

## Iron(II) coordination to bipyridyl-based hydrogel polymers

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Hydrophilic membranes composed of copolymers of 0.3% by weight 4-methyl-4'-vinyl-2,2'-bipyridyl with 2-hydroxyethyl methacrylate were prepared, and the coordination of iron(II) from aqueous solutions of the sulfate, perchlorate and chloride salts to form the tris(2,2'-bipyridyl)iron(II) species was studied at a range of temperatures in order to extend earlier findings. In the case of the chloride the rate equation was found to differ from that previously reported. Values for the enthalpy and entropy changes for an equilibrium involving the obstruction of potential ligand sites by existing coordination centres, and the activation enthalpies and entropies for the slow steps during complex formation, are determined. They are interpreted as showing that the slow steps in all cases involve segmental rotation within the copolymer chains to permit further coordination to occur. Copyright © 1996 Elsevier Science Ltd.

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### Introduction

There is widespread interest in syntheses and separations using functional polymers; see for example ref. 1. Advantage is often taken of the interactions which occur between metal ions and these functionalized polymers. This can range from the use of polymer-supported complex catalysts through separation and hydrometallurgy<sup>2</sup>, and polymer-modified electrodes<sup>3</sup>, to the investigation of purely physical processes<sup>4</sup>. Closely related studies of the transport of metal ions through hydrogel membranes have been reported by other workers<sup>5</sup>. Here we focus on some aspects of the coordination process itself.

2,2'-Bipyridyl (bipy) is a very well known and extensively investigated ligand<sup>6-9</sup>. Studies of the incorporation of the bipy group into hydrogels, and of the use of these copolymers for coordination, have already been reported<sup>10-14</sup>. In that work the copolymer was formed into a membrane of thickness 0.4 mm, a convenient physical form for investigation. The work described here was undertaken as a simple experimental extension of the earlier studies. This investigation concerns the effect of temperature on the variation of the rate of formation of the *tris*-bipyiron(II) colour centre within a membrane. An improved method for sample handling was achieved by mounting membrane samples in two small notched polytetrafluoroethylene blocks, one of which served as a weight to hold down the bottom of the membrane in a spectrophotometric cuvette containing the appropriate salt solution, while the other block served both as a holder for the top of the membrane and as a lid for the cuvette. This arrangement enabled us to keep the flexible membrane upright while it remained immersed in a reactant solution within a spectrophotometer, a marked improvement on the earlier technique in which

membrane samples were manually transferred from the immersion in a reagent solution to the spectrophotometer. In all other respects, the experimental procedures were the same as those previously reported<sup>13</sup>.

Membrane samples at a previously unstudied copolymer ratio, 0.3% by weight of the bipy-based monomer, but still containing 1% by weight of ethylene glycol dimethacrylate as cross-linker, were prepared and both the kinetics of their interaction with Fe<sup>2+</sup> ions in aqueous solution and the final degree of *tris*-complex formation were studied as functions of temperature.

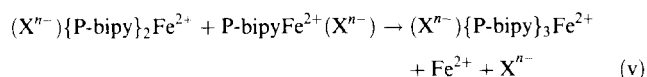
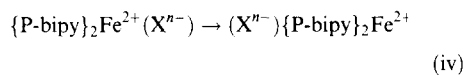
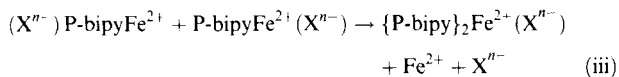
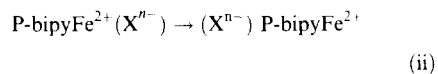
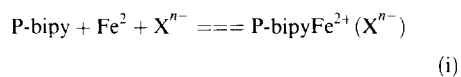
In an earlier paper from our research group<sup>13</sup> we reported that, when solutions of iron(II) sulfate at 25°C are allowed to diffuse into hydrogel copolymers formed from mixtures of monomers containing 0.5% of 4-methyl-4'-vinyl-2,2'-bipyridyl, the *tris*-colour centre is formed in a process that for more than two half-lives is first order with respect to the unreacted ligand concentration, but independent of the Fe<sup>2+</sup> concentration. The final visible absorbance due to the *tris*-complex, equivalent to the eventual utilization of (66 ± 5)% of the ligands present, was also found to be independent of [Fe<sup>2+</sup>].

In the cases of the perchlorate and chloride salts the rate equation was different, being second order in ligand but again zero order in [Fe<sup>2+</sup>]. For these counterions, the degree of formation of *tris*-complex that was finally achieved varied with [Fe<sup>2+</sup>]. A mechanism for complex formation, applicable to all three cases, was proposed. It can be described in the following way, using X<sup>n-</sup> to represent the anion.

As an iron(II) salt diffuses through the membrane it reacts with ligand sites one at a time. Since these complexed sites are close to the polymer chains we assume that the anions remain close by, forming ion-pairs, which will confer some anion dependence on the overall process. Under our experimental conditions the formation of the *mono*-complex is a rapidly

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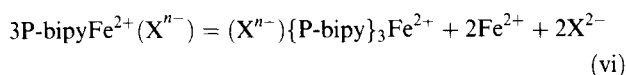
maintained equilibrium which favours essentially complete formation of the complex. Some structural reorganization is required after each coordination event before the attachment of the next ligand group to the cation becomes possible. Thus the mechanism can be written as



We use P-bipy to represent a coordination site within the copolymer, while the nearby ( $\text{X}^{n-}$ ) is written to the left to indicate an arrangement for which further coordination can occur, and to the right when further coordination is not yet possible.

As the data obtained using  $\text{FeSO}_4$  exhibit a rate equation which is first order in [ligand] and zero order in  $[\text{Fe}^{2+}]$ , step (i) must be displaced far to the right and step (ii) must be the slow step. For a reaction to be second order in [ligand] and zero order in  $[\text{Fe}^{2+}]$ , step (iv), the rearrangement of the *bis*- complex is deduced to be rate determining.

By analogy with the known solution chemistry of the parent bipyridyl ligand, the concentration of the *bis*- complex can be assumed to be negligibly small. Thus only coordination equilibrium (vi) need be considered to explain the observed variation with  $[\text{Fe}^{2+}]$  of the amount of *tris*- complex formed upon completion:



For each of the salts used, even after equilibrium (vi) is taken into account, the maximum achievable yield of *tris*- complex was found to be less than 100%. The values were 83, 57 and 66% for the chloride, perchlorate and sulfate respectively. Thus a further factor must intrude, affecting the availability of some ligand sites for coordination. That was not further discussed at the time as its impact could not be determined from data obtained at only one temperature, but it is relevant to the present paper. Here we report results that are explicable in terms of an equilibrium involving each coordinated

**Table 1** Experimental data obtained for the interaction of solutions of  $\text{Fe}(\text{SO}_4)$  with the 0.3%-ligand-loaded copolymer at various temperatures and the calculated fits to them (see text)

Temperature (K)	$10^3 k$ ( $\text{min}^{-1}$ )		$p^a$	
	observed	calculated <sup>b</sup>	observed	calculated <sup>b</sup>
298	17	16	55	55
308	20	24	60	60
318	38	34	65	66
328	48	48	73	73
338	87	65	81	81

<sup>a</sup>  $p$  is the percentage utilization of bipyridyl sites in *tris*- complexes, see (vii)

<sup>b</sup> Calculated values use the appropriate activation parameters of Table 3

**Table 2** Experimental data obtained for the interaction of solutions of  $\text{Fe}(\text{ClO}_4)_2$  and  $\text{FeCl}_2$  with the 0.3%-ligand-loaded copolymer at various temperatures and the calculated fits to them (see text)

Temp. (K)	$\text{Fe}(\text{ClO}_4)_2$			$\text{FeCl}_2$		
	$p_{\text{obs}}^a$	$10^2 k$ ( $\text{min}^{-1}$ )		$p_{\text{obs}}^a$	$10^3 k$ ( $\text{min}^{-1}$ )	
		obs.	calc. <sup>b</sup>		obs.	calc. <sup>b</sup>
298	16	60	51	27	66	55
308	24	94	82	37	71	80
318	25	150	130	42	110	110
328	26	210	200	48	150	160
338	30	320	290	53	250	220

<sup>a</sup>  $p$  is the percentage utilization of bipyridyl sites in *tris*- complexes

<sup>b</sup> Calculated values using the appropriate activation parameters of Table 3

ligand of a *tris*- complex in an independent interaction with, on average, one, but only one, adjacent ligand site. See equilibrium (vii) below.

### Results

In the studies reported here, a 0.3% ligand loading in the copolymer and 0.25 M salt concentrations in the interacting solution were used throughout. Except for the change in membrane mounting mentioned above, which enabled us to record continuously the absorbance of the membrane at 534 nm while it remained immersed in the ferrous salt solution, all preparations and experimental techniques used have been described previously<sup>13</sup>. We again found that the kinetic data for interaction with  $\text{FeSO}_4$  are well described by a first-order rate law over more than two half-lives. The rate constant varies with temperature, and at 25°C is comparable to that reported for the 0.5% hydrogel. The quantity of *tris*- complex formed upon completion of the reaction also varies with temperature. The data are collected together in Table 1.

**Table 3** Calculated values for entropy and enthalpy changes

Anion	Process	$K_{\text{closure}}$ (25°C)	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )
$\text{SO}_4^{2-}$	vii	0.22	$-55 \pm 2$	$-173 \pm 5$
Anion	Process	$k$ (25°C)	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )
$\text{SO}_4^{2-}$	ii	$0.017 \text{ min}^{-1}$	$32 \pm 4$	$-207 \pm 13$
Cl	ii	$0.066 \text{ min}^{-1}$	$26 \pm 4$	$-217 \pm 13$
$\text{ClO}_4^-$	iv	$0.60 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$	$34 \pm 3$	$-230 \pm 10$

In Table 2 we have collected the data for the reactions with  $\text{Fe}(\text{ClO}_4)_2$  and  $\text{FeCl}_2$ , discussed below. The only point that need be made here is that the rate equation which best describes the reaction profile for the chloride is definitely first order, while that found previously was second order. For the perchlorate here, as before, we found that second-order kinetics are obeyed. In every case, curve fitting for the results collected was undertaken to at least 80% completion, using the commercially available SigmaPlot software.

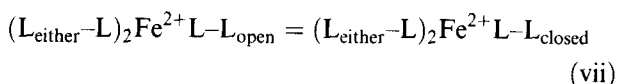
In order to apply transition state theory, the rate constants of the second-order process for the perchlorate salt must be computed relative to the fractional conversion of reagent, so that values of  $k$  with the required dimensions of  $\text{kT h}^{-1}$  (i.e.  $t^{-1}$ ) are obtained. They are presented in Table 2 in that format rather than in the usual second-order form.

All computed activation parameters are collected together in the summary table, Table 3. For comparison purposes, data fits computed from them are shown in Tables 1 and 2 alongside the experimental values.

We have made no attempt to isolate products containing the perchlorate ion; anyone attempting to do so should be aware of the safety problems associated with perchlorates.

### Discussion

Firstly we discuss the data obtained when sulfate is the anion. Lewis and Miller<sup>13</sup> showed that, since the final degree of formation of the *tris*- complex is  $[\text{FeSO}_4]$ -independent, the  $[\text{Fe}(\text{bipy})_3]^{2+}$  species is the only complex occurring to any significant extent when the reaction is complete. For the 0.5%-loaded copolymer at 25°C, 66% of the ligand sites were involved in *tris*-complex centres, and so essentially all the remaining ligand sites must be unavailable for complexation. Some form of site shielding must occur. Here we found that the degree of site availability changes with temperature. We found, by testing a range of different curve fitting procedures, that the observed variation with temperature can best be explained by equilibrium (vii). In this equation, a potential ligand site is shown as L. The subscript 'closed', 'either' or 'open' shows the site's status for coordination with metal ions. When coordination to a site L has already taken place, indicated by writing its symbol adjacent to  $\text{Fe}^{2+}$ , on average one other nearby site can be affected. That interaction is independent of all other sites. We can represent this as



If the equilibrium constant for (vii) is labelled  $K_{\text{closure}}$ , then  $p$ , the percentage of all the bipyridyl sites actually involved in *tris*- complex formation, is given by

$$p = 100(1 + K_{\text{closure}})/(1 + 2K_{\text{closure}}) \quad (\text{viii})$$

We fitted this equation to all the sulfate data to yield the values of  $K_{\text{closure}}$  (25°C),  $\Delta H_{\text{closure}}$  and  $\Delta S_{\text{closure}}$  listed in the summary table, Table 3. The very good agreement between the experimentally observed values of  $p$  and those calculated from these constants is shown in Table 1.

In the earlier study of the perchlorate and chloride salts, Lewis and Miller<sup>13</sup> found that the final degree of

*tris*- complex formation varied with  $[\text{Fe}^{2+}]$ . That is, for these ions equilibrium (vi) cannot lie far over to the right, as the concentration of the *mono*-  $\text{P-bipy Fe}^{2+}(\text{X}^{n-})$  complex must be significant. Spectroscopic evidence of its presence was also cited in that paper. The position of equilibrium (vi) will be similar in our studies of the temperature variation studies of these salts. Therefore both  $K_{\text{closure}}$  and the equilibrium constant of reaction (vi),  $K_{\text{vi}}$ , will affect the observed values of  $p$  quoted in Table 2. Neither the quality nor the quantity of these data is sufficient to permit two independent exponential terms to be separated with any accuracy. Only if the questionable assumption is made that  $K_{\text{closure}}$  is the same for all anions, can we estimate  $K_{\text{vi}}$  for  $\text{ClO}_4^-$  or  $\text{Cl}^-$ . As an exercise we have carried out that estimation. The outcome compares well with the value of  $10^{4.6}$  computed from tabulated data<sup>9</sup> for the parent 2,2'-bipyridyl ligand reacting with  $\text{Fe}^{2+}$  in aqueous solution. We have made no attempt to estimate  $\Delta H$  or  $\Delta S$  for reaction (vi).

The analysis of the rate data is of considerable interest. Firstly there is the form of the rate equations themselves. We agreed with the earlier findings, made with batches of copolymer with a different ligand loading, that the rate of formation of the *tris*- colour centre is first order in ligand when  $\text{FeSO}_4$  is used as the metal-containing reactant, but second order when  $\text{Fe}(\text{ClO}_4)_2$  is used. However, we found a change for the order of reaction when using  $\text{FeCl}_2$ . For our data with this salt, a second-order rate equation definitely does not fit; they describe a first-order process. For all the temperatures studied by us in this work, the rate data are well fitted by this mathematical form to more than 80% completion, and do not conform to the second-order alternative. In terms of the proposed mechanism, step (ii) must be the slow step for the sulfate and here also for the chloride, while the closely analogous stem (iv) is rate determining for the perchlorate. Clearly, little change is needed to alter the relative rates of these steps, and so either step might be rate determining for a particular set of experimental conditions. Such a changeover must occur for interactions of chloride with the different batches copolymers, but we cannot identify the crucial factor.

In Table 3 we tabulate the activation parameters for reaction with all three salts, and for the equilibrium governing the availability of ligand for their final conversion to the  $\text{Fe}(\text{p-bipy})_3\text{SO}_4$  form. They provide further strong evidence of the mechanism operating during complex formation. Both the enthalpies and entropies of activation change little from one salt to another, even when the order of the reaction changes. Therefore, while the identity of the particular rate-determining step is anion-dependent, their common characteristics are anion-independent. For the first-order reactions the rate equation must be step (ii), a rearrangement of the environment of the *mono*- complex. The slow step for the second-order reaction with  $\text{Fe}(\text{ClO}_4)_2$  must be the analogous rearrangement for the *bis*- complex. The equivalence of their parameters leads us to believe that we have measured the activation parameters for segmental rotation within the copolymer chains. We have not found suitable data in the literature from which we can draw comparisons. However, we note that the molar entropy of water is  $70 \text{ J K}^{-1} \text{ mol}^{-1}$  at

25°C. Motion of a copolymer chain in a swollen hydrogel could not occur without accompanying effects on nearby water molecules. Therefore, as water molecules must be moved during rotation, large values for activation entropies are readily acceptable.

Although there is not direct, logical connection between the equilibrium and rate data of *Table 3*, we note the similarity in magnitudes of the determined constants. If our deduction that the rate data refer to steps in which ligands are made available for coordination, then effectively they are equivalent to the back reaction of equilibrium (vi).

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