer

$$P_{cx}=zP_{c0}(EWC_x-29)^2/EWC_0-29)^2 \qquad (4)$$

If the diffusion process were totally unchanged by the incorporation of vinylpyridine groups into the polymer, except for any effects due to changes in the equilibrium water content and the amount of freezing water, the value of z would be unity. If z is treated as an unchanging constant for all the salts with monovalent anions, its value of 0.82 ± 0.27 is not significantly different from unity. By contrast, the incorporation of vinylpyridine markedly affects the time lag. If the intimate process of diffusion were unchanged from that occurring in pure poly(HEMA), time lags similar to those in *Table 1* should be expected, but the strongly coordinating cations exhibit much longer time lags. They are clearly related to the stability constants for complex formation with pyridine. The more strongly does the pyridine group coordinate to the cation, the more of it is held back in the membrane, and so the longer is the lag time lag. we assume that the rate of permeation during the time lag is the same as that measured afterwards, then the function $[(T_L)_x-(T_L)_0](dm/dt)_x$ is a direct measure of the extra quantity of salt transported into the membrane before the passage of any is detected on the output side of the membrane. Again the subscript x is used to indicate the copolymer composition. In *Tables 3* and *4* the calculated ratios of this quantity to the amount of ligand in the membrane aperture are quoted as the retained ratios of $[M^{2+}]/[VPy]$ and $[M^{2+}]/[VBpy]$, respectively. These ratios provide very strong support for the suggestions that coordination occurs within the membrane and that the extended time lag reflects the capture of the appropriate amount of cation by the copolymer ligand sites.

The data are not sufficiently precise to allow the accurate computation of stability constants for all the metal ions, but a pattern can be discerned similar to that observed in aqueous solution. Estimates of the constants can, however, be made, given some reasonable assumptions. The experimental values of retained $[M^{2+}]/[VPy]$ are consistent with the simplifying assumptions that equilibria are maintained and that bis(pyridyl) and higher complexes can be neglected. The activity of any salt within the hydrogel will be unknown and different from that in the aqueous phase. Therefore only $K_1 f_M$ rather than K_1 can be estimated, where f_M is the activity of the hydrated cation within the hydrogel. On the assumption that only mono(pyridyl) complexes need be considered when the swollen membrane is at equilibrium with the permeant solution, values of $\log K_1 f_M$ of approximately -0.4, -0.7, 0.2, 0.8 and 1.5 for Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, respectively, are obtained. The formation of the mono(pyridyl) complex of Cu^{2+} appears to be essentially complete in the 2% w/w copolymer, and so the data used to provide this estimate are those obtained for the 0.5% w/w copolymer. In every case $K_1 f_M$ seems to be approximately one order of magnitude smaller than is K_1 for aqueous solutions.

Our observation that the experimental ratios for $[Cu^{2+}]/[VPy]$ (see *Table 3*) are close to unity, except under conditions of high ligand loading or low Cu^{2+} concentraton, must indicate that the mono(pyridyl) complex is predominant, and therefore K_2 must also be lower for the hydrogel than for aqueous solutions. This is easily seen by considering the following generalized reaction, for which the equilibrium constant is $K_2/K_1 f_M$

$$2[ML]^{2+} \rightleftharpoons [ML_2]^{2+} + M^{2+} \qquad (5)$$

If, for L = VPy, K_2 were unchanged on moving from aqueous solution to the hydrogel environment, then 30% of the vinylpyridine groups would be in the bis(pyridyl) complex form when 0.25 M $CuCl_2$ is the permeant solution. By contrast, if K_2 were also reduced by a factor of 10, then an acceptable level of only 6% bis(pyridyl) complex would occur, while $[Cu^{2+}]/[VPy]$ would be 0.94.

Equation (5) can be used in a different argument. It clearly shows that when the concentration of hydrated cations in the imbibed water is lower, the concentration of the crosslinking bis(pyridyl) complex is higher. Thus, when a permeating $CuCl_2$ solution first reaches a non-complexed region of the membrane, the concentration of hydrated ions in the imbibed water will be small, and so the percentage of the crosslinking bis(pyridyl) complex will be higher than the eventual equilibrium level. If crosslinking retards permeation, it will tend to hold back the permeating solution front and force the solution to pass through the membrane as a plug. If the solution contains salts of two different cations, both will be held back for the same time, even though one of them might not be involved in coordination to any significant extent. In *Table 5* we illustrate this argument quantitatively with the results of calculations for the Cu^{2+} system using the previously estimated value of $K_1 f_{Cu}$ and $K_2=(K_2)_{aq}/10$. If the formation of tris(pyridyl) and tetrakis(pyridyl) complexes were also included in the calculations, the effect we demonstrate would be even more pronounced.

The only datum of *Table 3* which is not fully compatible with the preceding argument is the permeability coefficient for $CuCl_2$ passing through the 4% w/w vinylpyridine copolymer, for which z is only 0.36. This is probably due to experimental error. Although the increase in the pyridine concentration would increase the amount of crosslinked pyridine groups to 10% for the parameters of *Table 5*, that is not a large enough increase to account for the observed reduction in permeation.

Finally for this copolymer system, we studied the competitive transport of mixtures of ions through membranes. We chose two pairs of salts at the extremes of our data range, i.e. 0.25 M $CuCl_2$ plus 0.25 M $MnCl_2$ and the equivalent mixture containing calcium in place of manganese. *Figures 7a* and *7b* show the primary transport curves for the competitive transport of a binary salt solution containing Cu^{2+} and Mn^{2+} through ligand-based membranes. *Table 6* summarizes the important data, together with those from a similar study using Cu^{2+} and Ca^{2+} as competitors.

Table 5 Demonstration of crosslinking bis(pyridyl) complex formation according to equation (5)[a]

$(f_{Cu})_{transient}/(f_{Cu})_{final}$	$[Cu^{2+}]/[VPy]$ retained	Py as $[Cu(Py)_2]^{2+}$ (%)
1	0.94	6
0.2	0.89	18
0.1	0.81	23

[a] $Kf_{Cu}=32$, $K_2=3.6\ M^{-1}$ and $[VPy]_{total}=0.31$ M

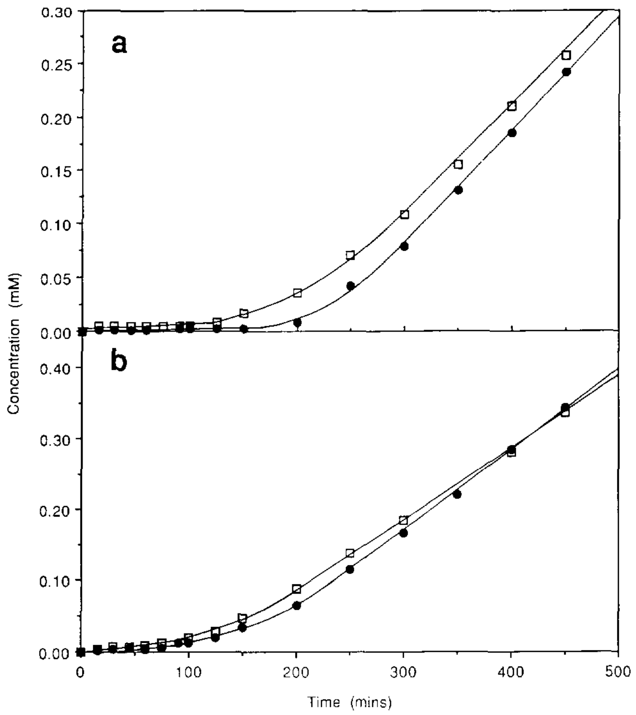

Figure 7 Competitive transport of Cu^{2+} (□) and Mn^{2+} (●) in binary chloride solutions through (a) 2% w/w HEMA/VPy and (b) 2% w/w HEMA/VBpy copolymer membranes

Table 6 Permeability data for binary solutions of metal chlorides through ligand-modified membranes

Membrane type (2% w/w ligand)	Binary system (0.25 M each)	Ion monitored	T_L (min)	P_c ($cm^2 min^{-1}$)
VPy	Cu^{2+}/Mn^{2+}	Cu^{2+}	180	3.5×10^{-6}
VPy	Cu^{2+}/Mn^{2+}	Mn^{2+}	210	3.9×10^{-6}
VBpy	Cu^{2+}/Mn^{2+}	Cu^{2+}	120	4.0×10^{-6}
VBpy	Cu^{2+}/Mn^{2+}	Mn^{2+}	130	3.5×10^{-6}
VPy	$Ca^{2+}Cu^{2+}$	Cu^{2+}	180	5.3×10^{-6}
VPy	Ca^{2+}/Cu^{2+}	Ca^{2+}	200	7.7×10^{-6}

To our initial surprise we found that there is no selectivity in the system. When two ions are in competition, the lag times and steady-state permeability values are very similar for both. These results are genuine, as the concentrations of both metal ions in the receiving compartment were determined by atomic absorption spectroscopy. The common lag times are explicable in terms of the model we advanced above. As the stability constant ratio $^{Cu}K_1/^{Mn}K_1$ is 240 for aqueous solutions, we can expect the membrane ligand sites to be almost entirely saturated with Cu^{2+} in both cases. The initial formation of crosslinking bis(pyridyl) to tetrakis(pyridyl) complexes with copper, followed by reconversion to a predominantly mono(pyridyl) state, will enforce plug flow for both ions and so give a common lag time controlled by the coordination of Cu^{2+}. These membranes thus appear to exhibit an antiselective nature, and cannot easily be used to separate species from mixed metal solutions. Therefore we did not pursue those investigations any further. That leaves some behavioural features unexplained, namely the reduced lag time compared to $CuCl_2$ alone, and the relative enhancement of P_c for the poorly coordinating cation. We note that since the more strongly coordinating cation dominates coordination to the ligand groups, while both salts may play a part in altering the equilibrium water content of the equilibrated membrane, some variation could be expected in both transport parameters.

Permeation through vinylbipyridine-containing copolymer membranes

In aqueous solution 2,2′-bipyridine is a much better ligand than is pyridine, and we can expect the difference to be retained in the hydrogel copolymers. Spectroscopic evidence for the Cu^{2+}- and Co^{2+}-soaked membranes, already reported elsewhere[12], shows that formation of both bis(bipyridyl) and tris(bipyridyl) complexes occurs very readily for this chelating ligand. It also shows that as the concentration of metal ions within the membrane increases, equilibria involving lower orders of complexation are again established, e.g. that between the mono(bipyridyl) and bis(bipyridyl) species shown in equation (5).

First, we consider the lag times. The order for the bipyridine-containing copolymer, i.e. $Cu^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+}$, does not reflect either the Irving–Williams series nor $\log K_1$. All are much larger than those seen for the parent poly(HEMA) membrane. The retained $[M^{2+}]/[VBpy]$ ratios, calculated in the same way as for $[M^{2+}]/[VPy]$, are listed in *Table 4*. They are very close to unity for the poorly coordinating Mn^{2+} and Ca^{2+} cations, and also for Cu^{2+}, which has an unusually large value for K_1/K_2 in aqueous solutions. When $[M^{2+}]/[VBpy] = 1$, this shows that the permeation of these cations leads to the essentially complete formation of $[M(VBpy)]^{2+}$ centres within the membrane. For cobalt the ratio is a little greater than 0.33, which is strong evidence for the predominant formation of $[Co(VBpy)_3]^{2+}$ centres. Only for nickel is the interpretation of the ratio uncertain. A value slightly greater than 0.5 probably indicates the presence of significant amounts of mono(bipyridyl), bis(bipyridyl) and tris(bipyridyl) centres. Clearly, essentially complete complexation of the ligand sites always occurs as the divalent transition metal cations pass through the membranes. In the case of Ni^{2+} a significant amount of crosslinking must occur, while the Co^{2+}-treated membrane is very heavily crosslinked.

When the permeability coefficients for the various MCl_2 salt solutions are compared using equation (4), the value of z varies in the manner expected for salts which produce widely differing degrees of crosslinking. The most heavily crosslinking permeant, the cobalt salt, gives $z = 0.06$; z for $NiCl_2$ is 10 times greater, and there is a further increase by a factor of three on changing to $MnCl_2$. Thus the presence of 2,2′-bipyridyl groups in a copolymer membrane affects the permeability in two distinct ways. The formation of hydrated complexes within the membrane will affect the equilibrium water content and hence the amount of freezing water available for transport. Additionally, the formation of crosslinking complexes, especially tris(bipyridyl) complexes, will reduce permeability further.

The results of a competitive permeability experiment involving 0.25 M Cu^{2+} and 0.25 M Mn^{2+} again show a common lag time consequent upon the enforcement of plug flow. Again, the adjusted lag time $[(T_L)_x-(T_L)_0]$ is lower than that for $CuCl_2$ alone. If this phenomenon is to be investigated further, many more experiments over a range of concentration ratios are needed, and the use of Co^{2+} rather than Cu^{2+} is indicated.

CONCLUSIONS

Ligand groups within a hydrogel copolymer membrane alter the transport profile for transition metal salts. The most dominant feature is the characteristic lag time before steady-state permeation is achieved, which can be mainly attributed to the differing degrees of interaction between particular metal–ligand pairings. The effect on permeability is more complex. The coordination of a large hydrated metal ion to a ligand site will enforce some reorganization in the three-dimensional structure of the polymer, so that the environment within the transient pore is altered in some manner – perhaps a constriction or expansion in size.

Increasing the ligand concentration within the copolymer membrane has little effect on the value of P_c for the permeating species, which precludes an active transport mechanism in which the ligand sites are directly involved in the ion transport process. However, coordination does occur and causes modifications in the membrane and its transport properties. These arise through the changes in equilibrium water content that occur as the membrane is exposed to a salt solution and the varying degrees of complexation and crosslinking complexation afforded by the particular cation–ligand combinations.

The different degrees of ion selectivity demonstrated by the parent ligands in aqueous solutions do not translate into the hydrogel membrane system. Rather, the membranes display an antiselectivity in which metal species that individually show different permeability characteristics behave similarly when transported as a binary salt mixture. These systems may therefore find use in applications where it is desirable to enhance the transport of species that normally permeate slowly.

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