

Kinetic and mechanistic aspects of copper(II) coordination to bis-*N,N'*-(salicylidene)-1,2-diaminoethane-based hydrogel polymer membranes, and the permeation of cations through them

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A range of hydrophilic membranes composed of copolymers of bis-*N,N'*-(5-vinylsalicylidene)-1,2-diaminoethane with 2-hydroxyethylmethacrylate have been synthesised. Over a period of approximately 2 h these membranes coordinate copper(II) ions from aqueous solution to yield tetradeinate species in a first-order process. However, only a small fraction of the potentially ligating sites are fully used in this way. Kinetic studies of the interactions with the nitrate, chloride and sulfate salts of copper(II) are described and a detailed mechanism is proposed. Molecular rotations at the ligand site are suggested to be the rate determining steps of the overall process. Values of individual rate and equilibrium constants have been determined, and shown to be consistent with the equivalent data found for simpler ligands involved in reactions in homogeneous solutions. The permeation of the nitrates of Co^{II}, Ni^{II} and Cu^{II} through membranes of these copolymers is also described. Due to the slow rates of complex formation, the ligand sites have no significant effect on either the permeability of the salts through the membrane, or the time lags before salt passage is detected. For comparison purposes, permeation data for the passage of the nitrate of the substitutionally inert [Cr(H₂O)₆]³⁺ ion through 4-methyl-4'-vinyl-2,2'-bipyridyl-containing membranes are also reported.

There is widespread interest in syntheses and separations using functional polymers.¹ Advantage is often taken of the interactions which occur between metal ions and these functionalised polymers. This can range from the use of polymer supported complex catalysts through separation and hydrometallurgy,² and polymer-modified electrodes,^{3,4} to the investigation of more purely physical processes.⁵ The closely related studies of the transport of metal ions through hydrogel membranes has been reported by other workers.^{6,7} Here we touch on transport but mainly focus on some aspects of the coordination process itself.

Studies involving two different hydrogel copolymers, incorporating well known ligand groups, are described here. The first, 2,2'-bipyridyl (bipy), has been extensively studied as a monomeric ligand in solution.⁸⁻¹¹ It has also been functionalised, usually as 4-methyl-4'-vinyl-2,2'-bipyridine (vbpy) and incorporated into copolymers. Members of this research group have concentrated on hydrogel copolymers, and used them in coordination studies.¹²⁻¹⁷ The other ligand group described in this paper is bis-*N,N'*-(salicylidene)-1,2-diaminoethane (H₂salen). Again it has been studied as a discrete ligand¹⁸⁻²⁰ and as a functionalised component of copolymers, e.g. using the 5,5'-divinyl derivative (H₂dvsalen) which we have examined here.^{21,22}

The main emphasis in this report is upon kinetic and mechanistic studies involving the coordination of the Cu²⁺ ion, but we begin by briefly describing some relevant transport studies.

Experimental

Monomers

Optical grade 2-hydroxyethyl methacrylate (HEMA) was used as supplied by Kelvin Lenses Limited. Ethylene glycol dimethacrylate (EGDM) cross-linking agent was obtained from BDH and used without further purification. The free radical initiator azobisisobutyronitrile (AIBN) was obtained from Aldrich and recrystallised before use. 4-Methyl-4'-vinyl-2,2'-bipyridine (vbpy) was prepared in an overall 30% yield by the method of

Abruna *et al.*,²³ while bis-*N,N'*-(5-vinylsalicylidene)-1,2-diaminoethane (H₂dvsalen) was prepared by the method of Wulff and Akelah.²⁴

Satisfactory characterisation of both monomers was achieved. Elemental analysis for vbpy gave C, 79.3; H, 6.3; N, 14.0% (expected values being 79.6, 6.2 and 14.3%). ¹H NMR (CDCl₃) δ: 8.49/8.55 (H 6/6'), 8.20/8.35 (H 5/5'), 7.08/7.27 (H 3/3'), 6.67/6.7/6.72/6.76 (=CH₂: position 4'), 5.45/5.56, 6.01/6.07 (=CH: position 4') and 2.39 (CH₃: position 4). ¹³C NMR (CDCl₃) δ: 155.8/156.8 (C 2/2'), 148.8/149.3 (C 6/6'), 145.7/148.1 (C 4/4'), 121.9/124.7 (C 5/5'), 118.7 (=CH₂: position 4'), 118.4/120.5 (C 3/3') and 21.1 (CH₃: position 4).

The other functionalised-ligand monomer, H₂dvsalen, was prepared in 85% yield from its immediate precursor 5-vinyl salicylaldehyde (Found: C, 72.4; H, 5.2. Calc. for H₂dvsalen: C, 73.0; H, 5.4%). ¹H NMR (CDCl₃) δ: 13.25 (br, H 9/9'), 8.33 (H 7/7'), 7.35/7.36/7.38/7.39 (H 3/3'), 7.22/7.23/7.24 (H 5/5'), 6.88/6.91 (H 6/6'), 6.56/6.59/6.61/6.65 (=CH: positions 4/4'), 5.09/5.12, 5.54/5.59 (=CH₂: positions 4/4') and 3.93 (H 8/8'). ¹³C NMR (CDCl₃) δ: 166.4 (C 7/7'), 160.8 (C 1/1'), 135.6 (=CH: positions 4/4'), 130.0 (C 5/5'), 129.4 (C 4/4'), 118.3 (C 2/2'), 111.6 (=CH₂: positions 4/4') and 59.7 (C 8/8'). The melting point of our product is 167–170 °C, which compares with the literature value of 168–170 °C.

Membrane fabrication

Membranes of approximately 0.4 mm unhydrated, but accurately measured, thickness were prepared by a previously described method.¹³ The desired mixture of monomers, also containing 0.5% AIBN and 1% EGDM, was purged with nitrogen, injected into a glass mould through a G22 syringe needle, and heated at 60 °C for three days, followed by 2 h postcure at 90 °C. The membrane was then extracted from the mould, inspected and measured. The variations in thickness measured at different positions on a sheet were found to be within 2% of the average value, while films showing defects such as pinholes were discarded at this stage. Membranes were then left to hydrate in deionised water for 2 weeks, with daily changes of water. The membranes were stored in deionised water until required.

All the membranes behave as hydrogels, as shown by their equilibrium water contents. Within experimental error, the incorporation of ligand groups has no effect on the values; thus hydrogels containing dvsalen contain $(37.5 \pm 1)\%$ water, while those containing vbpy yield a value of $(38.0 \pm 1)\%$.

In previously reported studies we occasionally obtained individual results that were greatly at variance with others from the same sets of experiments.¹²⁻¹⁶ We believe them to be attributable to pinholes. Here, we always made careful visual inspections for membrane defects, and we obtained no large data discontinuities. We assume that minor variations in film thickness and the presence of small pores will have occurred in some individual experiments, as evidenced by discrepancies between observed and expected constants; but they are not large. Therefore we believe that where systematic variations in experimental parameters are seen, they can be attributed to chemical effects.

Transition-metal salt solutions

Analytical grade $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were obtained from BDH, while $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was obtained from Aldrich. All were used as supplied. The salt solutions were prepared using deionised water.

Permeation apparatus

The permeability cell used in these experiments has been described previously. A membrane sheet is mounted between rigid backing plates and solution can permeate through a circular 4 cm diameter aperture.¹⁶ A dip conductivity cell (cell constant $K=1$) was used to detect ions permeating into the 'low' concentration side of the cell during a given experiment. The conductivity cell was connected to an AGB-1000 conductivity meter (Cambridge Scientific Instruments) which in turn was interfaced with a BBC microcomputer. Appropriate software, written in-house, allowed the automatic acquisition of data at set times during a permeation experiment. The conductivity cell itself was calibrated with a 1 mmol dm^{-3} solution of KCl. Calibration curves for the conversion of conductivities to concentrations were also constructed for each of the transition-metal ions being studied.

On assembly of the unit, deionised water and the salt solution under test were poured simultaneously into the respective chambers of the cell. Stirring, timing and data collection were started immediately.

Coordination studies

To study the coordination between the polymer-appended ligands and transition-metal ions in solution, membrane strips ($4 \times 1 \text{ cm}$) were immersed in the appropriate salt solution in a cuvette using inert PTFE securing devices described elsewhere.¹⁷ The HEMA/vbpy copolymer membranes are optically clear with absorptions appearing below *ca.* 300 nm, while HEMA/ $\text{H}_2\text{dvsalen}$ copolymer membranes show an absorption due to the ligand at *ca.* 340 nm.

Spectra were recorded by placing the immersed membrane strips in the sample beam of a Pye-Unicam SP8-100 double-beam spectrophotometer, while using a membrane strip immersed in distilled water as reference. It should be noted that here, unlike the permeation study, stirring of the solution in which the membrane is immersed can not be undertaken.

For the kinetics experiments, the spectrophotometer was fitted with a thermostatted four-cell carriage. The appropriate wavelength for monitoring complex formation was chosen. The test samples were exposed to the sample beam and the absorbance reading taken at regular intervals, with time zero being the time when the membrane strips were first immersed

in their respective transition-metal salt solutions. The reference was a membrane sample immersed in distilled water.

Permeation of transition-metal ions through membranes

In this section we discuss transport through both $\text{H}_2\text{dvsalen}$ - and vbpy-containing membranes. The latter studies were made to add to our understanding of the behaviour of ligand-containing copolymers.

Transport phenomena involving hydrogel membranes have been extensively investigated within this research group, *e.g.* Hamilton *et al.*⁶ and Lewis and Miller.¹⁶ The same technique was applied here to investigate the passage of cobalt(II), nickel(II), and copper(II) nitrates through prepared membranes both of pure poly(HEMA) and of dvsalen-containing copolymers, to be detected by conductivity measurement at the low concentration side of the apparatus. The results are summarised in Table 1. As expected, they show a time lag while the salts are passing through the membrane, before increasing conductivity begins to be detected at the low concentration side. That is followed by a period in which a constant permeation rate can be measured. We found that, within experimental error, the presence of up to 1% by mass of dvsalen in the copolymer membrane has no detectable effect on either the time lag before salts pass through the membrane, or the permeation rates of the salts, as shown by the arithmetic means and standard deviations of the parameters obtained from linear regression and quoted in Table 1. By contrast, the presence of comparable quantities of bipyridyl ligands in HEMA copolymers has a very dramatic effect with salts of these metal ions.¹⁶ In both cases the presence of ligand groups has no detectable effect on the equilibrium water contents of the copolymers.

The interpretation of our complex formation studies, given later in this paper, casts light on this unexpected finding, as does the qualitative observation that colour within the membranes only developed weakly during the early stages of the transport experiments. Our mechanistic interpretation shows that only ligand sites capable of tetradeinate coordination strongly complex with $\text{Cu}(\text{NO}_3)_2$. Initially less than 3% of the dvsalen, and after 2 h only 12%, is open to tetradeinate coordination. The retention of salts by such a small percentage of the dvsalen sites would be insufficient to lengthen the time lag by detectable amounts.

Our earlier published studies, in which comparable quantities of functionalised 2,2'-bipyridyl ligands were incorporated into hydrogel copolymers, exhibited a different feature.¹⁶ The lag times for the passage of substitutionally labile²⁵ cations through those copolymers were found to be increased at least tenfold in comparison with that for pure poly(HEMA), although the permeation rates were again little altered. The crucial difference in these two cases is that most of the 2,2'-bipyridyl sites in those copolymers are immediately available for rapid 1:1 complex formation, and can even form tris-complexes.

We confirmed these deductions by studying the passage of the substitutionally inert $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ cation, as the nitrate salt, through vbpy-containing copolymer membranes. The results of linear regression fitting are given in Table 2.

As expected, $[\text{Cr}(\text{H}_2\text{O})_6][\text{NO}_3]_3$ passes through fresh membranes with lag times and permeation rates which are essentially unaffected by the presence of ligand sites, and without the retention of detectable levels of chromium. However, if a membrane sample is allowed to stand in an excess of a chromium nitrate solution and equilibrate for nine months, complexation occurs, as indicated by the appearance of a broad visible absorption band at 535 nm in the spectrum of the membrane specimen. Experiments using such precomplexed membranes, from which the imbibed $[\text{Cr}(\text{H}_2\text{O})_6][\text{NO}_3]_3$ -containing water has not been flushed, exhibit no detectable lag time while their permeation rates are

Table 1 Permeability data for the transport of 0.25 mol dm^{-3} transition-metal(II) nitrates through $\text{H}_2\text{dvsalen-HEMA}$ copolymer membranes

| $\text{H}_2\text{dvsalen}$ (% by mass) | membrane thickness/cm | time lag/min | steady-state flow per unit area/ $10^{-9} \text{ mol min}^{-1} \text{ cm}^{-2}$ | steady-state flow rate/ $10^{-7} \text{ mol min}^{-1} \text{ cm}^{-3}$ |
|--|--------------------------|--------------|---|--|
| Co(NO_3) ₂ transport | | | | |
| 0 | 0.036 | 28 ± 5 | 52 ± 1.2 | 14 ± 0.5 |
| 0.1 | 0.035 | 29 ± 7 | 39 ± 1.4 | 11 ± 0.4 |
| 0.25 | 0.037 | 26 ± 9 | 51 ± 2.1 | 14 ± 0.6 |
| 0.5 | 0.038 | 21 ± 4 | 42 ± 1.3 | 11 ± 0.3 |
| 1.0 | 0.036 | 40 ± 16 | 40 ± 2 | 10 ± 0.5 |
| overall | | 29 ± 7 | | 12 ± 2 |
| Cu(NO_3) ₂ transport | | | | |
| 0 | 0.040 | 25 ± 3 | 36 ± 0.7 | 9.9 ± 0.3 |
| 0.1 | 0.035 | 34 ± 3 | 53 ± 1.0 | 13 ± 0.3 |
| 0.25 | 0.037 | 41 ± 3 | 49 ± 1.0 | 13 ± 0.3 |
| 0.5 | 0.038 | 29 ± 4 | 51 ± 1.1 | 13 ± 0.3 |
| 1.0 | 0.036 | 27 ± 8 | 40 ± 0.4 | 10 ± 0.1 |
| overall | | 31 ± 6 | | 12 ± 1.7 |
| Ni(NO_3) ₂ transport | | | | |
| 0 | 0.040 | 25 ± 4 | 34 ± 1.0 | 9.3 ± 0.2 |
| 0.1 | 0.035 | 31 ± 6 | 40 ± 1.1 | 9.7 ± 0.3 |
| 0.25 | 0.037 | 35 ± 7 | 39 ± 1.4 | 9.9 ± 0.3 |
| 0.5 | 0.038 | 38 ± 8 | 40 ± 1.5 | 10 ± 0.4 |
| 1.0 | 0.036 | 10 ± 1 | 28 ± 1.2 | 7.0 ± 0.3 |
| overall | | 28 ± 11 | | 9.2 ± 1.2 |

Table 2 Permeability data for the transport of 0.25 mol dm^{-3} Cr(NO_3)₃ through vbpy-HEMA copolymer membranes

| % vbpy (P_{vbpy}) (by mass) | membrane thickness/cm | time lag/min | steady-state flow per unit area/ $10^{-8} \text{ mol min}^{-1} \text{ cm}^{-2}$ | steady-state flow rate/ $10^{-7} \text{ mol min}^{-1} \text{ cm}^{-3}$ |
|--|--------------------------|----------------|---|--|
| fresh membrane | | | | |
| 0 | 0.033 | 22 ± 3 | 21 ± 0.2 | 47 ± 0.5 |
| 1 | 0.038 | 19 ± 1 | 17 ± 0.1 | 45 ± 0.3 |
| 2 | 0.035 | 25 ± 1 | 17 ± 0.1 | 42 ± 0.3 |
| 4 | 0.033 | 37 ± 1 | 16 ± 0.1 | 35 ± 0.2 |
| linear regression | | | | |
| precomplexed membrane ^a | | | | |
| 0 | 0.033 | -8.0 ± 0.5 | 22 ± 0.5 | 50 ± 1 |
| 1 | 0.038 | -2.3 ± 0.2 | 17 ± 0.2 | 46 ± 0.6 |
| 2 | 0.035 | -1.2 ± 0.4 | 20 ± 0.4 | 48 ± 1 |
| 4 | 0.033 | -4.0 ± 0.3 | 16 ± 0.3 | 37 ± 0.7 |
| linear regression | | | | |
| $\text{time lag} = (18 \pm 3) + (4.2 \pm 1.4)P_{\text{vbpy}}$ | | | | |
| $\text{flow rate} = (48 \pm 0.5) - (3.1 \pm 0.2)P_{\text{vbpy}}$ | | | | |
| $\text{flow rate} = (51 \pm 2) - (3.1 \pm 1)P_{\text{vbpy}}$ | | | | |

^aIt should be noted that the lag times for these experiments can be negative since some nitrate solution may be present on the surface of the membrane at the start of an experiment.

still the same as those found for untreated membranes. Over the timescale of a transport experiment neither coordination of the substitutionally inert $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ cations to, nor dissociation from, the ligand sites occurs to a significant extent. This is in marked contrast to the behaviour when solutions containing the substitutionally labile metal ions pass through specimens of the vbpy-HEMA copolymer. There complexation does occur, is manifested by the lengthened time lag, and can rapidly be detected spectroscopically, as here.¹⁶ In the results of the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ -based experiments we also note that the coordination present in the precomplexed membranes has no detectable effect on the permeation rates of salt through the membrane. Both sets of data show the same slight variation of the steady-state flow rate with copolymer composition.

In summary, at the copolymer composition levels used by us, coordination of metal ions during the passage of their salts through a hydrogel membrane has no effect on the permeation rates for those salts. However, if it occurs, coordination is accompanied by an increase in the time lag before passage of the salt is detected. Except at very low levels of coordination, that increase is detectable and can be used diagnostically.

Kinetic studies of complex formation

Results. When a copolymer membrane sample is immersed in a copper(II) nitrate solution, complex formation occurs

within the membrane, with the development of a dark green colouration. This process is conveniently monitored at 400 nm. Similar spectral changes have been reported^{21,22} for other dvsalen-containing copolymers.

The investigation of the rate of complex formation in heterogeneous systems such as this is complicated by the extra step of initial electrolyte diffusion into the membrane. By trial and error, we reconfirmed our group's earlier finding that the effects of diffusion through copolymer membranes based on poly(HEMA), as evidenced by their impact on the computed rate equation, can be eliminated by neglecting all measurements made during the first few, usually five, minutes after immersion of a membrane into the reagent solution. Using data obtained after that point, for a period of up to 1–2 h, the experimental data can be closely described by a pseudo-first order rate equation in this instance. We applied curve-fitting procedures to all our results, fitting data up to at least 85% attainment of the highest recorded absorption. In calculation we treated both the pseudo-first order rate constant, k_{obs} , and the finally achieved absorbance reading, A_{ach} , as unknowns. The latter constant could not be measured directly as after the main first order dependence had almost reached its conclusion, a subsequent, very slow, slight drop in absorbance occurs. However, over the period of study, typically between 2 and 3 h, the standard of curve fitting was extremely good. Unfortunately

we were unable to obtain enough accurate measurements over a much longer time period to carry out a mathematical analysis of the late, very slow drop in absorbance, other than to note its magnitude as being between 5 and 10% of the value of A_{ach} .

Of necessity, the need to make spectrophotometric observations of the membrane precludes the stirring of the salt solution in which it is immersed. The experimental conditions are therefore not identical to those used in the permeation experiments.

During our studies we first completed systematic sets of 4×4 experiments to investigate the interaction of each of several salt concentrations with membrane specimens made from batches of copolymers each with different ligand loadings. It was apparent that A_{ach} was a linear function of the dvsalen loading of the copolymer, and that both k_{obs} and A_{ach} were varying with $[\text{Cu}^{2+}]$. However, except where CuCl_2 was used, the variability inherent in such heterogeneous experiments was too large to support complete quantitative analyses of the parameter relationships for these small sets of data. Therefore we undertook a much larger set of experiments with $\text{Cu}(\text{NO}_3)_2$ as the electrolyte. Every membrane specimen in this set was

Table 3 Curve-fitted values of k_{obs} and A_{ach} for a first order description of the interaction of a 1%-loaded copolymer membrane with $\text{Cu}(\text{NO}_3)_2$. The final column shows the fraction of A_{ach} determined by extrapolation of the fitted curve back to $t=0$

| $[\text{Cu}^{2+}] / \text{mol dm}^{-3}$ | $k_{\text{obs}} / \text{min}^{-1}$ | A_{ach} | A_0/A_{ach} |
|---|------------------------------------|------------------|----------------------|
| 0.500 | 0.116 | 0.997 | 0.23 |
| 0.475 | 0.115 | 0.863 | 0.13 |
| 0.450 | 0.126 | 1.02 | 0.15 |
| 0.425 | 0.0924 | 1.43 | 0.30 |
| 0.400 | 0.135 | 1.08 | 0.13 |
| 0.375 | 0.0923 | 1.19 | 0.23 |
| 0.350 | 0.0864 | 1.12 | 0.18 |
| 0.325 | 0.0975 | 1.18 | 0.29 |
| 0.300 | 0.0802 | 1.15 | 0.13 |
| 0.275 | 0.0637 | 1.07 | 0.21 |
| 0.250 | 0.0610 | 1.11 | 0.18 |
| 0.250 | 0.0706 | 1.04 | 0.19 |
| 0.225 | 0.0646 | 1.17 | 0.17 |
| 0.200 | 0.0959 | 0.897 | 0.15 |
| 0.175 | 0.0627 | 0.848 | 0.14 |
| 0.150 | 0.0605 | 0.948 | 0.17 |
| 0.125 | 0.0489 | 0.937 | 0.21 |
| 0.100 | 0.0418 | 0.733 | 0.18 |
| 0.100 | 0.0518 | 0.892 | 0.15 |
| 0.075 | 0.0391 | 0.752 | 0.19 |
| 0.050 | 0.0420 | 0.666 | 0.18 |
| 0.025 | 0.0253 | 0.485 | 0.14 |
| 0.025 | 0.0332 | 0.540 | 0.15 |

taken from the same prepared sheet of copolymer, one containing 1% by dry mass of dvsalen. The results are collected together in Table 3, in which we list the values of k_{obs} and A_{ach} computed by allowing each to vary independently to give the best fit to the experimental data obtained once diffusional effects had become negligible. Table 4 contains the results of the smaller sets of experiments for the chloride and sulfate salts. As has been demonstrated elsewhere,^{15,16} we also found here that the diffusion of the sulfate into copolymeric HEMA hydrogels is slower than that for the chloride or nitrate salt, and so the delay before first order kinetics are followed is longer.

It should be noted that, although in homogeneous solutions such investigations are normally carried out at a constant ionic strength, we did not adopt that strategy here. We were unable to identify an inert electrolyte whose cation would not interact with the strongly complexing coordination sites or affect the pH of the reaction solutions, while still exhibiting similar permeation properties to Cu^{2+} . Our interpretations should therefore be judged against that fact.

An inspection of these results confirms that both k_{obs} and the achieved absorbance vary with the concentration of Cu^{2+} . There is a non-zero intercept at $[\text{Cu}^{2+}] = 0$ for the rate constant, while a plot of absorbance against $[\text{Cu}^{2+}]$ is curved. The simplest relationships between $[\text{Cu}^{2+}]$ and these computed constants that show good agreement between observed and calculated values of k_{obs} and A_{ach} are summarised in eqn. (1) and (2).

$$k_{\text{obs}} = \{\alpha + \beta[\text{Cu}^{2+}]\} \text{ min}^{-1} \quad (1)$$

$$A_{\text{ach}} = \gamma \delta P_{\text{dvs}} [\text{Cu}^{2+}] / \{1 + \delta[\text{Cu}^{2+}]\} \quad (2)$$

In these equations α , β , γ and δ represent constants whose values for the various copper salts are collected together in Table 5. These constants are empirical, being obtained from the curve fitting of our experimental data. Our sets of 4×4 experiments for the interaction of copper salts with the hydrogel membranes show that the achieved absorbances varied linearly with the percentage of the dvsalen monomer (see for example Table 4), and therefore we incorporate that percentage, P_{dvs} , into eqn. (2). That is, for the data of Table 3, $P_{\text{dvs}} = 1$. Its use is necessary when values of rate and equilibrium constants are obtained from the data of Table 4.

Discussion

The forms of eqn. (1) and (2) suggest that the attainment of an equilibrium is being observed. However, it must be more

Table 4 Curve-fitted values of k_{obs} and A_{ach} for a first order description of the interaction of copolymer membranes with $\text{Cu}(\text{NO}_3)_2$, CuCl_2 and $\text{Cu}(\text{SO}_4)_2$

| $[\text{Cu}^{2+}] / \text{mol dm}^{-3}$ | L loading/ % by mass | $\text{Cu}(\text{NO}_3)_2$ | | CuCl_2 | | $\text{Cu}(\text{SO}_4)_2$ | |
|---|-------------------------|------------------------------------|------------------|------------------------------------|------------------|------------------------------------|------------------|
| | | $k_{\text{obs}} / \text{min}^{-1}$ | A_{ach} | $k_{\text{obs}} / \text{min}^{-1}$ | A_{ach} | $k_{\text{obs}} / \text{min}^{-1}$ | A_{ach} |
| 0.25 | 1.0 | 0.071 | 1.04 | 0.047 | 0.94 | 0.0079 | 0.70 |
| 0.10 | 1.0 | 0.052 | 0.89 | 0.036 | 0.71 | 0.0091 | 0.62 |
| 0.05 | 1.0 | 0.042 | 0.67 | 0.027 | 0.61 | 0.0088 | 0.44 |
| 0.025 | 1.0 | 0.033 | 0.54 | 0.019 | 0.38 | 0.0074 | 0.40 |
| 0.25 | 0.50 | 0.12 | 0.58 | 0.044 | 0.47 | 0.011 | 0.25 |
| 0.10 | 0.50 | 0.060 | 0.59 | 0.032 | 0.50 | 0.013 | 0.33 |
| 0.05 | 0.50 | 0.049 | 0.54 | 0.031 | 0.33 | 0.011 | 0.24 |
| 0.025 | 0.50 | 0.035 | 0.44 | 0.027 | 0.22 | 0.010 | 0.27 |
| 0.25 | 0.25 | 0.11 | 0.31 | 0.046 | 0.16 | 0.0070 | 0.19 |
| 0.10 | 0.25 | 0.063 | 0.34 | 0.036 | 0.16 | 0.010 | 0.20 |
| 0.05 | 0.25 | 0.074 | 0.28 | 0.026 | 0.18 | 0.010 | 0.18 |
| 0.025 | 0.25 | 0.044 | 0.24 | 0.013 | 0.18 | | |
| 0.25 | 0.10 | 0.10 | 0.16 | 0.092 | 0.08 | | |
| 0.10 | 0.10 | 0.063 | 0.17 | 0.031 | 0.07 | | |
| 0.05 | 0.10 | 0.064 | 0.16 | 0.029 | 0.08 | | |
| 0.025 | 0.10 | 0.050 | 0.14 | 0.025 | 0.09 | | |

Table 5 Values of the constants obtained by fitting the individual rate profiles for the various copper salts to eqn. (1) and (2)

| eqn. | constant ^a | NO ₃ ⁻ | Cl ⁻ | SO ₄ ²⁻ |
|------|---|------------------------------|-------------------|-------------------------------|
| (1) | α/min^{-1} | 0.025 ± 0.004 | 0.019 ± 0.005 | 0.010 ± 0.001 |
| (1) | $\beta/\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ | 0.20 ± 0.015 | 0.16 ± 0.03 | 0 ± 0.0071 |
| (2) | γ | 1.22 ± 0.05 | 1.06 ± 0.07 | 0.71 ± 0.06 |
| (2) | $\delta/\text{dm}^3 \text{ mol}^{-1}$ | 24 ± 6 | 26 ± 6 | 56 ± 22 |

^aSee text.

complicated than a single step equilibrium (3)



since such a process requires the function $k_{\text{obs}} A_{\text{ach}} / [\text{Cu}^{2+}]$ to be constant. That is not found here.

Salen can be regarded as two planar substituted phenols bearing conjugated imine groups, which are linked together by a flexible dimethylene bridge. Here we indicate that as $-\text{LH}-\text{LH}-$. Although salen normally forms tetradentate complexes in which both phenolic protons are lost and only one cation coordinates, complexes are known in which salen behaves as a bis-bidentate ligand.²⁰ However, there are no known mono- or ter-dentate complexes which, given the impact of the chelate effect,²⁶ is not surprising. Therefore only bi- and tetra-dentate interactions need be considered in a mechanistic scheme here.

Within our copolymeric structure each potentially bidentate half of the salen function might be open or closed towards complexation by Cu²⁺, as indicated in our subscripts. Thus we envisage $-\text{LH}_{\text{closed}}-\text{LH}_{\text{closed}}-$, $-\text{LH}_{\text{closed}}-\text{LH}_{\text{open}}-$ and $-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}-$ as the possible alternative salen configurations. In a hydrogel their slow interconversion through rotation can occur.

Therefore all the individual steps which could be involved in the overall scheme can be written as steps (4)–(10), Scheme 1. Some simplifying notation is needed. Therefore we show the attachment of H⁺ or Cu²⁺ to a ligand site by writing it immediately adjacent to a ligand symbol. Also each equilibrium constant, K_2 , K_4 , K_5 , and K_6 , is the ratio of the appropriate stability constants for the protonation of and for the complex formation with the phenolate at the pH prevailing in the imbibed water.

Because the experimental observations of eqn. (1) and (2) are simple, the majority of the steps in this scheme must play little part in determining the reaction profile over the period of our observations. We have found only one set of simplifying

assumptions that fit the observations. They are summarised in the 'comments' column of the proposed scheme. The main points of our arguments are as follows.

It is well known that in homogeneous reactions in aqueous solutions, the substitution reactions of Cu²⁺ complexes are extremely rapid, often very close to the diffusion controlled limit for such reactions.²⁵ Therefore here, once diffusion has produced an essentially constant salt concentration within the imbibed water of the hydrogel membrane, all complex formation steps in any overall reaction can be assumed to be maintained in dynamic equilibrium.

As complex formation will be extremely rapid, the rate determining steps in our system must be those which involve large-scale molecular movement within the copolymer itself; *i.e.* some or all of steps (4)–(6). The equivalent point has been demonstrated earlier for other complexing hydrogels. In one study it was even possible to assign activation parameters to segmental rotation.¹⁷

The dark green parent tetradentate complex, [Cu(salen)], absorbs visible radiation at 400 nm. From published spectra¹⁸ its absorption coefficient is estimated to be *ca.* $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. A similar value should hold for the tetradentate complexes formed within our membranes, which also absorb at 400 nm. Therefore, if all ligand sites in a 0.4 mm, 1% loaded membrane were to yield tetradentate complexes, the final absorbance at this wavelength would be *ca.* 10. That is eight times greater than A_{max} , the value of the observed A_{ach} extrapolated to high [Cu(NO₃)₂]. That absorbance value is reached *via* a first order process over a period of one or two hours, too short a period for the occurrence of two consecutive slow rotations to be significant. Therefore step (4) must be essentially stationary on this timescale, with the bulk of the unused sites remaining in the $-\text{LH}_{\text{closed}}-\text{LH}_{\text{closed}}-$ form. Hence, $K_0 \geq A_{\text{max}} / (10 - A_{\text{max}})$. If $K_0 = 0$ then this relationship becomes an equality.

Although we can not measure the equivalent of $A_{t=0}$ for rapidly mixed homogeneous reactions, the absorbance initially observed, we can make an approximation to it, A_0 , the value of the absorbance extrapolated back to the time of immersion of the copolymer membrane into the reactant solution. Because diffusion is not rapid in our experiments, A_0 will be less than $A_{t=0}$ would have been. Fortunately its values, tabulated in Table 3, are a relatively constant fraction of A_{ach} . Using the average value of that fraction, a limit for K_1 can be calculated [eqn. (11)],

$$K_1 \geq A_0 / (A_{\text{max}} - A_0) \quad (11)$$

| step | | comment |
|---|------|---|
| $-\text{LH}_{\text{closed}}-\text{LH}_{\text{closed}} \xrightleftharpoons[k_{-0}]{k_0} -\text{LH}_{\text{closed}}-\text{LH}_{\text{open}}-$ | (4) | K_0 affects start of reaction only essentially stationary |
| $-\text{LH}_{\text{closed}}-\text{LH}_{\text{open}} \xrightleftharpoons[k_{-1}]{k_1} -\text{LH}_{\text{open}}-\text{LH}_{\text{open}}-$ | (5) | K_1 affects start of reaction k_{-1} not detected |
| $-\text{LH}_{\text{closed}}-\text{LH}_{\text{open}}- + \text{Cu}^{2+} \xrightleftharpoons{K_2} [-\text{LH}_{\text{closed}}-\text{LH}_{\text{open}}\text{Cu}-]^+ + \text{H}^+$ | (6) | mainly as free ligand |
| $[-\text{LH}_{\text{closed}}-\text{LH}_{\text{open}}\text{Cu}-]^+ \xrightleftharpoons[k_{-3}]{k_3} [-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}\text{Cu}-]^+$ | (7) | major rate determining step |
| $-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}- + \text{Cu}^{2+} \xrightleftharpoons{K_4} [-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}\text{Cu}-]^+ + \text{H}^+$ | (8) | both at low concentrations |
| $[-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}\text{Cu}-]^+ \xrightleftharpoons{K_5} [-(\text{L}_{\text{open}}-\text{L}_{\text{open}})\text{Cu}-]^+ + \text{H}^+$ | (9) | mainly in tetradentate form |
| $[-\text{LH}_{\text{open}}-\text{LH}_{\text{open}}\text{Cu}-]^+ + \text{Cu}^{2+} \xrightleftharpoons{K_6} [-\text{CuL}_{\text{open}}-\text{L}_{\text{open}}\text{Cu}-]^{2+} + \text{H}^+$ | (10) | not detected |

Scheme 1 Proposed mechanistic scheme

Table 6 Limiting values for the equilibrium constants found here, and calculated comparison values using published data²⁸ for Cu^{2+} -salicylamide complexes

| constant | this work | lit. comparison ²⁸ |
|------------------------------|----------------------------|-------------------------------|
| pH of imbibed water | | 5 |
| K_2 | $\leq 10^{-5}$ | $< 10^{-3.4}$ |
| K_4 | $\leq 10^{-5}$ | $< 10^{-3.4}$ |
| $K_4 K_5/\text{mol dm}^{-3}$ | $\geq 10^{-10}$ | $< 10^{-4.5+1.7}$ |
| K_6 | $\ll K_5/[\text{Cu}^{2+}]$ | $< 10^{-3.4}$ |

Table 7 Values of rate and equilibrium constants obtained by fitting the composite constants of eqn. (1) and (2) to the mechanistic scheme of steps (4)–(10)

| constant | NO_3^- | Cl^- | SO_4^{2-} |
|---|-------------------|-------------------|-----------------------------------|
| K_0 | ≥ 0.11 | ≥ 0.12 | ≥ 0.08 |
| K_1 | ≥ 0.25 | ≥ 0.22 | ≥ 0.27 |
| k_1/min^{-1} | 0.016 ± 0.006 | 0.013 ± 0.006 | 0.010 ± 0.01 |
| $K_2 K_3 K_5/\text{dm}^3 \text{ mol}^{-1}$ | 24 ± 6 | 26 ± 6 | 56 ± 22 |
| $(k_{-3}/K_5)/\text{min}^{-1}$ | 0.008 ± 0.004 | 0.006 ± 0.003 | $> 9 \times 10^{-5}$ ^a |
| $K_2 k_3/\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ | 0.20 ± 0.015 | 0.16 ± 0.07 | 0.0036 ± 0.0036 ^a |

^aSee text.

and is quoted in Table 7. The more rapid is diffusion into the membrane, the closer this relationship will be to an equality.

The mathematical forms of eqn. (1) and (2) are surprisingly simple and can be reached from our proposed set of steps only if k_{-1} , K_2 and K_6 are unimportant in controlling the rate of reaction. Note also that one equilibrium constant is superfluous since $K_1 K_4 = K_2 K_3$. Neither the pH of the imbibed water in our hydrogel nor the pK_a of its phenolic groups is known, but by comparison to salicylamide we assume that the pK_a will be *ca.* 9. Salicylamide rather than phenol is chosen as that same molecule also provides comparison stability constants used later in the argument. Given a pK_a of 9, the uncoordinated ligand sites in a 1% copolymeric hydrogel will maintain the pH in the imbibed water at *ca.* 5. The evaluated limits on the equilibrium constants calculated from that pH are quoted in Table 6.

Under conditions such that the concentration of Cu^{2+} in the imbibed water remains essentially constant and step (4) is too slow to be detected, we can equate eqn. (1) and (2) to eqn. (12) and (13).

$$k_{\text{obs}} = k_1 + (k_{-3}/K_5) + K_2 k_3 [\text{Cu}^{2+}] \quad (12)$$

$$A_{\text{ach}} = K_2 K_3 K_5 [\text{Cu}^{2+}] A_{\text{max}} / \{1 + K_2 K_3 K_5 [\text{Cu}^{2+}]\} \quad (13)$$

Numerical values can then be assigned to some of the constants of Scheme 1. They are also quoted in Table 7.

Where stability constants for homogeneous systems have been compared with those prevailing in polymer-heterogeneous systems, it has been found that coordination to the polymeric ligands involves somewhat smaller values of the stability constants than does coordination to the analogous ligands in homogeneous solution.^{15,27} Therefore, we can use such comparisons to set upper limits for the range of expected values for our system. The arguments for these limits are set out below and their values are given in Table 6.

There is no available data for stability constants involving $\text{H}_2\text{dvsalen}$ or H_2salen , but the closely related bidentate ligand salicylamide has been studied. The equilibrium constants for the formation of mono- and bis-complexes of Cu^{2+} , equivalent to K_4 and $K_4 K_5$, are known.²⁸ Here, comparisons applied to K_4 can also be applied to K_2 and K_6 . For a strict comparison

of the bis-salicylamido datum with that for the tetradeinate dvsalen complex, an entropy term must be added.²⁶ That is indicated in Table 6 by showing the multiplication of the literature equilibrium constant of $10^{-4.5}$ by $10^{1.7}$. A comparison of the tabulated values of Table 6 is extremely encouraging. In our view it strongly supports our mechanistic interpretation.

We now turn to the data of Table 7. One presentational feature should first be noted, for the data involving CuSO_4 . The estimated mean value of β for this salt is much smaller than its estimated deviation; but since $\beta = K_2 k_3$, it can not be negative. Therefore its value is presented differently in Tables 3 and 5, to show that only a limit for k_{-3}/K_5 , which equals δ/β , is available.

One very interesting observation can be made on the data of Table 7. Only in the cases of k_3 and k_{-3} are there marked differences in the values of the constants measurable for the different salts. There the rate constants for sulfate are distinctly slower. Anions will be closely associated with cationic complexes within a membrane, and therefore they must affect the rates at which nearby segmentation rotation can occur. Therefore a change from a structure-making to a structure-breaking anion⁶ should have a significant impact on this step, but not on the others.

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References

- 1 *Syntheses and Separations using Functional Polymers*, ed. D. C. Sherrington and P. Hodge, J. Wiley and Sons, London, 1988.
- 2 See ch. 3, 10 and 11 of ref. 1.
- 3 A. J. Frank and K. Honda, *J. Photochem.*, 1985, **29**, 195.
- 4 R. W. Murray, *Electroanal. Chem.*, 1984, **13**, 191.
- 5 *Macromolecular Complexes: Dynamic Interactions and Electronic Processes*, ed. E. Tsuchida, VCH, New York, 1991.
- 6 C. J. Hamilton, S. M. Murphy, N. D. Anderton and B. J. Tighe, *Polymer*, 1988, **29**, 1988.
- 7 B. A. Gregg and A. Heller, *J. Phys. Chem.*, 1991, **95**, 5976.
- 8 W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 959.
- 9 H. Irving and D. H. Mellor, *J. Chem. Soc.*, 1962, 5222.
- 10 L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.*, 1967, **2**, 173.
- 11 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
- 12 A. L. Lewis and J. D. Miller, *J. Chem. Soc., Chem. Commun.*, 1992, 1029.
- 13 A. L. Lewis and J. D. Miller, *J. Mater. Chem.*, 1993, **3**, 897.
- 14 A. L. Lewis and J. D. Miller, *Polymer*, 1993, **34**, 2453.
- 15 A. L. Lewis and J. D. Miller, *J. Mater. Chem.*, 1994, **4**, 729.
- 16 A. L. Lewis and J. D. Miller, *Polymer*, 1995, **36**, 331.
- 17 R. J. Chaggard, A. J. Hall and J. D. Miller, *Polymer*, 1996, **37**, 5313.
- 18 J. Csaszar, *Acta Phys. Chem.*, 1984, **30**, 61.
- 19 D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
- 20 P. Pfeiffer, *Angew. Chem.*, 1940, **53**, 93.
- 21 A. Akelah, M. M. Abbasi and M. K. H. Awad, *Ind. J. Chem., Sect. A*, 1986, **25**, 923.
- 22 D. Wohrle, H. Bohlen and G. Meyer, *Polymer Bull.*, 1984, **11**, 143; 150.
- 23 H. D. Abruna, A. I. Breikss and D. B. Collum, *Inorg. Chem.*, 1985, **24**, 987.
- 24 G. Wulff and A. Akelah, *Makromol. Chem.*, 1978, **179**, 2647.
- 25 R. G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VCH, Cambridge, 2nd edn., 1991.
- 26 G. Beech, *Quart. Rev. Chem. Soc.*, 1969, **23**, 410.
- 27 J. D. Miller and D. S. Morton, *J. Chem. Soc., Dalton Trans.*, 1983, 1511.
- 28 L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, The Royal Society of Chemistry, London, 1964.