Analysis of the Effects of Solvent on the Initial and Transition States in the Kinetics of Reaction between Tris(1,10-phenanthroline)iron(II) cation and Hydroxide Ions in Methanol– and Acetone–Water Mixtures

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Rate constants at 298 K are reported for the reaction of $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) with hydroxide ion in methanol–water and acetone–water mixtures. From known solubilities of naphthalene in these mixtures, and using the method of Van Meter and Neumann, the effect of added solvent on the solvation of this iron complex has been calculated. Thence, the kinetic results have been split into the effects of solvent on the initial and transition states. The treatment of Van Meter and Neumann has been extended to an analysis of the effect of solvent on the transition state, using solubility data obtained from 2-naphthol in methanol–water mixtures. The results support a mechanism in which hydroxide attacks initially at the 2(9) position of the co-ordinated phen; considerable interaction between this carbon-bonded hydroxyl group and the central iron atom is indicated.

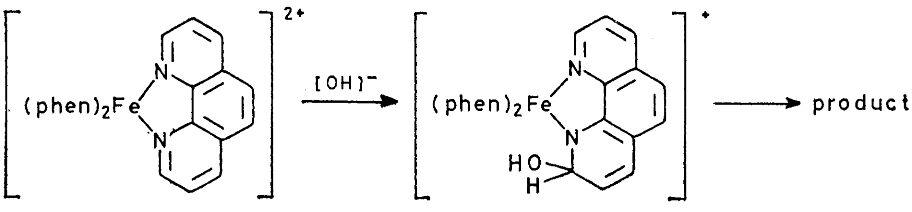
In aqueous solutions the reaction between tris(1,10-phenanthroline)iron(II) cation and hydroxide ions follows the kinetic laws summarised in equations (1) and (2).

$$-d[Fe(phen)_3{}^{2+}]/dt = k_{obs.}[Fe(phen)_3{}^{2+}] \quad (1)$$

$$k_{obs.} = k_1 + k_2[OH^-] \quad (2)$$

Thus $k_{obs.}$ is the experimental first-order rate constant measured under conditions where $[OH^-] \gg [Fe(phen)_3{}^{2+}]$; k_1 and k_2 are the corresponding first- and second-order rate constants respectively. When a co-solvent (*e.g.* acetone) is added the second-order rate constant increases. A similar pattern was observed [1] for the reaction between $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) and hydroxide ions in water when either dimethyl sulphoxide (dmso) or t-butyl alcohol was added. This observation was attributed for the most part to destabilisation of hydroxide ions as the mole fraction of organic co-solvent, x_2, increased. However, comparison [1] of kinetic data for alkaline hydrolysis of a range of inorganic substrates in water–dmso mixtures showed that the effect of co-solvent on the initial and transition states was not unimportant in determining the overall pattern of behaviour.

The aim of the work reported in this paper was to extend the investigation to an examination of the effect of added co-solvent on the kinetics for the alkaline hydrolysis of $[Fe(phen)_3]^{2+}$. In addition an attempt has been made to estimate the effect of the co-solvent on the initial state of the complex and the transition state. The basis of our method follows the extra-thermodynamic analysis of the solvation energy for the $[Fe(phen)_3]^{2+}$ cation as suggested by Van Meter and Neumann.[2] Their method involves calculating the contribution to the solvation energy arising from ligand–solvent interactions. This contribution is obtained from the solubility data for naphthalene. In our work we have extended this analysis to a consideration of solvent effect in aqueous mixtures. Thus, in addition to the kinetic data, the solubility of naphthalene in the same mixtures was incorporated into the analysis. It is therefore possible to obtain a fairly complete picture of the effect of added solvent on the kinetic parameters. In these terms we show that both the initial state of the complex and the transition state are stabilised, although to slightly different extents. Thus in methanol–water mixtures the transition state is stabilised to a lesser degree than the iron complex in the initial state as x_2 increases. The reverse trend however is obtained for acetone–water mixtures. Nevertheless, the effect of co-solvent on both the transition state and initial state of the complex is very similar and the overall trend in rate constant is controlled by the gradual destabilisation of hydroxide ions as x_2 increases.



(1)

SCHEME

These calculations served as a basis for an extension of the method to a consideration of the interactions between the transition state and the solvent. Thus we wished to explore an extension of the Van Meter and Neumann method in terms of a model for ligand–solvent interactions in the transition state. For the reaction considered here, two possible positions of attack of the hydroxide ion on the complex have been discussed:[3]

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[1] M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *J.C.S. Dalton*, 1977, 165.

[2] F. M. Van Meter and H. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 1382.

[3] R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67.

(*i*) directly at the iron atom and (*ii*) at the ligand[4] (Scheme). The attraction of the latter path is that it obviates the implausible proposal of direct attack by hydroxide at the iron atom. Attack of hydroxide at the ligand, which may be reversible, gives a species [(1) in the Scheme] in which the aromatic character of one pyridine ring has been partially lost. The consequent weakening of this iron–nitrogen bond, and the proximity of the hydroxide to the iron atom, should facilitate S_Ni transfer of the hydroxide from carbon to iron, with concomitant breaking of the Fe–N bond and easy subsequent loss of the phen ligand. Recent work[3] has indicated that this mechanism is the more likely and we have accepted it in our analysis.

Thus we started from the basis that incorporation of an OH group into one phen ring would drastically alter the interaction of this ligand with the solvent. If the OH group was extensively hydrogen bonded to the solvent then the effect of co-solvent on the change in ligand–solvent interactions in going from the initial to the transition states of the complex would be equivalent to the effect of co-solvent on the difference in solubility of naphthalene and naphthol. We also postulated that the actual contribution of the OH group was less than predicted, if the OH group was in close proximity and interacting with the central iron atom. Indeed this seems to be the case and we discuss some implications of our calculations on the mechanism of alkaline hydrolysis of $[Fe(phen)_3]^{2+}$.

EXPERIMENTAL

Kinetics.—A concentrated solution of tris(1,10-phenanthroline)iron(II) sulphate (Koch–Light Ltd.) was used without further purification. The other reagents and techniques were as previously described.[1] Absorbance readings at 510 nm (Unicam 1800) were recorded for a period of at least 2.5 half-lives and the rate constants, $k_{obs.}$ [equation (2)], were calculated using the method suggested by Moore[5] suitably incorporated into a computer program (FORTRAN).

Solubilities.—2-Naphthol (May and Baker) was recrystallised and then dried in a vacuum desiccator. Solutions of 2-naphthol in water–methanol mixtures were thermostatted at 298.1 K for several days. The solutions were centrifuged and the absorbance at 265 nm recorded using a Unicam SP 1800 spectrophotometer. The molar absorption coefficient of naphthol was assumed to be independent of solvent.

RESULTS

The measured first-order rate constants, $k_{obs.}$, for the reaction [equation (1)] are summarised in Table 1 for aqueous mixtures where the co-solvent is either methanol or acetone. For both systems $k_{obs.}$ increases with increase in either x_2 or $[OH^-]$. The data were analysed using equation (2) in conjunction with a least-squares procedure. Values of k_1 are very small; the calculated values of the required rate constants k_2 are summarised in Table 2. For both sets of mixtures k_2 increases with increasing x_2.

The solubility of 2-naphthol (Table 3) increases with increasing mol fraction of methanol (Figure 1).

Analysis of Kinetic and Solubility Data.—At a fixed temperature and pressure, the second-order rate constant (Table 2) can be related, using transition-state theory, to the corresponding Gibbs activation function $\Delta G^‡$ which can be re-expressed [equation (3)], in terms of the corresponding standard-state chemical potentials for the initial [*i.e.*

TABLE 1

Rate constants, $k_{obs.}$, for the reaction between $[Fe(phen)_3]^{2+}$ and hydroxide ions in aqueous mixtures at 298.1 K as a function of the mol fraction of added co-solvent, x_2

	x_2				
[NaOH]/mol dm^{-3}	0.033	0.067	0.100	0.133	0.167
(*a*) Methanol–water	$10^4\ k_{obs.}/s^{-1}$				
0	4.32	8.23	14.6	23.3	32.8
0.081	5.94	12.5	19.9	31.3	47.7
0.182		22.2	34.6	51.9	66.5
0.307	21.8	47.6	75.9	111	154
0.470	51.7	104	149	228	309
0.593	72.8	171	218	402	462
	x_2				
(*b*) Acetone–water	0.0033	0.0067	0.01	0.0133	0.0167
0	1.25	1.94	2.74	3.58	4.30
0.047	1.90	3.27	4.62	5.05	6.36
0.109	3.87	6.36	8.10	11.1	13.9
0.196	7.30	17.1	26.0	38.1	48.3
0.328	27.8	65.0	98.1	143	164

The total ionic strength of the solution was 0.167 in (*a*) and 0.016 7 mol dm^{-3} in (*b*).

TABLE 2

Calculated second-order rate constants for the reaction of $[Fe(phen)_3]^{2+}$ with hydroxide ions in binary aqueous mixtures; x_2 = mol fraction of non-aqueous co-solvent *

Mixture	x_2	$10^2k_2/dm^3\ mol^{-1}\ s^{-1}$
Methanol–water	0	2.03
	0.081	2.98
	0.182	4.48
	0.307	9.37
	0.470	18.9
	0.593	29.8
Acetone–water	0	2.33
	0.047	3.23
	0.109	7.39
	0.196	30.8
	0.328	105

* Ionic strengths as in Table 1.

TABLE 3

Solubility of 2-naphthol in methanol–water mixtures at 298.1 K as a function of the mol fraction of alcohol

x_2	Solubility/mol dm^{-3}
0.0	0.006 1
0.081	0.012 0
0.182	0.075 3
0.307	0.389 6
0.470	1.818
0.593	10.38

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[4] See, for example, R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51; R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, p. 226; R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *ibid.*, 1977, **2**, 12.

[5] P. Moore, *J.C.S. Faraday I*, 1972, 180.

$\mu^{\ominus}$(complex)] and transition (*i.e.* $\mu^{\ddagger}$) states and for the hydroxide ion [*i.e.* $\mu^{\ominus}(OH^-)$]. The standard states used here refer to a hypothetical solution having unit molarity and activity coefficient. We adopt the aqueous solution where $x_2 = 0$ as a reference and express the dependence of each quantity in equation (3) on x_2 using the solvent operator,[6] δ_m[equation (4)]. Thus the quantity $\delta_m\Delta G^{\ddagger}$ in equation (4)

$$\Delta G^{\ddagger} = \mu^{\ddagger} - \mu^{\ominus}(\text{complex}) - \mu^{\ominus}(OH^-) \qquad (3)$$

$$\delta_m\Delta G^{\ddagger} = \delta_m\mu^{\ddagger} - \delta_m\mu^{\ominus}(\text{complex}) - \delta_m\mu^{\ominus}(OH^-) \qquad (4)$$

can be calculated from the dependence of k_2 on x_2 and separated into contributions arising from each term on the right-hand side of equation (4). However, this latter task is not straightforward. Thus the terms $\delta_m\mu^{\ominus}(OH^-)$ and $\delta_m\mu^{\ominus}$(complex) describe the solvent dependence of single-ion quantities and cannot be calculated without invoking extra-thermodynamic assumptions. The major aim of this section is to examine how these various terms can be calculated.

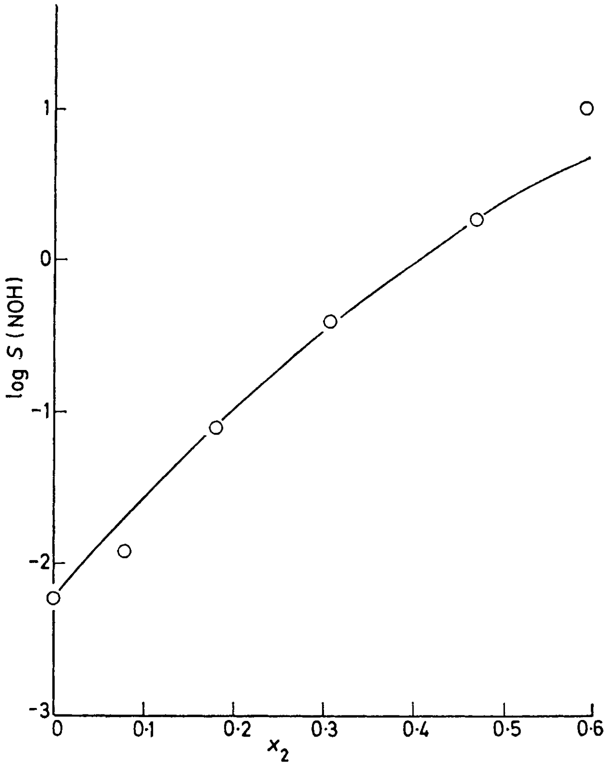

FIGURE 1 Dependence of the solubility of 2-naphthol on the mol fraction of methanol in aqueous mixtures at 298.1 K

(*i*) $\delta_m\mu^{\ominus}(OH^-)$. Wells calculated[7] the transfer function $\delta_m\mu^{\ominus}(H^+)$ in methanol- and in acetone–water mixtures by treating the process in two stages. In the first stage the contribution is calculated for transfer of $H^+(OH_2)_5$ from water to the mixture using the Born expression for the dependence of chemical potential on solvent permittivity. In the second stage the effect of replacing one of the five water molecules by co-solvent is calculated. Using the resulting $\delta_m\mu^{\ominus}(H^+)$ quantity Wells tabulated[7] values of $\delta_m\mu^{\ominus}(OH^-)$ in methanol–water mixtures using the mol fraction scale. These were converted into the molar

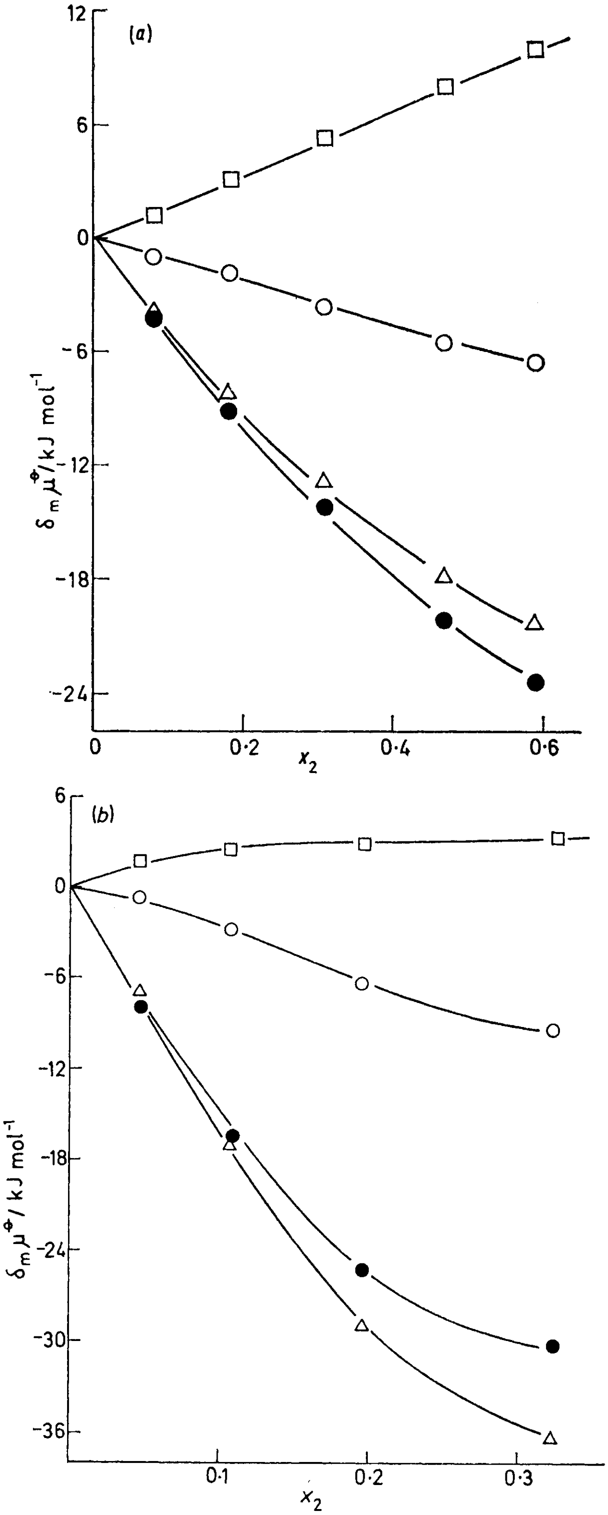

FIGURE 2 Dependence of the Gibbs activation function, $\delta_m\Delta G^{\ddagger}$, and related standard-state chemical potentials on the mol fraction of added co-solvent for the reaction between $[Fe(phen)_3]^{2+}$ and hydroxide ions in water at 298.1 K: (●) $\delta_m\mu^{\ominus}$(complex), (□) $\delta_m\mu^{\ominus}(OH^-)$, (△) $\delta_m\mu^{\ddagger}$, (○) $\delta_m\Delta G^{\ddagger}$; co-solvent = (*a*) methanol and (*b*) acetone

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[6] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, London, 1963.

[7] C. F. Wells, *J.C.S. Faraday I*, 1973, 984.

scale using the densities of the mixtures.[8] Transfer functions for $\delta_m\mu^\ominus(OH^-)$ in acetone–water mixtures were calculated using the values of $\delta_m\mu^\ominus(H^+)$ tabulated by Wells [9] (following conversion to the molar scale [10]), pK_w values in this mixture,[11] and vapour-pressure data.[12] The method is described by Gillet *et al.*[13] The vapour-pressure data for acetone–water mixtures [12] show considerable scatter [9] about a smooth curve and in our calculations we used interpolated values along smoothed curves drawn through the data points. The results of these calculations are summarised for both sets of mixtures in Figure 2. Values of $\delta_m\mu^\ominus(OH^-)$ in mixtures having the same composition as in the kinetic experiments were obtained by interpolation.

(*ii*) $\delta_m\mu^\ominus$(complex). This quantity was calculated along the lines suggested by Van Meter and Neumann.[2] The expression given by these workers for the Gibbs function for solvation of $[Fe(phen)_3]^{2+}$ can be readily modified to express the medium effect on the chemical potential of the iron complex in its solution standard state [equation (5)]. Here

$$\delta_m\mu^\ominus(\text{complex}) = -[N(Z_ie)^2/8\pi r_i\varepsilon_0](\varepsilon_w^{-1} - \varepsilon_x^{-1}) + cRT\ln[S_w(N)/S_x(N)] \quad (5)$$

Z_i is the valency of the ith ion, e is the electronic charge, ε_0 is the permittivity of free space, ε_w and ε_x are the relative permittivities of water and the mixture respectively [2] in which the solubilities of naphthalene [2] are $S_w(N)$ and $S_x(N)$. The radius parameter r_i was taken as the effective radius of the $[Fe(phen)_3]^{2+}$ ion and the value (4.13 Å) obtained by Van Meter and Neumann [2] was used here. The proportionality constant c [equation (5)] is assumed to be independent of solvent and is the ratio of the solvation energy of the ligand to that of naphthalene. Van Meter and Neumann calculated a value for c of 2.053 and this was used in the present calculations together with the solubility data reported by these workers.

(*iii*) *Combination of* δ_m *quantities.* The value of $\delta_m\Delta G^\ddagger$ together with the value of $\delta_m\mu^\ominus(OH^-)$ and $\delta_m\mu^\ominus$(complex) obtained above can be substituted into equation (4) and values of $\delta_m\mu^\ddagger$ calculated. The outcome of this analysis is summarised in Figure 2 for the two systems acetone– and methanol–water.

(*iv*) $\delta_m\mu^\ddagger$. In the previous section, this quantity was calculated, knowing the three other terms in equation (4). In this part of the analysis we have attempted to express $\delta_m\mu^\ddagger$ using an equation similar to equation (6). However, it is now argued that in the transition state the total ligand–solvent interactions can be represented by contributions modelled on naphthalene for two ligands and by a contribution modelled on naphthol for one ligand. Thus the corresponding equation [*cf.* (5)] for $\delta_m\mu^\ddagger$ is now given by (6).

$$\delta_m\mu^\ddagger = -[N(Z_ie)^2/8\pi r_\ddagger\varepsilon_0](\varepsilon_w^{-1} - \varepsilon_x^{-1}) + c'RT\ln[S_w(NOH)/S_x(NOH)] + (2cRT/3)\ln[S_w(N)/S_x(N)] \quad (6)$$

Here $S_w(NOH)$ and $S_x(NOH)$ are the solubilities of naphthol in water and an aqueous mixture respectively. The quantity c is defined above and c' is the corresponding factor for naphthol and the substituted phenanthroline ring in the transition state. Therefore, using the previously calculated value for $\delta_m\mu^\ddagger$ in methanol–water mixtures, equation (6) can be rearranged such that a plot of $\{\delta_m\mu^\ddagger - (2cRT/3)\ln[S_w(N)/S_x(N)]\}/(\varepsilon_w^{-1} - \varepsilon_x^{-1})$ against $\ln[S_w(NOH)/S_x(NOH)]/(\varepsilon_w^{-1} - \varepsilon_x^{-1})$ yields a straight line (Figure 3)

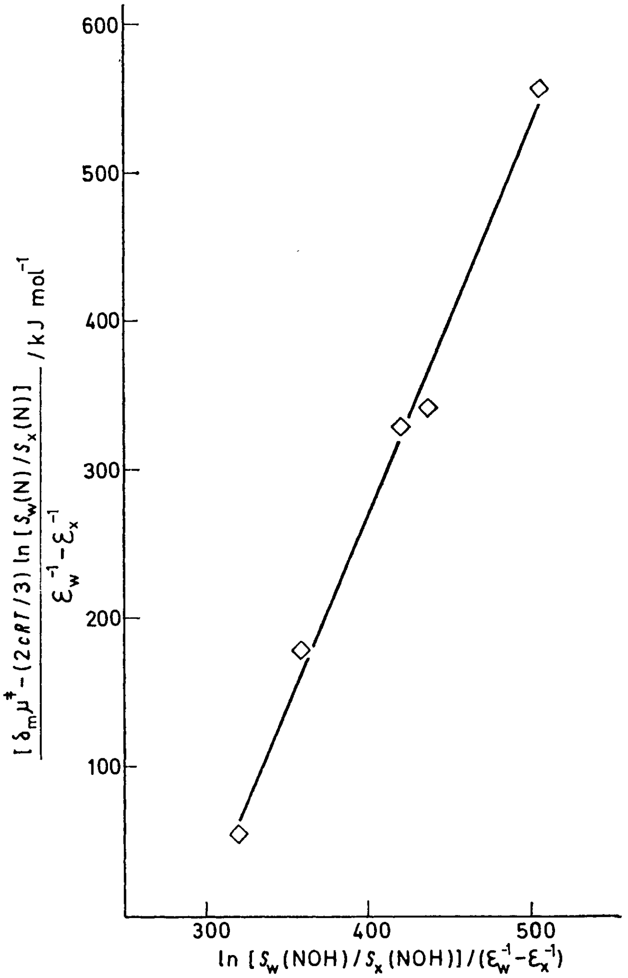

FIGURE 3 Plot to obtain the solubility coefficient for naphthol in the transition state, as defined in equation (6)

yielding from the gradient and intercept the values $r_\ddagger$ = 3.55 Å and c' = 0.462.

DISCUSSION

The model for the solution characteristics of $[Fe(phen)_3]^{2+}$ as advanced by Van Meter and Neumann [2] is very similar to the model for ionic solvation described by Gurney [14] and extended by Friedman and his co-workers [15,16] to the analysis of ion–ion interactions in solution. Thus solvent molecules in close proximity to an ion are described as lying inside a co-sphere such that

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[8] N. G. Foster and E. S. Amis, *Z. phys. Chem.*, 1956, **7**, 360

[9] C. F. Wells, *J.C.S. Faraday I*, 1974, 694.

[10] S. Schiavo and B. Scrosati, *Z. phys. Chem.* (*Frankfurt*), 1976, **102**, 9.

[11] E. M. Wooley, D. G. Hurkot, and L. G. Hepler, *J. Phys. Chem.*, 1970, **74**, 3908.

[12] A. E. Taylor, *J. Phys. Chem.*, 1900, **4**, 355, 675.

[13] H. Gillet, L. Avedikian, and J-P. Morel, *Canad. J. Chem.*, 1975, **53**, 455.

[14] R. W. Gurney, 'Ionic Processes in Solution,' McGraw-Hill, New York, 1953.

[15] H. L. Friedman and C. V. Krishnan, 'Water—A Comprehensive Treatise,' ed. F. Franks, Plenum, New York, 1973, vol. 3, ch. 1.

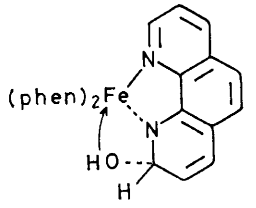
[16] P. S. Ramanathan and H. L. Friedman, *J. Chem. Phys.*, 1971, **54**, 1086.

interactions between the ion and neighbouring water molecules are dominated, in the present case, by the hydrophobic phenanthroline rings. The situation is therefore analogous to the case of tetra-alkylammonium ions in water where the hydration characteristics are determined to a considerable extent by the hydrophobic alkyl chains.[17] Beyond the co-sphere, ion–solvent interactions can be treated using a Born-type expression[15] in which the solvent is characterised by the permittivity of the solvent.

The data summarised in Figure 2 show a fairly complete picture of the parameters controlling the kinetic behaviour. Thus the overall trend confirms our previous hypothesis that to a first approximation $\delta_m\mu^\ominus$(complex) $\simeq$ $\delta_m\mu^\ddagger$; the quantity $\delta_m\mu^\ominus(OH^-)$ is the controlling factor. However, there remain important features which warrant comment. Thus for mixtures where methanol is the co-solvent $\delta_m\mu^\ominus$(complex) decreases more rapidly as x_2 increases than does $\delta_m\mu^\ddagger$. However, in mixtures where acetone is the co-solvent the reverse trend is observed. The overall trend in $\delta_m\mu^\ominus$(complex) and $\delta_m\mu^\ddagger$ is in agreement with the conclusions drawn by Abraham[18] with reference to ionic-transfer parameters for alkylammonium ions from water to a range of organic solvents. These observations confirm the dominant role played by hydrophobic groups in relation to the properties of ions in water. The data summarised in Figure 2 also show that the magnitudes of both $\delta_m\mu^\ominus$(complex) and $\delta_m\mu^\ddagger$ are larger in a mixture with acetone than in those containing methanol. It is noteworthy that, according to Abraham, $\delta_m\mu^\ominus(AsPh_4^+)$ is larger on going from water to acetone than to methanol. However, there is a paucity of information in the literature concerning transfer parameters for large and multivalent ions in aqueous mixtures and so it is dangerous to draw detailed conclusions at this stage.

We now consider the extension of Van Meter and Neumann's model[2] to the transition state of our reaction. The new feature in our reaction is the attachment of a hydroxyl group to the 2(9) position of the co-ordinated 1,10-phenanthroline. This converts one ligand from hydrophobic into predominantly hydrophilic character. This modification can best be paralleled by comparing the change in solubility on going from naphthalene to 2-naphthol. In doing this we have ignored secondary effects arising from the partial loss of aromaticity in the phen ligand on adding the hydroxide to the 2(9) position (phen ⟶ ' phen-OH ').

For this reason too much emphasis cannot be placed on the calculated parameters. Nevertheless the general trend is informative. Thus the low value of *c'* indicates that the change on going from phen to ' phen-OH ' in the transition state is not so dramatic as the change from naphthalene to 2-naphthol in terms of interaction between the ligand and solvent. Thus if the OH group was exposed to and hydrogen bonded with the solvent a value of *c'* close to unity would be expected. That *c'* is less than 50% indicates that the OH group is not completely exposed to the solvent and that there has already developed in the transition state considerable HO · · · Fe interaction from the OH group attached to the ligand (2).



(2)

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[17] M. J. Blandamer, *Adv. Phys. Org. Chem.*, 1977, **14**, 204.

[18] M. H. Abraham, *J.C.S. Faraday I*, 1973, 1375.