A study of the electron-transfer reaction between $Fe(CN)_2(bpy)_2$ and $S_2O_8{}^{2-}$ in solvent mixtures: the translational component of solvent reorganization

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The kinetics of the oxidation of dicyanobis(2,2′-bipyridine) iron(II) [$Fe(CN)_2(bpy)_2$] by peroxodisulfate ($S_2O_8{}^{2-}$) has been studied in different water–cosolvent mixtures. The cosolvents used were methanol, *tert*-butyl alcohol, ethylene glycol and glycerol. The results are explained assuming an additional component of the reorganization free energy of the solvent in the mixtures, caused by a translation of the solvent molecules, as a consequence of the changes in the composition of the (at least) innermost solvation shell. A quantitative estimation of this component is attempted.

Understanding solvent effects on chemical reactivity is of prime importance in chemistry. These effects, as is well known, are extremely different, depending on the solvent and the reaction under study; sometimes the solvent simply provides a physical environment for the reaction. At the other extreme, it participates as a reactant. For electron-transfer reactions the solvent plays an essential role that is well understood, since the seminal papers of Marcus[1], Hush[2] and others.[3]

In the last few years, we have studied electron-transfer reactions in mixed solvents, constituted of water and an organic cosolvent, as well as aqueous electrolyte solutions. Solvent effects in these media are more difficult to explain because in the mixed solvents the reactivity can depend on preferential solvation phenomena. Indeed, there are at least three different solvent–solvent interactions that can also have kinetic influences. However, these kinds of solvents are of interest in relation to many areas of chemistry and biology. In particular, it is possible, by using mixed solvents, to continously change the macroscopic properties of the reaction media. They have, therefore, become a subject of both experimental and theoretical interest [4].

This paper was motivated by previous results, on optical[5] and thermal[6] electron-transfer reactions in mixed solvents, that seemed to point to the possibility of anomalous behaviour in these media: reactivity trends are the opposite of those expected, based on the continuum model of the solvent. To confirm this finding and to quantify the magnitude of the deviation from the model, if any, is the objective of this work. This question is of interest in relation to the types of models to be used for solvent mixtures. Thus, although simple continuum models seem to be sufficient for pure solvents,[7] the application of these models to mixed solvents has been criticised and still remains an open question.[8]

In order to deal with the questions raised above, we have studied the kinetics of the oxidation of $Fe(CN)_2(bpy)_2$ by $S_2O_8{}^{2-}$ in different water–cosolvent mixtures. This system is appropriate for several reasons: first of all, the zero charge of the iron complex implies that the true electron-transfer rate constant, k_{et}, differs only by an approximately constant factor, K_{IP}, from the observed rate constant, k_{obs}; K_{IP} is the equilibrium constant corresponding to the formation of the precursor (encounter) complex from the reactants. On the other hand, the iron complex, after the electron-transfer reaction, becomes a positively charged species. This circumstance will probably cause a significant change in the (preferential) solvation of this reactant, this being the point we want to address here. The iron complex is also useful as a reactant because of a recently published paper[9] concerning the electrochemical reduction of $Fe(CN)_2(bpy)_2{}^+$. This paper gives the value of the internal reorganization free energy of this reactant, a datum that, as will be seen later, permits the calculation of the internal reorganization free energy for $S_2O_8{}^{2-}$. This calculation is important in order to check the reliability of our calculations (see point iii in the Appendix). As for the other reactant, the peroxodisulfate, there are data on the redox potential of the $S_2O_8{}^{2-}/S_2O_8{}^{3-}$ couple in water. These data and the transfer free energies of the peroxodisulfate ions from water to the aqueous mixtures, also available, permit a reasonable estimation of the free energy for the reaction studied in these mixtures (see below). More importantly, in the oxidations by peroxodisulfate, the inner-shell reorganization energy of this reactant controls the kinetics of these reactions (but not the solvent effects). So, the use of this oxidant guarantees the constancy of the preexponential factor in k_{et} (see Discussion). This is especially useful in order to obtain the variations of the activation free energy caused by the solvent.

Results

Table 1 contains the second-order rate constants, k_{obs}, for the process studied in the different water–cosolvent mixtures (D = dielectric constant). The standard formal potentials of the $Fe(CN)_2(bpy)_2{}^+/Fe(CN)_2(bpy)_2$ couple, collected in Table 2, were corrected for liquid junction potentials using those of the $Fe(\eta^5\text{-}Cp)_2{}^+/Fe(\eta^5\text{-}Cp)_2$ couple, which also appear in the same table. After correction for liquid junction potentials, a correction for ionic strength effects (from 0.1 to 0.069 mol dm^{-3}) was also taken into account.

Table 3 presents the true rate constants for the electron-transfer process. These constants can be obtained from k_{obs} through:

$$k_{et} = \frac{k_{obs}}{K_{IP}} \qquad (1)$$

In this case, as the formation of the encounter (precursor complex) involves a neutral species, K_{IP} can be considered independent of the dielectric constant of the reaction media.

Table 1 Second-order rate constants ($10^2\ k_{obs}/s^{-1}\ mol^{-1}\ dm^3$) for the reaction of $Fe(CN)_2(bpy)_2$ with $S_2O_8^{2-}$ at 298.2 K in different water–cosolvent mixtures

D	Methanol	*tert*-Butyl alcohol	Ethylene glycol	Glycerol
76	(0.033) 9.91	(0.007) 24.8	(0.028) 2.28	(0.020) 1.87
74	(0.060) 6.00	(0.013) 19.6	(0.051) 1.66	(0.036) 1.73
70	(0.112) 4.81	(0.025) 15.1	(0.110) 1.03	(0.077) 1.47
66	(0.169) 3.00	(0.040) 11.5	(0.174) 0.75	(0.131) 1.24
64	(0.200) 2.41	(0.047) 9.24	(0.215) 0.49	(0.165) 1.18
60	(0.265) 1.56	(0.062) 7.64	(0.289) 0.36	(0.234) 0.98

* Parenthesis correspond to molar fractions of the cosolvent used. $k_{obs}(\text{water}) = 30.9 \times 10^{-2}\ mol^{-1}\ dm^3\ s^{-1}$.

For this reason, the same value of this parameter was used in all the media ($K_{IP} = 1.839$) $mol^{-1}dm^3$).[10]

Table 4 contains the calculated redox potentials for $S_2O_8^{2-}/S_2O_8^{3-}$. The calculation of these redox potentials was performed as follows: the starting point is the value of this potential in water (1.39 V).[11] From this value, the redox potential in the mixtures can be calculated if the free energies of transfer of $S_2O_8^{2-}$ and $S_2O_8^{3-}$ from water to the mixtures are known. These free energies are known, for $S_2O_8^{2-}$ [12] but not for $S_2O_8^{3-}$ (an unstable species). So, we have estimated the latter using the following approximation:

$$\frac{\Delta G_t(S_2O_3^{3-})}{\Delta G_t(S_2O_8^{2-})} = \frac{Z^2(S_2O_8^{3-})}{Z^2(S_2O_8^{2-})} = \frac{9}{4} \quad (2)$$

where *Z* is the charge of the ion being transferred. This permits the calculation of standard redox potentials for this couple in the different solvents through:

$$(E^0) = E^0_{H_2O} + \frac{RT}{F} \ln \frac{\gamma_t(S_2O_8^{2-})}{\gamma_t(S_2O_8^{3-})} \quad (3)$$

and

$$RT \ln \gamma_t(i) = \Delta G_t(i) \quad (4)$$

However, we are more interested in the standard formal redox potentials corresponding to the actual conditions of the reaction, the latter being carried out at an ionic strengh of 0.069 mol dm^{-3}. Thus a Debye–Hückel correction was applied to give the results appearing in Table 4. The procedure used to calculate the variations of the redox potential of the $S_2O_8^{2-}/S_2O_8^{3-}$ redox couple could be considered a rather crude approximation. However, hydration free energies of anions are proportional to the square of their charges (see point ii in the Appendix). The validity of eqn 2 depends on the supposition that the radii of $S_2O_8^{2-}$ and $S_2O_8^{3-}$ are similar. After electron transfer the —O—O— bond will increase its length though there are no data on this length increase. However, for cobalt complexes that, like $S_2O_8^{2-}$, present a high value of the internal reorganization free energy, this increase after electron transfer is about 6%.[13] This is thus about the difference in the radii to be expected in the present case. (The differences in radii of the anions in Fig. A-1 of the Appendix are of this order and as can be seen, eqn 2 holds.) Finally, the average transfer of $S_2O_8^{2-}$ for water to the mixtures studied in this work is about 5 kJ mol^{-1}. Six per cent of this value is about 0.3 kJ mol^{-1}, which is of the order of magnitude of the uncertainty in the values of the redox potentials measured directly.

From data in Tables 2 and 4 the free energy of reaction, ΔG°, can be easily calculated. However, for the reason given in the discussion, we are interested in $\Delta G^{\circ\prime}$, the free energy of the process:

$$\text{precursor complex} \xrightarrow{k_{et}} \text{successor complex} \quad (5)$$

rather than in ΔG°, the free energy of the reaction:

$$\text{reactants} \xrightarrow{k_{obs}} \text{products} \quad (6)$$

The corrections to ΔG° in order to obtain $\Delta G^{\circ\prime}$ were done as in reference 14:

$$\Delta G^{\circ\prime} = \Delta G^\circ + w_p - w_r \quad (7)$$

with w_p and w_r being the work corresponding to the formation of the succesor complex from the products and the precursor complex from the reactants, respectively. The work w_i (i = r or p) can be calculated with the following equation:

$$w_i = \frac{Z_i Z_j e^2 N_A}{DR(1 + \kappa R)} \quad (8)$$

where Z_i and Z_j are the charges on the two reactants or products, considered with their corresponding signs, and κ the inverse Debye length:

$$\kappa = \left(\frac{8\pi N_A e^2}{1000 D_s k_B T}\right) I^{1/2} \quad (9)$$

The values of $\Delta G^{\circ\prime}$ calculated in this way are given in Table 5. According to these data the reaction becomes less favourable, from a thermodynamic point of view, when the amount of cosolvent in the mixtures is increased.

Table 2 Standard formal redox potentials ($E^{\circ\prime}$/mV *vs.* NHE)[a] of the $Fe(CN)_2(bpy)_2^+/Fe(CN)_2(bpy)_2$ (a) and ferrocinium/ferrocene $[Fe(\eta^5\text{-}Cp)_2^+/Fe(\eta^5\text{-}Cp)_2]$ (b) couples at 298.2 K in different water–cosolvent mixtures

	Methanol		*tert*-Butyl alcohol		Ethylene glycol		Glycerol	
D	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
78.5	water				775	514		
76	776	506	782	522	758	506	779	507
74	776	502	789	516	768	515	773	506
70	778	495	803	513	779	515	779	502
66	780	491	815	515	788	522	779	498
64	787	492	819	516	792	526	780	490
60	781	486	834	516	804	530	783	493

[a] Potentials measured in the presence of 0.1 mol dm^{-3} $NaClO_4$ as supporting electrolyte after correction for liquid junction potentials and ionic strength effects from 0.1 to 0.069 mol dm^{-3}.

Table 3 Electron-transfer rate constants ($10^2\ k_{et}/s^{-1}$) values for the reaction of $Fe(CN)_2(bpy)_2$ with $S_2O_8^{2-}$ at 298.2 K in different water–cosolvent mixtures

D	Methanol	*tert*-Butyl alcohol	Ethylene glycol	Glycerol
78.5	water		16.8	
76	5.40	13.5	1.24	1.02
74	3.26	10.7	0.90	0.94
70	2.61	8.21	0.56	0.80
66	1.63	6.25	0.40	0.67
64	1.31	5.02	0.27	0.64
60	0.85	4.15	0.20	0.53

Table 4 Standard formal redox potentials ($E^{\circ\prime}$/V *vs.* NHE) of the $S_2O_8^{2-}/S_2O_8^{3-}$couple at 298.2 K in different water–cosolvent mixtures

D	Methanol	*tert*-Butyl alcohol	Ethylene glycol	Glycerol
78.5	water		1.421	
76	1.418	1.437	1.405	1.425
74	1.414	1.430	1.386	1.420
70	1.406	1.421	1.368	1.410
66	1.398	1.410	1.352	1.404
64	1.393	1.405	1.341	1.401
60	1.383	1.393	1.338	1.396

Table 5 $-\Delta G^{\circ\prime}$/kJ mol^{-1} values for the reaction of $Fe(CN)_2(bpy)_2$ with $S_2O_8^{2-}$ at 298.2 K in different water–cosolvent mixtures

D	Methanol	*tert*-Butyl alcohol	Ethylene glycol	Glycerol
78.5	water		65.59	
76	65.33	66.61	65.84	65.59
74	65.06	65.31	63.15	65.96
70	64.26	63.20	60.52	64.54
66	63.40	61.23	58.27	64.08
64	62.35	60.38	56.81	63.86
60	62.19	58.00	55.66	63.26

It is worth pointing out that w_i, as given in eqn 8, does not include the cavity terms. However, these terms would be similar for reactants and products and, consequently, they would cancel. This term, however, has been taken into account in the calculation of K_{IP} (for this reason a K_{IP} value different from unity appears).

Discussion

First, it is interesting to note that, as can be seen in Tables 1 and 3, the addition of a small amount of cosolvent decreases the rate constant by about an order of magnitude. This apparently abnormal situation is clearly shown in Fig. 1 and 2, which are plots of ln k_{et} *vs.* two polarity parameters. The first one, *Y*, (Grundwald–Winstein)[15] is obtained from kinetic measurements and the second one $E_T(30)$,[16] from spectrophotometric measurements. In both cases the points corresponding to the rate constants in water are outside the correlation. The figures correspond to water–ethylene glycol mixtures, but similar behaviour is found for methanol–water and glycerol–water mixtures. However, for *tert*-butyl alcohol–water mixtures the linear correlation includes the water point. This special situation can be understood by considering the molar fraction of cosolvent in the mixtures (Table 1), which are much lower in the case of *tert*-butyl alcohol. This suggests, at first, that the deviation of the water point in the other cases can be related to the phenomenom of preferential solvation. If this is so, it is clear that the treatments based on simple continuum models of the solvent cannot explain quantitatively the kinetic behaviour. So we need to consider the solvent from a molecular point of view.

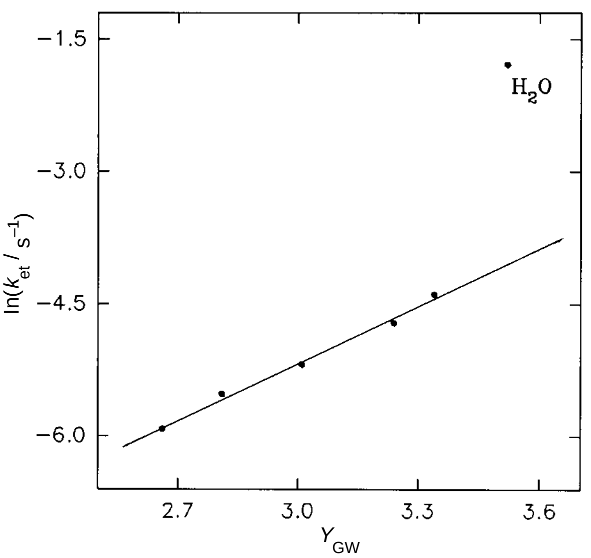

Fig. 1 Plot of the logarithm of k_{et}/s^{-1} *vs.* the Grundwald–Winstein polarity parameter, Y_{GW}, in ethylene glycol–water mixtures at 298.2 K

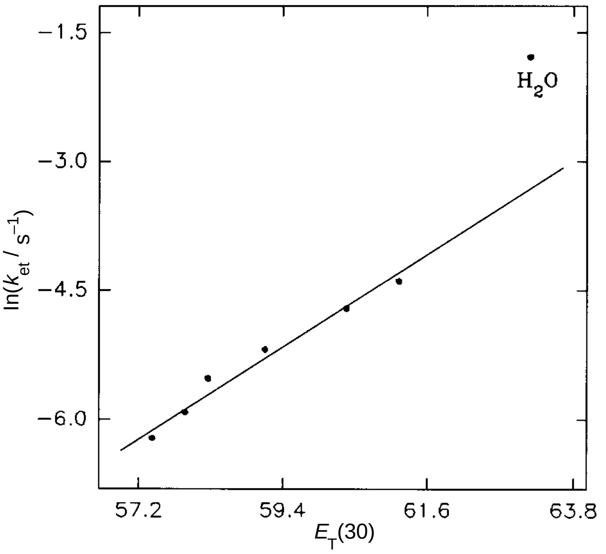

Fig. 2 Plot of the logarithm of k_{et}/s^{-1} *vs.* the Reichardt polarity parameter, $E_T(30)$, in ethylene glycol–water mixtures at 298.2 K

As a starting point we will consider the expresion of k_{et} given by classical electron-transfer theory:[14]

$$k_{et} = \kappa_{el}\,\upsilon_n \exp(-\Delta G^{\neq}/RT) \tag{10}$$

Here, κ_{et}, υ_n and $\Delta G^{\neq}$ are the electronic transmission coefficient, the nuclear frequency factor and the (Gibbs) free energy of activation for the electron-transfer process. The latter is given by:

$$\Delta G^{\neq} = \frac{(\lambda + \Delta G^{\circ\prime})^2}{4\lambda} \tag{11}$$

The λ parameter appearing in this equation is the so-called (free) energy of reorganization for the electron-transfer process. This free energy is considered to consist of a solvent contribution, λ_o, and a contribution arising from the reorganization of the bonds within the donor and aceptor, λ_i. The latter contribution to the reorganization energy can be safely considered as independent of the reaction media. The values of $\Delta G^{\neq}$ can be obtained from the data in Table 3 once the value of the preexponential term in the rate constant is known. Assuming adiabatic behaviour ($\kappa_{el} \approx 1$),[11] we need to know υ_n. This parameter is given by:[17]

$$\upsilon_n = \left(\frac{\upsilon_{in}^2 \lambda_i + \upsilon_{out}^2 \lambda_o}{\lambda_o + \lambda_i}\right)^{1/2} \qquad (12)$$

υ_{in} and υ_{out} being the characteristic frequencies for the internal and external (solvent) reorganization. If $\lambda_i \gg \lambda_o$ (as will be shown to be the case for our process) one can safely assume:

$$\upsilon_n = \upsilon_{in} \qquad (13)$$

because υ_{in} is nearly two orders of magnitude greater than υ_{out}. That is, the preexponential factor in the rate constant can be considered independent of the reaction media. According to this, a value of $\upsilon_n \approx 10^{13}$ s^{-1} seems reasonable. We have used a value of 6.62×10^{12} s^{-1} corresponding to the value of $k_B T/h$ at 298 K. However, it is important to indicate that we have performed calculations with preexponential factors in the range 10^8–10^{14} s^{-1}. In this range, although there are variations in the values obtained for $\Delta G^{\neq}$, the trends in this parameter and the conclusions reached from these trends do not change.

Once the values of $\Delta G^{\neq}$ have been calculated, obtaining λ is a straightforward matter, using the data in Table 5 and eqn 11. These λ values appear in Table 6, which also includes the values of λ_o calculated from:[1]

$$\lambda_o = N_A e^2 \left(\frac{1}{2r_A} + \frac{1}{2r_B} - \frac{1}{d_{AB}}\right)\gamma \qquad (14)$$

where $\gamma = 1/n^2 - 1/D$ is Pekar's factor, r_A and r_B the acceptor and donor radii, respectively ($r_A = 3.4$ Å and $r_B = 5.6$ Å),[18] and d_{AB} is the donor–acceptor distance in the precursor complex (assumed to be the sum of the reactant radii). From the values of λ_o and λ in the table, the value of λ_i can be obtained. This value is about 330 kJ mol^{-1}and, consequently, the above assumption ($\lambda_i \gg \lambda_o$) is supported.

It is of interest to consider the λ values, which are greater in the mixtures than in water. This circumstance is unexpected since Pekar's factor decreases as the amount of cosolvent in the mixtures increases. Given that λ_i is a constant, a decrease in λ should be expected. According to this, λ_o must have another component, which is not included in eqn 14. This equation is based on the consideration of the solvent as a continuum and, consequently, does not include contributions arising from preferential solvation, which probably influences the kinetics, as suggested by Fig. 1 and 2. In fact, as a consequence of the electron transfer, the neutral iron complex becomes a (positively) charged species and a change in the preferential solvation is expected. This change will produce an extra reorganization of the solvent caused by a translational movement of some solvent molecules, because at the transition state the position of the molecules of the two components of the solvent (and not only the solvent polarization) must be intermediate between the positions corresponding to the (preferential) solvation of the initial and final states. It is important to realize that the cause of the extra component in λ is not the preferential solvation itself, but the *changes* in this preferential solvation in the activation process, which implies a movement of solvent molecules in this process. This extra contribution in mixed solvents has been suggested by Curtis *et al.*[19] from thermodynamic measurements and by Hupp and Weydert[4] from a study of the spectra of some complexes in mixed solvents. Also, Piotrowiak and Miller[20] and others[21] have explained results corresponding to optical electron-transfer processes in electrolyte solutions as caused by an extra component of the reorganization free energy due to the translational movement of the ions of the supporting electrolyte. But, to the best of our knowledge, no previous results have been reported showing the influence of this component of λ on the kinetics of electron-transfer processes in mixed solvents. However, related effects in the kinetics of the electron-transfer processes have been pointed out by Nielsen *et al.*[22] in relation to primitive recognition effects in electron-transfer reactions (see also ref. 23). The magnitude of this contribution to λ, caused by the translational movement of the solvent molecules, λ_t, can be calculated from:

$$\lambda_t = (\lambda)_{mix} - \lambda_i - (\lambda_o)_{mix} \qquad (15)$$

and:

$$\lambda_i = (\lambda)_{H_2O} - (\lambda_o)_{H_2O} \qquad (16)$$

Notice that $\lambda_t = 0$ in pure water, because preferential solvation is absent.

The values of λ_t obtained in this way are given in Table 6. Fig. 3 gives the plot of λ_t in methanol–water mixtures *vs.* the diffusion coefficient of the organic component in the mixtures.[24] The increase of λ_t when the diffusion coefficient decreases, that is, when the translational movement of the molecules becomes more hindered, supports the idea of a translational origin of λ_t in such a way that, as established before, the *movement* of solvent molecules in the activation process, rather than the preferential solvation itself, is at the origin of λ_t.

As to the λ_t values obtained (except for *tert*-butyl alcohol–water mixtures), it is worth pointing out that they represent an important fraction of λ_o. Since λ_t increases when λ_o decreases, this extra component can cause changes in reactivity trends, as observed in this work, in relation to the predictions of the continuum model. The importance of λ_t will be outstanding in the cases where λ_i is small. Indeed, the phenomena causing λ_t can produce a breakdown of the linear response of the solvent when substantial differences exist between solute–solvent interactions in the initial and final states.[25]

The observed solvent effects can now be explained: after the addition of the first portions of methanol, ethylene glycol or glycerol there is a marked decrease in the rate constant. This

Table 6 Reorganization energies (λ), outer reorganization energies (λ_o) and 'translation' reorganization energies (λ_t), (all in kJ mol^{-1}) for the reaction of Fe(CN)$_2$(bpy)$_2$ with $S_2O_8{}^{2-}$ at 298.2 K in different water–cosolvent mixtures

	Methanol			*tert*-Butyl alcohol			Ethylene glycol			Glycerol		
D	λ	λ_o	λ_t	λ	λ_o	λ_t	λ	λ_o	λ_t	λ	λ_o	λ_t
78.5	water			431	99.6	0						
76	442	99.0	10.6	435	98.5	3.4	458	97.6	27	460	97.3	31
74	447	98.5	16.1	436	98.3	3.6	457	96.6	28	460	96.0	33
70	448	98.0	17.6	434	97.2	4.7	457	94.5	31	460	93.3	35
66	451	97.5	21.1	434	96.5	5.1	456	92.5	33	461	90.5	38
64	452	97.3	22.3	434	96.2	5.7	458	91.5	34	461	89.2	39
60	456	96.9	26.7	432	95.3	6.6	459	89.9	35	462	87.0	42

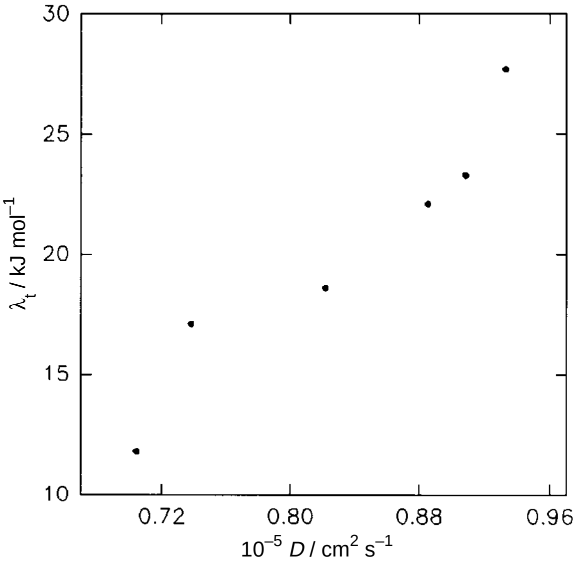

Fig. 3 Plot of the translational reorganization energy, λ_t/kJ mol^{-1}, *vs.* the diffusion coefficient of methanol in methanol–water mixtures at 298.2 K

decrease comes from the fact that the free energy of reorganization, λ, increases by about 10–30 kJ mol^{-1} when going from water to the first water–cosolvent mixtures (see Table 6). Indeed, the addition of cosolvents makes the process somewhat less favourable from a thermodynamic point of view (see Table 5). Further addition of the cosolvents glycerol and ethylene glycol does not significantly change λ. This happens since the extra component compensates for the decrease in λ_o due to the change in the dielectric properties of the mixtures (in all cases Pekar's factor decreases with increasing concentration of the organic component). The decrease in the rate constant in these media must be ascribed, consequently, to the fact that the reaction becomes thermodynamically less favourable with increasing cosolvent amount (see Table 5). In methanol–water mixtures, both the kinetic parameter, λ, and the thermodynamic one, $\Delta G^{\circ\prime}$, contribute to the decrease of k_{et}.

In conclusion, we have shown that a simple continuum dielectric model is unable to explain the 'fine structure' of the solvent effects in solvent mixtures, due to the preferential solvation phenomena. In relation to electron transfer, this model cannot (obviously) account for an extra component of the solvent reorganization caused by molecular translations, which contribute substantially to the total solvent reorganization energy, as shown here.

Experimental

Materials

The iron complex $Fe(CN)_2(bpy)_2 \cdot 3H_2O$ was prepared according to the literature.[28] Its purity was tested by UV-visible spectroscopy and by CHN analysis. EDTA (disodium salt) was obtained from Merck (P.A. grade) and sodium peroxodisulfate from Carlo Erba (P.A. grade). Ferricinium was synthesized according to the method given in the literature.[27] All the solutions were prepared with deionized water (conductivity $< 10^{-8}$ S m^{-1}).

Kinetics

Kinetic runs were performed using a Hitachi 150-20 spectrophotometer at 298.2 K employing a matched 1 cm quartz cell. The temperature was maintained within a range of ±0.1 K by using a Julabo thermostat. All the experiments were carried out under pseudo-first-order conditions using an excess of oxidant. The reactant concentrations used were the following: $[Fe(CN)_2(bpy)_2] = 1.18 \times 10^{-4}$ mol dm^{-3}, $[Na_2S_2O_8] = 2.25 \times 10^{-2}$ mol dm^{-3} and $[EDTA^{2-}] = 5 \times 10^{-4}$ mol dm^{-3}. The kinetics were followed at 520 nm. Rate constants were obtained from the slopes of the plots of $\ln(A - A_\infty)$ *vs.* time, A being the absorbance at time t and A_∞ the final absorbance. These rate constants were found to be reproducible within about 5%.

Electrochemical measurements

The apparatus and electrodes used in this study have been previously described.[28] The concentration of the iron complex used in these experiments was 2×10^{-4} mol dm^{-3}. To measure the redox potential of the $Fe(\eta^5\text{-}Cp)_2{}^+/Fe(\eta^5\text{-}Cp)_2$ couple, a 1.5×10^{-4} mol dm^{-3} concentration of the oxidized component of this couple was used. In all cases potentials were obtained in the presence of 0.1 mol dm^{-3} $NaClO_4$.

Acknowledgements

The authors thank D.G.I.C.Y.T. (PB92-0677), the Consejería de Educación y Ciencia de la Junta de Andalucía and Fundación Cámara for their support of this work.

Appendix: Checking calculations

In the previous paragraphs some assumptions and approximations have been used. Therefore it seemed necessary to check them in order to support our conclusions. The main approximations are: (i) The use of the Eigen–Fuoss treatment for the calculation of the association constants (K_{IP}). (ii) The approximations made in the calculation of the redox potential of the $S_2O_8{}^{2-}/S_2O_8{}^{3-}$ couple. (iii) The assumption that λ_{in} is a constant in the water–cosolvent mixtures. We will try to justify the assumptions we have made.

(i) In order to calculate K_{IP} we have used the Eigen–Fuoss treatment. Even if these equilibrium constants are in error by a factor of two, this would imply an error in $\Delta G^{\neq}$ of about 2 kJ mol^{-1} which is probably smaller than the error in the other approximations.

(ii) To estimate the redox potential of the $S_2O_8{}^{2-}/S_2O_8{}^{3-}$ couple, we have used the Debye–Hückel formulation. This approach, in the range of concentrations used in our experiments ($I_{total} \leqslant 0.1$ mol dm^{-3}), can be applied safely. Indeed we have used eqn 2 in order to estimate the transfer free energies of $S_2O_8{}^{3-}$ from those of $S_2O_8{}^{2-}$. It is important to realize that eqn 2 *is not* based on any model. It simply supposes that the free energy of transfer of an anion is proportional to the square of its charge. Fig. A-1 gives the experimental free energy of hydration of I^-, $SO_4{}^{2-}$ and $PO_4{}^{3-}$ *vs.* the square of their charges.[29] This figure supports our approximation.

(iii) In order to check that the variations of λ are not due to the influence of the solvent on λ_i, due to the (possible) dissociative character of our electron-transfer process, we will consider Fig. A-2. This figure gives a plot of λ values in methanol–water mixtures *vs.* the values of this parameter obtained for the same mixtures by an independent procedure. The λ values on the x axis correspond to an (optical) electron-transfer reaction within the binuclear complex:[5] $[(NH_3)_5RuNCRu(CN)_5]^-$. In this complex, a MMCT band is observed ($\lambda = 683$ nm, $\varepsilon \approx 3000$ mol^{-1} dm^3 cm^{-1} in water). The maximum energy for this band, E_{op}, is related to the λ and $\Delta G^{\circ\prime}$ parameters characterizing the electron transfer through:[18]

$$E_{op} = \lambda + \Delta G^{\circ\prime} \qquad (18)$$

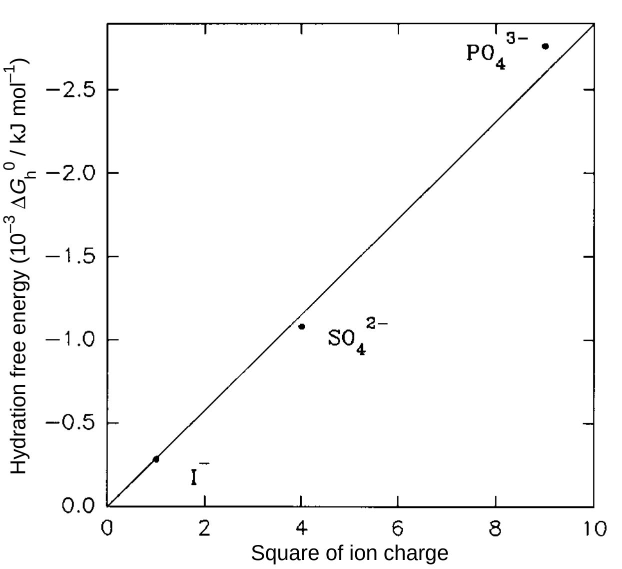

Fig. A-1 Plot of the free energy of hydration (kJ mol^{-1}) of some anions *vs.* the square of their charge

As $\Delta G^{\circ\prime}$ can be obtained by performing electrochemical measurements on both ruthenium centers of the type described above, λ can be obtained directly from two experimental magnitudes without any additional hypothesis. As can be seen in Fig. A-2, a correlation is observed between the λ values obtained in this work by using a kinetic procedure and the values of this parameter obtained from spectroscopy measurements. In the case of the binuclear complex λ_i is small, (26.84 kJ mol^{-1})[30] and consequently a dissociative character of the electron transfer is ruled out in this case. This correlation shows that the changes in λ are due to the influence of the solvent only on λ_o, as we have supposed, because in the case of a binuclear complex it can be safely assumed that the solvent does not influence λ_i.

Finally, a word in relation to the high λ_i value for this reaction. As mentioned above, this parameter measures the energy required to change the internal bonds of the reactant in order to reach the configuration of the transition state. The contribution of the iron complex to λ_i has been obtained recently by Terrettaz *et al.*[9] They give a value to this parameter of 0.04 eV molecule^{-1} = 3.86 kJ mol^{-1}. According to this, the main contribution to λ_i comes from the other reactant, the $S_2O_8^{2-}$ ions. Taking into account that:

$$\lambda_i \approx \frac{\lambda_i^{ox} + \lambda_i^{red}}{2} \tag{19}$$

we estimated λ_i ($S_2O_8^{2-}$) to be about 660 kJ mol^{-1}, in reasonable agreement with the value of about 600 kJ mol^{-1} that can be estimated from the study of Fürholz and Haim[11] on the oxidation of $Ru(NH_3)_5pz^{2+}$ by peroxodisulfate. This agreement also gives support to our calculations. Indeed, this result can explain the relatively low rate of reaction observed when the oxidant is $S_2O_8^{2-}$, in spite of its high redox potential.

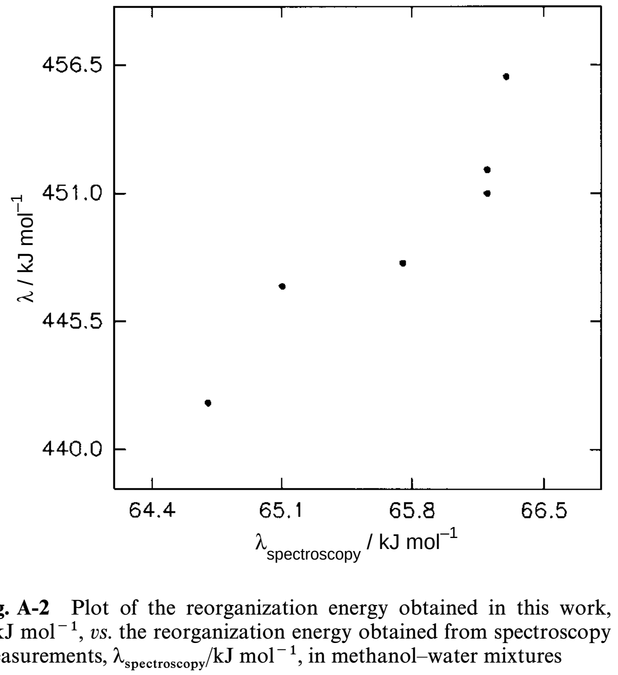

Fig. A-2 Plot of the reorganization energy obtained in this work, λ/kJ mol^{-1}, *vs.* the reorganization energy obtained from spectroscopy measurements, $\lambda_{spectroscopy}$/kJ mol^{-1}, in methanol–water mixtures

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Received 27th January 1997; *Paper* 7/06747D