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Electron transfer reactions in solvent mixtures: the excess component of solvent reorganization free energy

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Abstract

In this paper, experimental and simulation results corresponding to studies of electron transfer processes in solvent mixtures are presented. The methodology is presented to obtain the relevant parameters controlling the elementary electron transfer step, namely, the reorganization free energy, λ, and the driving force, $\Delta G^{\circ\prime}$. It is shown that in solvent mixtures there appears an additional component of the solvent reorganization free energy. An attempt is carried out to quantify its magnitude. The conclusions corresponding to the existence and origin of this extra component are supported by the results of Monte Carlo

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simulations. It is concluded that continuum models of the solvent, in particular Marcus' model, can give good results for a single component solvent if the critical parameters, the ion sizes, are taken as adjustable parameters and fitted accordingly. However, when these fitted values are used in solvent mixtures, the continuum model fails, even in the absence of any specific solvent effects.

Keywords: Electron transfer; Reorganization free energy; Solvent mixtures

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1. Introduction

Thermal electron transfer processes are nonradiative processes in which an electron is transferred from a donor to an acceptor without the formation or breaking of chemical bonds. In this sense they are one of the simplest chemical processes of interest.

In order to achieve a nonradiative electron transfer, the Franck–Condon Principle and the Energy Conservation Principle must hold. Consequently, during the transfer: (i) the nuclear degrees of freedom remain at fixed configurations; and (ii) the electronic levels at the donor and the acceptor have the same energies. According to current treatments of electron transfer, conditions (i) and (ii) generally require an activation process, which implies a reorganization of the bonds of the reactants as well as a solvent reorganization. Accordingly the role of solvent in electron transfer processes is critical, as has been shown in the pioneering work of Marcus and Hush, using a continuum dielectric description [1]. This description yields results that are in qualitative agreement with the experiment. However, classical dielectric models are an oversimplification and, consequently, a quantitative agreement between the predictions of the models and experiments is rarely observed [2]. Nevertheless, recent progress has been made in understanding the role of single component solvents in electron transfer processes. This progress concerns the role of both the static as well as dynamic solvent effects. Some recent reviews on this topic are those in reference [3].

The situation is more involved when dealing with solvent mixtures in spite of some recent progress in this area [4]. This is due the fact that in mixtures, the reactivity may depend on preferential solvation phenomena, which are determined by the reactant (and product) interactions with the two kinds of solvent molecules as well as by different solvent–solvent interactions. Relaxation phenomena, affecting the dynamic solvent effects, are also more complicated in mixtures than in pure solvents. However, solvent mixtures are interesting in relation to many areas of chemistry and biology. In particular, using mixed solvents, it is possible to continuously change the macroscopic properties of the reaction media. They are, therefore, a subject of both experimental and theoretical interest [5].

In the last few years we have been interested in the study of solvent effects on electron transfer reactions involving, in most cases, transition metal complexes. Generally, these complexes carry a high charge, and therefore, most of our studies have been carried out in aqueous solvent mixtures (as well as in electrolyte solutions), in order to avoid problems related to the low solubility of highly charged reactants in low dielectric constant solvents. In relation to the interpretation of kinetic results we have used the classical (Marcus–Hush) model for electron transfer reactions [1]. As is well known, this model describes the multidimensional free energy surfaces of the reactant and product states as parabolic surfaces in terms of a suitable reaction coordinate. In this model, the activation free energy, $\Delta G^{\neq}$, is related to the reaction free energy, $\Delta G^{\circ\prime}$, and the reorganization energy, λ (see below). The model is based, as mentioned above, on the continuum description of the solvent, in such a way that $\Delta G^{\circ\prime}$ and λ depend only on the dielectric properties of the reaction medium. In order to overcome the limitations of the continuum description several approaches have been used. Molecular descriptions of the solvent are, in principle, capable of overcoming some of the difficulties associated with a continuum treatment of the solvent. The mean spherical approximation (MSA) allows calculation of the reorganization energy and the free energy of the reaction recognizing the solvent molecularly, by describing the solvent molecules as hard spheres with point dipoles in their centers. Within the MSA [6], an expression for λ involving an effective hard sphere radius of the solvent molecules has been used [7,8]. A second approach is based on use of the nonlocal electrostatic theory [9] of solute–solvent interactions. This is a convenient frame for incorporating both short-range solvent structure and long-range interionic interactions in the appropriate kinetic and equilibrium quantities. In this model, the structural characteristics of the solvent are described in terms of short-range dielectric constants and polarization fluctuation correlation lengths. In fact, this approach has been used to calculate the relevant parameters for electron transfer processes [10]. The results reveal significant deviations from the expectation based on classical electrostatic theory. A third approach has been used by Hupp and co-workers [11]. This relies on the use of a continuum model of the solvent but with ‘effective’ electron transfer distances, in such a way that solvent specificities are incorporated in the effective distance parameter. This approach has recently received theoretical support [12]. In this work, the authors suggest that the results of quantum mechanical calculations of the reorganization energies can be reproduced by using an ‘effective’ cavity size in the calculations performed with the Marcus formula. As will be seen later, we have used this approach in the interpretation of kinetic data corresponding to electron transfer processes in solvent mixtures.

The conclusion emerging from our studies is that the Marcus treatment, when used in combination with ‘effective’ parameters, gives a good estimation of the reorganization energy, but it cannot reproduce the *fine structure* of this parameter. We have hypothesized that, in solvent mixtures, a new component of the reorganization energy appears. This new component arises from the changes in the preferential solvation of the sites as a consequence of the electron transfer.

In this paper the methodology and the results of our studies are presented.

2. Deriving the relevant parameters for electron transfer processes from kinetic data

The first step towards deriving the parameters controlling the kinetics of electron transfer processes from kinetic data is to extract the true (unimolecular) electron transfer rate constant, k_{et}, from the experimentally measured rate constant, k_{exp}. This need arises from the fact that the latter is a complex parameter, which contains contributions from several processes. The complex character of k_{exp} arises from the fact that, as in other solution processes, electron transfer occurs in, at least, the following steps:

$$A + D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A/D \tag{1}$$

$$A/D \overset{k_{et}}{\rightleftarrows} A^-/D^+ \tag{2}$$

$$A^-/D^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A^- + D^+ \tag{3}$$

The first step represents the formation of the precursor, or encounter complex from the reactants; the second step corresponds to the activation of the precursor complex to produce the successor complex; and the third one represents the formation of the separate products from the successor complex. Thus, the experimental rate constant, k_{exp}, for the process reactants → products, contains contributions from all three steps above. Factorization into the different contributions can be done by selecting suitable systems: if the reaction is accompanied by a major decrease in free energy, contributions from the reverse processes of the second and third steps can be ignored. Nevertheless, the observed rate constant still contains contributions from the forward and backward processes of the first step and, of course, from the forward process in the second step. The rate constant corresponding to this latter process, k_{et}, is the derived parameter because this is the parameter considered by current treatments of the electron transfer reactions.

It can be easily shown that if the equilibrium (1) is rapid (in both, forward and reverse directions), working in an excess of one of the reactants, the rate constant obtained in a kinetic experiment is given by:

$$k_{exp} = \frac{k_{et} K_{IP}[R]}{1 + K_{IP}[R]} \tag{4}$$

In this equation K_{IP} is the equilibrium constant corresponding to step 1 ($K_{IP} = k_1/k_{-1}$) and [R] is the concentration of the reactant in excess. Notice that Eq. (4) can be applied only if $k_{et} \ll k_1, k_{-1}$.

According to Eq. (4), there are two limiting possibilities: (i) $K_{IP}[R] \ll 1$; in this case, $k_{exp} = k_{et} K_{IP}[R]$. (ii) $K_{IP}[R] \gg 1$; in this case k_{exp} directly yields k_{et}. The results presented in this review have been obtained under conditions corresponding to each of these limits. There are also intermediate situations that correspond to $K_{IP}[R] \sim 1$. Under these circumstances, k_{et} can still be obtained from k_{exp}. Thus, writing Eq. (4) as:

$$\frac{1}{k_{\rm exp}} = \frac{1}{k_{\rm et}K_{\rm IP}[{\rm R}]} + \frac{1}{k_{\rm et}} \tag{5}$$

it is clear that, using several values of [R] in the experiments, the quantities $k_{\rm et}$ and $K_{\rm IP}$ can be obtained from the intercept and the slope of a (linear) plot of $1/k_{\rm exp}$ versus 1/[R].

Then, by an appropriate choice of experimental system, it is possible to obtain $k_{\rm et}$. In case (i), it is the product $K_{\rm IP}k_{\rm et}$ that is in fact obtained. Obviously, in this case, $K_{\rm IP}$ must be obtained either by an independent procedure, or calculated. In relation to the results presented in this paper, $K_{\rm IP}$ has been obtained from calculations based on the Eigen–Fuoss approach [13,14]. This was possible because our data were obtained at low ionic strength, in such a way that this approach can safely be used.

Once $k_{\rm et}$ is known, its value can be considered in the light of the different models available to describe electron transfer processes. There are a variety of classical, semiclassical and quantum models. With respect to the interpretation of the results considered in this paper, only classical models [1] have been employed. According to these models, $k_{\rm et}$ is formulated as:

$$k_{\rm et} = Ae^{-\frac{\Delta G^{\neq}}{RT}} \tag{6}$$

The pre-exponential term in $k_{\rm et}$ contains electronic and nuclear contributions arising from the adiabatic or nonadiabatic character of the electron transfer process and from the nuclear relaxation. The latter is (or can be) solvent dependent. However, the dynamic dependence disappears for strongly non-adiabatic processes. On the other hand, according to the Sumi–Marcus model [15] although the nuclear dependence still exists, the pre-exponential term becomes independent of the solvent if the intramolecular (vibrational) contribution to the activation free energy is large, even if the electron transfer process is adiabatic. Some experimental studies exist which seems to contradict the predictions of the Sumi–Marcus theoretical analysis [16]. However, in these studies, the dynamic characteristic of the solvents as reflected in their dielectric relaxation times span a 10^2 range of values [16]. In our experiments, the corresponding range is of the order 2. Under these circumstances a value of 10^{13} s^{-1} (or simply k_BT/h as given by Classical Transition State Theory) seems adequate for the pre-exponential term of $k_{\rm et}$.

The classical treatments assume a linear response of the solvent and, consequently, the free energy surfaces corresponding to reactant and product states (or more properly, to precursor complex and successor complex states) are parabolic. In Marcus' treatment, it is also supposed that both surfaces have the same curvature. In this approach, the free energy of activation is given by:

$$\Delta G^{\neq} = \frac{(\lambda + \Delta G^{\circ\prime})^2}{4\lambda} \tag{7}$$

In Eq. (7), $\Delta G^{\circ\prime}$ is the free energy corresponding to the process precursor complex → successor complex. This free energy is distinct from the overall free energy ΔG° which corresponds to the process reactants → products. However both free energies are related through:

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + w_p - w_r \tag{8}$$

where w_r is the work corresponding to the precursor complex formation from the separate reactants and w_p is the equivalent work for the formation of the successor complex from the separate products. These terms can be calculated by using the Eigen–Fuoss treatment, provided that the circumstances mentioned in the case of K_{IP} hold, namely, that the ionic strength in the reaction medium is low enough. In this case,

$$w_\alpha = \frac{z_i z_j e^2 N_A}{D_s r(1+\kappa r)} \quad (\alpha = r, p) \tag{9}$$

where z_i and z_j are the charges of the reactants (products), considered with their signs, forming the precursor (successor) complex, r is the distance of closest approach and κ the inverse Debye length.

The parameter λ in Eq. (7) is the so-called free energy of reorganization. Its derivation is the central objective of our studies. This energy is usually assumed to be the sum of two different contributions: the inner sphere reorganization energy, λ_{in}, which is the reorganization free energy of the bonds in the reactants to achieve the configurations of the bonds corresponding to the product state and the outer sphere reorganization energy, λ_{out}, which is the reorganization free energy of the solvent.

It is worth pointing out that if one is interested in obtaining solvent effects on λ (in fact on λ_{out}), the selected system must satisfy the following conditions:

1. The direct and reverse processes in Eq. (1) must be rapid in relation to the electron transfer process.
2. The free energy of the global reaction (not necessarily of the electron transfer process (step 2)) must be highly favorable.
3. λ_{in} must be large, in such a way that, as mentioned above, the pre-exponential term of k_{et} remains a constant independent of the reaction medium.

Electron transfer processes in which peroxodisulphate and cobalt(III) complexes participate as oxidants are good examples of processes in which the conditions (i–iii) hold. However, there exists a drawback with these processes, arising from the fact that both, $S_2O_8^{2-}$ and many cobalt complexes suffer decomposition after electron transfer. Consequently, the redox potentials of these oxidants cannot be obtained by conventional electrochemical procedures. These data, of course, are necessary if one wants to obtain the reorganization free energy, λ, from the activation free energy, $\Delta G^{\neq}$ (see Eq. (7)).

In the case of peroxodisulphate oxidation we have overcome this problem by taking as a starting point the value of the (estimated) potential for the $S_2O_8^{2-/3-}$ couple in water, 1.39 V. From this value, the redox potential corresponding to a given solvent can be calculated if the transfer free energies of $S_2O_8^{2-}$ and $S_2O_8^{3-}$ from water to the solvent are available. These free energies, in fact, are known for $S_2O_8^{2-}$ for the solvents used by us [17–19], but not for $S_2O_8^{3-}$ (an unstable species). So we have estimated the latter using the following approximation:

$$\frac{\Delta G_t(S_2O_8^{3-})}{\Delta G_t(S_2O_8^{2-})} = \frac{Z^2(S_2O_8^{3-})}{Z^2(S_2O_8^{2-})} = \frac{9}{4} \tag{10}$$

where Z is the charge of the ion.

Once the transfer free energy (from water to the desired solvent) is known, the standard redox potential in the solvent can be calculated through:

$$(E°)_S = (E°)_{H_2O} + \frac{RT}{F} \ln \frac{\gamma_t(S_2O_8^{2-})}{\gamma_t(S_2O_8^{3-})} \tag{11a}$$

and

$$RT \ln \gamma_t(i) = \Delta G_t(i). \tag{11b}$$

In the case of cobalt complexes a different approach was used in order to obtain redox potentials. This approach is based on equations derived by Hush for optical electron transfer processes [20]. Hush obtained the equations for the reorganization free energies, λ, and reactions free energies, $\Delta G°'$, for these processes from band energies, E_{op}, and widths, $\Delta v_{1/2}$, corresponding to the associated optical electron transfer:

$$E_{op} = \lambda + \Delta G°' \tag{12}$$

and

$$\lambda \ (\mathrm{cm}^{-1}) = \frac{(\Delta v_{1/2})^2}{16 k_B T \ln 2} = \frac{(\Delta v_{1/2})^2}{2295} \quad (\text{at } 298.2 \text{ K}) \tag{13}$$

Thus, in principle, $\Delta G°'$ can be obtained from the optical transition. However, this approach is precluded from a practical point of view because of the phenomenon of inhomogeneous broadening [21–24]. This phenomenon increases the width of the experimental band (which, is in fact, an envelope of several bands). Consequently, an estimation of λ through Eq. (13) by using the experimental (observed) value of $\Delta v_{1/2}$ could yield an overestimated value of this parameter. Thus, according to Eq. (12), an underestimated value of $\Delta G°'$ would result.

Our approach consists in the use of Eq. (12), but without using the value of λ obtained from Eq. (13). Although this approach has been detailed in previous papers [25] it will be outlined in the following section. Consider two complexes with the same ligands, for example $Co(NH_3)_5L^{3+}$ (I) and $Ru(NH_3)_5L^{3+}$ (II). A metal-to-metal charge transfer (MMCT) band can be observed when those complexes are in solution with an anionic complex with high charge ($Ru(CN)_6^{4-}$ in our experiments). These bands can be related through Eq. (12):

$$(E_{op})_I - (E_{op})_{II} = [\lambda_I - \lambda_{II}] + [(\Delta G°')_I - (\Delta G°')]. \tag{14}$$

For two closely related complexes such as I and II, λ_{out} can be safely assumed to be the same, thus:

$$\lambda_I - \lambda_{II} = (\lambda_{in})_I - (\lambda_{in})_{II} \tag{15}$$

Now, Eq. (14) can be written as:

$$(\Delta G^{\circ\prime})_{\mathrm{I}} = [(E_{\mathrm{op}})_{\mathrm{I}} - (E_{\mathrm{op}})_{\mathrm{II}}] - [(\lambda_{\mathrm{in}})_{\mathrm{I}} - (\lambda_{\mathrm{in}})_{\mathrm{II}}] + (\Delta G^{\circ\prime})_{\mathrm{II}}. \tag{16}$$

So, $(\Delta G^{\circ\prime})_{\mathrm{I}}$ can be estimated from the difference between the energies corresponding to the optical electron transfers and $(\Delta G^{\circ\prime})_{\mathrm{II}}$, which are experimental quantities, after correction for the differences in the internal reorganization free energies. These reorganization energies have been obtained, in the present case, by using the classical expression for this parameter [1a]:

$$\lambda_{\mathrm{in}} = \frac{1}{2}\sum_i f_i(\Delta d_i)^2 \tag{17a}$$

$$f_i = \frac{2f_i^{\mathrm{r}}f_i^{\mathrm{p}}}{f_i^{\mathrm{r}} + f_i^{\mathrm{p}}} \tag{17b}$$

but other more exact expressions can be used when it is necessary [26]. In 17(a,b), f_i^{r} and f_i^{p} are the stretching (or breathing) force constants for the ith metal–ligand bond in the reactant and product states, respectively, and Δd_i is the change in the equilibrium value of the ith metal–ligand bond after electron transfer. The sum is over all the metal–ligand bonds.

In the case of cobalt complexes the value of $(\Delta G^{\circ\prime})_{\mathrm{I}}$ obtained through Eq. (16) must be corrected. The need for this correction arises because, in the case of these complexes, the products of optical and thermal electron transfer processes are different. The product of the thermal electron transfer is an (unstable) high-spin cobalt(II) species. On the contrary, a low-spin cobalt(II) species is produced in the optical electron transfer. The desired value of $\Delta G^{\circ\prime}$ is obtained as:

$$\Delta G^{\circ\prime} = (\Delta G^{\circ\prime})_{\mathrm{I}} + \Delta E_i \tag{18}$$

ΔE_i being the difference between free energies of thermally equilibrated high-spin and low-spin cobalt(II) complexes [27].

By using the procedure outlined above we have obtained the redox potentials (corresponding to $\mathrm{Co^{III}}$(low-spin)/$\mathrm{Co^{II}}$(high-spin) redox couples) appearing in Table 1. The reliability of the method can be checked considering the activation free energies for the oxidation of ferrocyanide by the complexes in Table 1: as is well known, for cases in which $(\Delta G^{\circ\prime})^2 \ll 4\lambda$ (as happens in these oxidations), a plot of the activation free energy versus $\Delta G^{\circ\prime}$ must be a straight line with a slope of 0.5. Fig. 1 shows this plot. It is seen that, in fact, a straight line is obtained, with a slope

Table 1
Estimated redox potentials vs. NHE for the couples $\mathrm{Co^{III}}$ (low-spin)/$\mathrm{Co^{II}}$ (high-spin), E°_{Co},in water ($I = 0.069$ mol dm^{-3}) at 298.2 K

Redox couple	E°_{Co} (V)
$\mathrm{Co(NH_3)_5DMSO^{3+/2+}}$	0.50
$\mathrm{Co(NH_3)_5py^{3+/2+}}$	0.35
$\mathrm{Co(NH_3)_4pzCO_2^{2+/+}}$	0.46
$\mathrm{Co(NH_3)_6^{3+/2+}}$	0.19

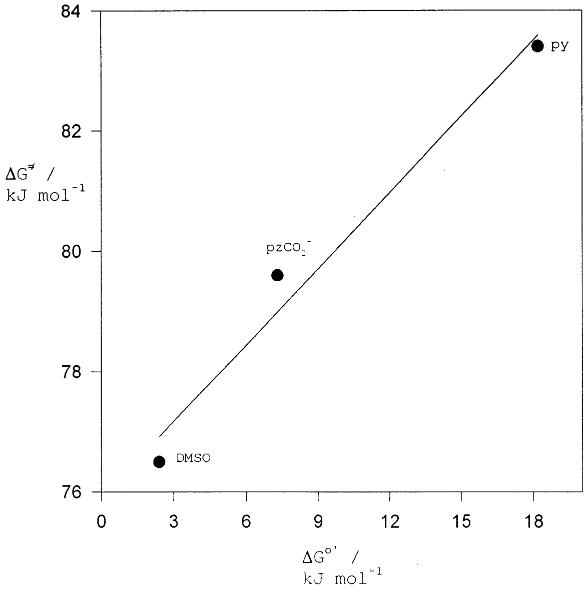

Fig. 1. Plot of $\Delta G^{\neq}$ vs. $\Delta G^{\circ\prime}$ for the electron transfer processes between the cobalt(III) complexes and $Fe(CN)_6^{4-}$.

of 0.42 ± 0.05 very close to the theoretical value. After these parameter values are obtained for water solution, it is straightforward to obtain them in other solvents (see Ref. [25]).

Once the values of $\Delta G^{\circ\prime}$ have been obtained in different solvents, the corresponding values of λ can easily be calculated using Eq. (7) and the experimental values of $\Delta G^{\neq}$ are given (in fact, from the experimental values of k_{et}). In Tables 2–4 the values of λ and $\Delta G^{\circ\prime}$, as well as those of k_{et} and $\Delta G^{\neq}$, are given for three representative examples which will be considered in this review. These examples correspond to the peroxodisulphate oxidation of $[Fe(bpy)_3]^{2+}$ [28], the oxidation of $[Fe(CN)_6]^{4-}$ by $[Co(NH_3)_5DMSO]^{3+}$ [25] and the intramolecular electron transfer whithin the binuclear complex $[(NH_3)_5Ru^{III}\text{–}NC\text{–}Ru^{II}(CN)_5]^{-}$ [29]. Although we limit ourselves to these three cases, similar results to those considered below have been found in other studies in solvent mixtures [30].

3. Discussion

3.1. General overview and the excess of solvent reorganization free energy

Let us first consider, the case of the peroxodisulphate oxidation of $Fe(bpy)_3^{2+}$. It can be seen in Table 2 (last column) that the addition of a small amount of cosolvent causes a decrease in the rate constant of about one order of magnitude.

This situation is clearly shown in Figs. 2 and 3, which are plots of k_{et} versus two polarity parameters. The first one, Y_{GW}, (Grunwald–Winstein) is obtained from kinetic measurements and the second one, $E_T(30)$, from spectroscopic measurements. The values of these parameters are taken from references [31] and [32], respectively. In both cases the point corresponding to the rate constant in water is outside the correlations. The figures correspond to water-methanol mixtures, but

Table 2
Electron transfer rate constant, k_{et}, reorganization free energy, λ, reaction free energy, $\Delta G^{\circ\prime}$, and activation free energy, $\Delta G^{\neq}$, for the reaction $Fe(bpy)_3^{2+} + S_2O_8^{2-}$ in different water–cosolvent mixtures at 298.2 K

X_S	γ [a]	$\Delta G^{\circ\prime}$ [b] (kJ mol^{-1})	λ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$k_{et} \times 10^3$ (s^{-1})
Water–methanol					
0	0.5505	−41.5	411.0	83.0	18.8
0.033	0.5486	−38.0	439.1	91.6	0.57
0.060	0.5472	−37.2	439.4	91.9	0.49
0.112	0.5445	−35.2	440.1	93.1	0.31
0.169	0.5419	−33.0	439.7	93.9	0.22
0.200	0.5406	−31.0	437.9	94.3	0.20
0.265	0.5383	−29.3	441.1	96.1	0.10
Water–tert-butyl alcohol					
0.007	0.5474	−42.1	419.0	84.8	9.3
0.013	0.5459	−40.8	419.4	85.3	7.1
0.025	0.5401	−38.5	420.2	86.6	3.9
0.040	0.5364	−35.2	421.7	88.4	2.1
0.047	0.5347	−34.8	425.3	89.6	1.3
0.062	0.5312	−31.7	429.6	92.0	0.5
Water–ethyleneglycol					
0.0278	0.5425	−39.5	436.3	90.1	1.00
0.0508	0.5369	−36.5	434.7	91.0	0.71
0.1050	0.5253	−33.5	435.1	92.6	0.37
0.1735	0.5139	−31.2	434.8	93.5	0.27
0.2145	0.5086	−29.3	435.4	94.6	0.19
0.2893	0.4996	−27.7	436.5	95.6	0.12
Water–glycerol					
0.0198	0.5404	−41.2	444.0	91.4	0.67
0.0364	0.5333	−40.3	444.4	91.8	0.55
0.0772	0.5183	−39.7	445.2	92.3	0.43
0.1312	0.5031	−37.7	445.7	93.2	0.30
0.1645	0.4957	−38.6	449.3	93.8	0.23
0.2326	0.4834	−37.5	454.2	95.5	0.12

[a] $\gamma = 1/n^2 - 1/D_S$; n and D_S values were taken from Refs. [57,58], respectively.

[b] Calculated from the value of $S_2O_8^{2-/3-}$ redox potential in water (1.39 V, Ref. [34]), as indicated in the text.

Table 3
Electron transfer rate constant, k_{et}, reorganization free energy, λ, reaction free energy, $\Delta G^{\circ\prime}$, and activation free energy, $\Delta G^{\neq}$, for the reaction $Co(NH_3)_5DMSO^{3+} + Fe(CN)_6^{4-}$ in different water–cosolvent mixtures at 298.2 K

%W [a]	γ [b]	$\Delta G^{\circ\prime}$ (kJ mol^{-1})	λ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$10k_{et}$ (s^{-1})
Water–methanol					
0	0.5505	2.4	303.6	76.5	2.5
10.0	0.5473	−2.1	309.1	74.8	4.9
20.0	0.5440	−3.5	309.9	72.0	15
30.0	0.5408	−5.3	312.9	69.8	36
40.0	0.5381	−8.0	318.2	67.8	83
Water–ethyleneglycol					
10.0	0.5422	−0.6	303.9	75.7	3.4
20.0	0.5336	−1.5	304.3	74.9	4.6
30.0	0.5251	−1.7	302.1	74.1	6.5
40.0	0.5162	−1.7	301.0	73.3	9.0
50.0	0.5083	−3.3	301.1	71.1	22
60.0	0.4992	−5.0	300.7	69.1	48
70.0	0.4906	−6.5	301.7	68.4	65
80.0	0.4817	−7.4	300.9	67.7	84
Water–acetonitrile					
10.0	0.5462	−4.1	306.4	74.2	6.2
20.0	0.5420	−7.6	305.4	72.1	15
30.0	0.5391	−8.6	307.8	68.6	60
40.0	0.5370	−8.6	308.6	67.0	115
50.0	0.5351	−7.9	308.3	66.4	142
Water–glucose					
6.4	0.5423	1.3	305.3	76.4	2.6
13.1	0.5337	2.7	304.6	76.7	2.3
19.6	0.5252	1.9	304.4	76.6	2.4
26.0	0.5163	1.9	304.6	77.0	2.0
37.7	0.4992	3.7	303.8	77.3	1.8
49.2	0.4817	2.8	302.1	77.1	1.9

[a] Percent of organic cosolvent weight in the mixtures.

[b] $\gamma = 1/n^2 - 1/D_S$; n values were measured (for these %W values), and D_S values were taken from Ref. [58].

similar behavior is found for ethyleneglycol and glycerol mixtures. However, for *tert*-butyl alcohol the linear correlation includes the water point. The (apparently, see below) special situation in the latter kind of mixtures can be understood by considering the molar fractions of the cosolvents in these mixtures appearing in Table 2. As can be seen, the molar fractions are much lower in the case of *tert*-butyl alcohol than in the other mixtures. This suggests, at first, that the deviation of the water point in the other cases could be related to the phenomenon of preferential solvation.

In Table 2, we also show the values of the reorganization free energy obtained as indicated above. A striking feature of the λ values is that they increase as the molar

Table 4
Values of $\Delta G^{\circ\prime}$, λ and $\Delta G^{\neq}$ for the electron transfer reaction within the $[(NH_3)_5Ru^{III}–NC–Ru^{II}(CN)_5]^-$ complex and Pekar's factor, γ, for different water–cosolvent media at 298.2 K

%*W* [a]	γ [b]	$\Delta G^{\circ\prime}$ (kJ mol^{-1})	λ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Water–methanol [c]				
0	0.5505	111.5	50.5	129.9
5.7	0.5486	110.7	50.3	128.8
10.2	0.5472	109.5	50.7	126.5
18.4	0.5445	107.4	51.5	122.6
26.5	0.5419	106.2	51.9	120.4
30.6	0.5406	105.4	51.9	119.2
39.2	0.5383	103.4	52.0	116.1

[a] Percent of organic cosolvent weight in the mixtures.

[b] $\gamma = 1/n^2 - 1/D_S$; *n* and D_S values were taken from Refs. [57,58], respectively.

[c] In the water–cosolvent mixtures a 0.2 mol dm^{-3} concentration $LiNO_3$ was always added.

fraction of cosolvent increases. This is unexpected, because, according to the Marcus treatment, the reorganization energy should decrease as the Pekar's factor does. This is because:

$$\lambda = \lambda_{in} + \lambda_{out} \tag{19}$$

and λ_{in} is solvent independent, whereas λ_{out} is given by:

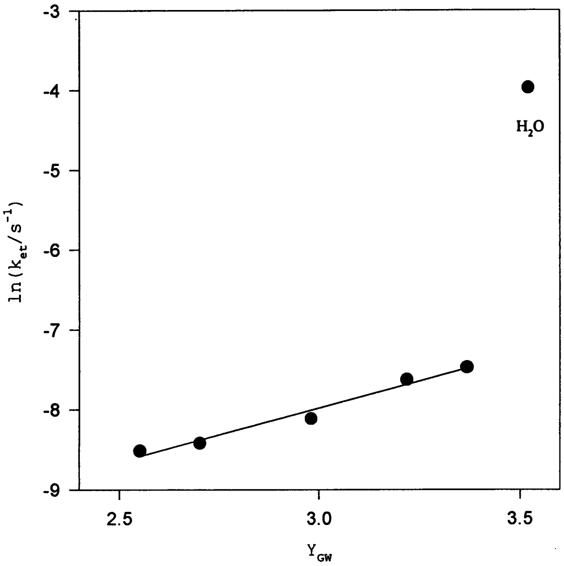

Fig. 2. Plot of $\ln(k_{et})$ (s^{-1}) vs. the Grunwald–Winstein polarity parameter, Y_{GW} (taken from reference [31]), in methanol–water mixtures at 298.2 K.

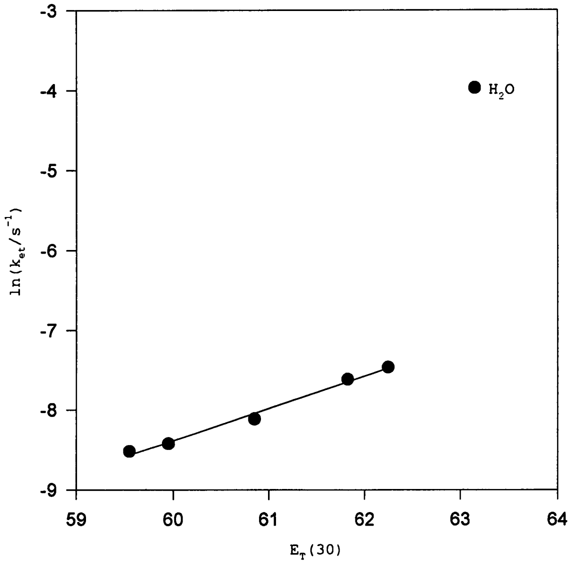

Fig. 3. Plot of $\ln(k_{et})$ (s^{-1}) vs. the Reichardt polarity parameter, $E_T(30)$ (taken from reference [32]), in methanol–water mixtures at 298.2 K.

$$\lambda_{out} = B\gamma \tag{20}$$

where $\gamma = 1/n^2 - 1/D_S$ is the Pekar's factor. In this factor, n^2 is the optical dielectric constant (corresponding to electronic polarization)and D_S the static dielectric constant of the solvent (corresponding to the total polarization, that is, to electronic and nuclear polarization).

As Pekar's factor for the mixtures is lower than those of water, a decrease in λ should be expected when the molar fraction of the organic component increases.

According to Marcus [1a], the factor B, appearing in Eq. (20) is given by:

$$B = Ne^2\left(\frac{1}{2r_A} + \frac{1}{2r_D} - \frac{1}{d_{AD}}\right) \tag{21}$$

where r_A and r_D are the acceptor and donor radii and d_{AD} is the donor–acceptor distance in the precursor complex (assumed to be the sum of the reactants radii). As is known, Eq. (20) overestimates the value for λ_{out}. In this regard Hupp et al. [11] have recently suggested that d_{AD} must be considered the effective distance of the electron transfer, and not the geometric distance between the centers of the reactants, calculated as mentioned above. This suggestion, as mentioned in the introduction, received theoretical support from the work of Jean and King [12], and has been used in the determination of λ_{out} by Paulson et al. [33]. In fact, our simulation results, presented in the last section of this paper also confirm this hypothesis. Notice that the use of an effective value of d_{AD} is equivalent to considering the parameter B as an adjustable parameter. So, instead of using B, as given by Eq. (21), we have fitted it by using data for water as:

$$B = \frac{(\lambda_{\mathrm{out}})_{\mathrm{water}}}{\gamma_{\mathrm{water}}} \tag{22}$$

The value of $(\lambda_{\mathrm{out}})_{\mathrm{water}}$ corresponds, according to Eq. (19):

$$(\lambda_{\mathrm{out}})_{\mathrm{water}} = \lambda_{\mathrm{water}} - \lambda_{\mathrm{in}} \tag{23}$$

and was calculated using λ_{in} values that have been reported for the two reactants considered here (540 kJ mol^{-1} for $S_2O_8^{2-}$ [34] and 1.93 kJ mol^{-1} for the iron complex [35]). In the present case, a value of $B = 254$ kJ mol^{-1} is obtained. From

Table 5

Experimental and calculated solvent reorganization free energies, $(\lambda_{\mathrm{out}})_{\mathrm{exp}}$ and $(\lambda_{\mathrm{out}})_{\mathrm{calc}}$, respectively, and excess reorganization free energies, λ^{exc}, for the reaction $\mathrm{Fe(bpy)_3^{2+}} + S_2O_8^{2-}$ in different water–cosolvent mixtures at 298.2 K

%W [a]	X_S [b]	$(\lambda_{\mathrm{out}})_{\mathrm{exp}}$ (kJ mol^{-1})	$(\lambda_{\mathrm{out}})_{\mathrm{calc}}$ (kJ mol^{-1}) [c]	λ^{exc} (kJ mol^{-1}) [d]
Water–methanol				
0	0	139.8	139.8	0
5.7	0.033	168.0	139.3	28.7
10.2	0.060	167.7	139.0	28.7
18.4	0.112	168.4	138.3	30.1
26.5	0.169	168.1	137.6	30.5
30.6	0.200	168.0	137.3	30.7
39.2	0.265	168.2	136.7	31.5
Water–tert-butyl alcohol				
2.9	0.007	147.7	139.0	8.7
5.3	0.013	148.0	138.7	9.3
10.0	0.025	149.4	137.2	12.2
14.6	0.040	149.9	136.2	13.7
16.9	0.047	153.9	135.8	18.1
21.5	0.062	158.5	134.9	23.6
Water–ethyleneglycol				
9.0	0.0278	164.0	137.8	26.2
15.6	0.0508	164.1	136.4	27.7
28.8	0.1050	163.9	133.4	30.5
42.0	0.1735	164.2	130.5	33.7
48.0	0.2145	163.8	129.2	34.6
58.4	0.2893	164.3	126.7	37.6
Water–glycerol				
9.4	0.0198	172.8	137.3	35.5
16.2	0.0364	173.1	135.5	37.6
30.0	0.0772	174.0	131.6	42.4
43.6	0.1312	174.6	127.8	46.8
50.2	0.1645	178.3	125.9	52.4
60.8	0.2326	183.2	122.8	60.4

[a] Percent of organic cosolvent weight in the mixtures.

[b] Molar fractions of cosolvent in the mixtures.

[c] Calculated by using Eq. (20).

[d] Obtained by using Eq. (24).

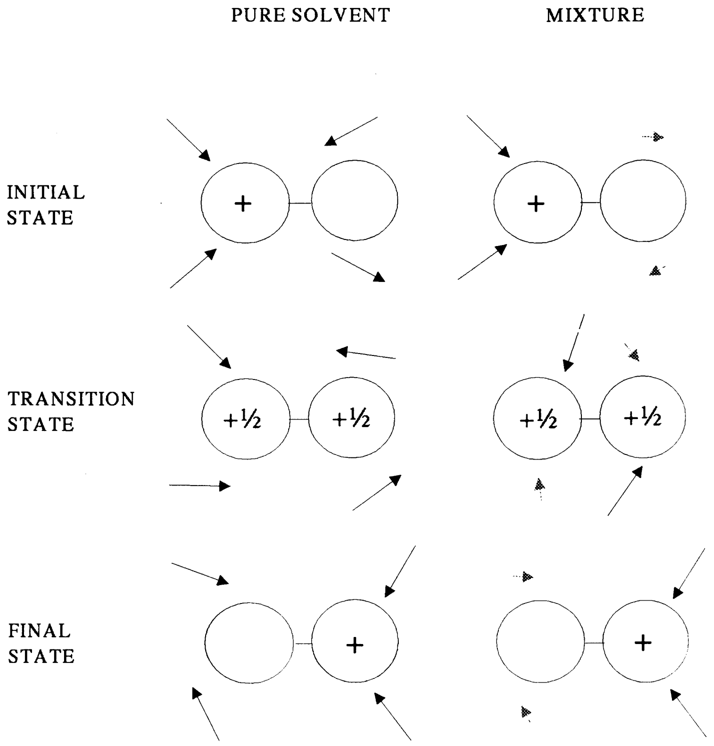

Fig. 4. Schematic representation of the movement of solvent molecules in the activation process corresponding to an electron transfer reaction (charge shift) in a pure solvent (left) and in a solvent mixture (right). In the first case, just the rotation of molecules is necessary to accomplish activation. In the second case, the sorting of molecules from the first solvation shells of the reactants is also necessary. Charges in the transition state are virtual.

this result, the values of $(\lambda_{out})_{calc}$ appearing in Table 5 were obtained. The tabulated values for λ^{exc} reported in references [28] and [30b] are somewhat different than those reported here. The discrepancy arises from an overestimation of λ_{in} of the peroxydisulfate of about 60 kJ mol^{-1} in these references. Table 5 also contains the experimental values of the solvent reorganization free energy, $(\lambda_{out})_{exp}$, obtained as indicated by Eq. (23), that is, $(\lambda_{out})_{exp} = \lambda^{exp} - \lambda_{in}$. Finally, the excess parameter, λ^{exc}, defined by:

$$\lambda^{exc} = (\lambda_{out})_{exp} - (\lambda_{out})_{calc} = \lambda - \lambda_{in} - 254\gamma \qquad (24)$$

is given. Notice that, in some sense, λ^{exc} represents an excess reorganization free energy with respect to that corresponding to a pure solvent with the same Pekar factor as the mixtures; i.e. with the same dielectric characteristics as the mixtures [36]. The extra contribution to the solvent reorganization (in solvent mixtures) can be attributed to the fact that, as a consequence of the electron transfer reaction, both reactants change their charges and consequently a modification of the preferential solvation is expected (which is, of course, absent in pure solvents [37]). The idea just outlined is depicted in a simplistic way in Fig. 4. The reorganization in the pure solvent involves configurations that differ mainly in the orientation of the dipoles around the reactants/products. On the other hand, in mixtures, an additional contribution arises from the different local compositions of the solvent around the reactants/products (preferential solvation).

The extra contribution that we are considering in mixed solvents was suggested by Curtis et al. [38], from the results obtained through thermodynamic (redox) measurements corresponding to some complexes in solvent mixtures, and by Hupp et al. [39,40] from the study of the spectra of some complexes in mixed solvents. In the work of Curtis et al., motivated by their interest in redox reactivity in mixed solvents, the thermodynamics of intramolecular electron transfer processes (in three binuclear transition metal systems) was studied in dimethyl sulfoxide–acetonitrile mixtures. In fact, the redox potentials (and free energies and entropies of electron transfer) were obtained. In the mixtures, the thermodynamic properties of the complexes go through an extrema when the solvent composition changes. This behavior arises from changes in the preferential solvation of the complexes. In particular, because the $Ru^{III}(NH_3)_5py$ moiety of the complexes 'is much more readily solvated by DMSO than the $Ru^{II}(NH_3)_5py$ moiety'.

On the other hand, in the work of references [39] and [40], also corresponding to dimethylsulfoxide/acetonitrile mixtures, the optical MMCT bands for these ruthenium complexes in the mixtures were discussed. According to the authors, in mixed solvents 'unusual (and kinetically significant) barrier effects which evidently are unique to mixed solvents' appear. In the case of optical MMCT, the transition energy goes through a maximum as the solvent composition changes. The explanation for this behavior given by those authors is very similar to ours (see Eq. (6) of reference [40]): after an (optical) electron transfer 'excited state relaxation requires either back electron transfer or the net translation of about five DMSO molecules from $Ru^{III}(NH_3)_5$ to $Ru^{II}(NH_3)_5$. To an electrochemist, the latter possibility would be immediately recognizable as an optical EC reaction — the C step being solvent translation'.

Also, Pitrowiak et al. [41] have explained the 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. Related effects in the kinetics of the electron transfer processes have been pointed out by Nielson et al. [42,43] in relation to primitive recognition effects in electron transfer reactions (see also reference [44]). However, although the concentration effects observed in these works with mixed solvents were pronounced, those experiments were not able to resolve the local contributions to the solvent reorganization energy from the bulk contribution [45], as it has been done in the present work.

The existence of this extra component of the solvent reorganization free energy has been predicted theoretically by Matyushov [46]. This author has constructed the free energy surfaces by a perturbative treatment of their exact representations as integrals in the phase space of the system. His treatment takes into account the fluctuations of the local structure of the solvent, near the reactants, due to thermal motions of the molecules. The picture emerging from this treatment is quite different from the one corresponding to continuos solvent models, when electron transfer results from long-range fluctuations in the polarization of the solvent. According to Matyushov, local structure fluctuations arise from fluctuations in the local density (pure solvents) or liquid composition (solvent mixtures). The treatment establishes that the dispersion of the energy of the localized electronic levels participating in the electron transfer (which is related to the reorganization energy) is the sum of a contribution from long-range solvent polarization fluctuations and a second contribution from local fluctuations. Part of this second contribution, in solvent mixtures, would correspond to the parameter λ^{exc} defined above.

In a somewhat different context, Yoshimori et al. [47] have stated differences between dynamic solvation in pure solvents and solvent mixtures, because 'in mixed solvents selective solvation is possible and this may require the redistribution of solvent species in the vicinity of a newly charged solute particle. The spatial redistribution of solvent particles will give slower overall and likely more complex dynamic process'. In fact, in binary 2-propanol–benzene mixtures the rate of change of the Stokes shift is proportional to the concentration of 2-propanol. This fact is attributed by the authors to a solvation process limited by the diffusion rate of 2-propanol.

In order to check the calculation of λ^{exc} it is important to realize that, according to previous considerations, the deviation of the water point from the general correlations in Figs. 2 and 3 must be considered a consequence of the excess of reorganization energy (λ^{exc}) in solvent mixtures. Thus, if the values of k_{et} in this mixture were calculated without this contribution, that is, as (see Eqs. (6) and (7))

$$(k_{\mathrm{et}})_{\mathrm{calc}} = A e^{-\frac{(\lambda - \lambda^{\mathrm{exc}} + \Delta G^{\circ\prime})^2}{4(\lambda - \lambda^{\mathrm{exc}})RT}} \tag{25}$$

a plot of $\ln(k_{\mathrm{et}})_{\mathrm{calc}}$ versus the polarity parameters should be linear including the water point. In Figs. 5 and 6 we show these plots for the same mixtures as in Figs. 2 and 3. Clearly these figures support our calculations and conclusions.

We have performed similar calculations to those detailed previously for the other two systems presented in this paper, that is, the oxidation of $[\mathrm{Fe(CN)_6}]^{4-}$ by $[\mathrm{Co(NH_3)_5DMSO}]^{3+}$ and the electron transfer process in the binuclear complex $[\mathrm{Ru^{III}(NH_3)_5NCRu^{II}(CN)_5}]^{-}$. The results of those calculations appear in Tables 6 and 7, respectively. The data corresponding to the binuclear complex are for the optical electron transfer reaction

$$[\mathrm{(NH_3)_5Ru^{III}{-}NC{-}Ru^{II}(CN)_5}]^{-} \rightarrow [\mathrm{(NH_3)_5Ru^{II}{-}NC{-}Ru^{III}(CN)_5}]^{-} \tag{26}$$

and they have been obtained as follows: the energy corresponding to the optical transition, as well as the redox potentials of both ruthenium centers (in this case they are both electrochemically reversible so a conventional electrochemical procedure was employed) were measured. From these data, Eq. (12) allows us to obtain λ. In relation to this procedure for obtaining λ, it is worth pointing out that one

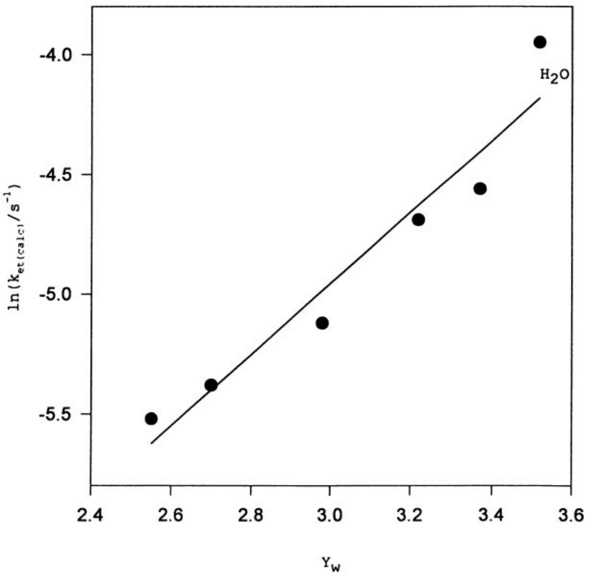

Fig. 5. Plot of $\ln(k_{et})_{calc}$ (s^{-1}) vs. the Grunwald–Winstein polarity parameter, Y_{GW}, in methanol–water mixtures at 298.2 K.

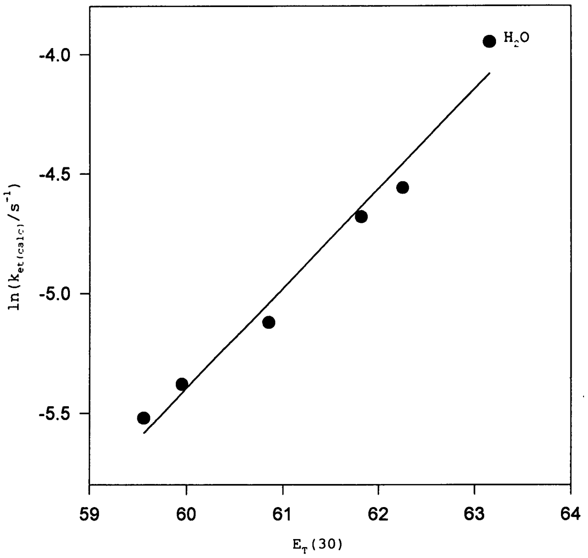

Fig. 6. Plot of $\ln(k_{et})_{calc}$ (s^{-1}) vs. the Reichardt polarity parameter, $E_T(30)$, in methanol–water mixtures at 298.2 K.

Table 6
Experimental and calculated solvent reorganization free energies, $(\lambda_{out})_{exp}$ and $(\lambda_{out})_{calc}$, respectively, and excess reorganization free energies, λ^{exc}, for the reaction $Co(NH_3)_5DMSO^{3+} + Fe(CN)_6^{4-}$ in different water–cosolvent mixtures at 298.2 K

%W [a]	Xs [b]	$(\lambda_{out})_{exp}$ (kJ mol^{-1})	$(\lambda_{out})_{calc}$ (kJ mol^{-1}) [c]	λ^{exc} (kJ mol^{-1}) [d]
Water–methanol				
0	0	113.2	113.2	0
10.0	0.0587	118.7	112.5	6.2
20.0	0.1232	119.5	111.9	7.6
30.0	0.1941	122.5	111.2	11.3
40.0	0.2726	127.8	110.6	17.2
Water–ethane-1,2-diol				
10.0	0.0312	113.5	111.5	2.0
20.0	0.0676	113.9	109.7	4.2
30.0	0.1106	111.7	108.0	3.7
40.0	0.1621	110.6	106.1	4.5
50.0	0.2249	110.7	104.5	6.2
60.0	0.3032	110.3	102.6	7.7
70.0	0.4037	111.3	100.9	10.4
80.0	0.5372	110.5	99.0	11.5
Water–acetonitrile				
10.0	0.0465	116.0	112.3	3.7
20.0	0.0989	115.0	111.4	3.6
30.0	0.1583	117.4	110.9	6.5
40.0	0.2263	118.2	110.4	7.8
50.0	0.3049	117.9	110.0	7.9
Water–glucose				
6.4	0.0068	114.9	111.5	3.4
13.1	0.0149	114.2	109.7	4.5
19.6	0.0237	114.0	108.0	6.0
26.0	0.0339	114.2	106.2	8.0
37.7	0.0571	113.4	102.6	10.8
49.2	0.0883	111.7	99.1	12.6

[a] Percent of organic cosolvent weight in the mixtures.
[b] Molar fractions of cosolvent in the mixtures.
[c] Calculated by using Eq. (20).
[d] Obtained by using Eq. (24).

could have some doubts about the applicability of Eq. (12), as it is written in terms of an energy parameter (E_{op}) and free energies ($\Delta G^{\circ\prime}$ and λ). It could be thought that on the right hand side of Eq. (12), instead of λ and $\Delta G^{\circ\prime}$, the corresponding energetic magnitudes should appear. Nevertheless, Marcus and Sutin [48] have convincingly argued that the parameter λ, appearing in Eq. (12) is better viewed as a free energy. It can also be argued that λ depends on the optical and static dielectric constants of the solvent while $\Delta G^{\circ\prime}$ depends on the static dielectric constant. As the temperature coefficient of these dielectric parameters is low, the entropic terms in $\Delta G^{\circ\prime}$ and λ must be low, and they indeed compensate to some extent [49]. This idea is supported by the fact that the intervalence absorption bands from symmetrical, localized, mixed valence compounds in aqueous solutions are nearly temperature independent. As, in these transitions, $\lambda = E_{\mathrm{op}}$, this result shows that the entropic term associated with λ is small [50]. On the other hand, the redox potentials obtained as mentioned above correspond, respectively, to processes (a)

$$[(\mathrm{NH_3})_5\mathrm{Ru^{III}}\text{–NC–}\mathrm{Ru^{II}(CN)_5}]^- \underset{-\mathrm{e}^-}{\overset{+\mathrm{e}^-}{\rightleftarrows}} [(\mathrm{NH_3})_5\mathrm{Ru^{II}}\text{–NC–}\mathrm{Ru^{II}(CN)_5}]^{2-} \quad (27)$$

and (b)

$$[(\mathrm{NH_3})_5\mathrm{Ru^{III}}\text{–NC–}\mathrm{Ru^{II}(CN)_5}]^- \underset{+\mathrm{e}^-}{\overset{-\mathrm{e}^-}{\rightleftarrows}} [(\mathrm{NH_3})_5\mathrm{Ru^{III}}\text{–NC–}\mathrm{Ru^{III}(CN)_5}]^{0} \quad (28)$$

instead of the process indicated in Eq. (26).

Consequently, the determination of $\Delta G^{\circ\prime}$ by the preceding method involves the following assumption: the redox potential of each ruthenium center is not affected by the oxidation state of the other (or at least that, if it is modified, the modifications compensate one another [51]). In this regard, some authors [52] have recently stated that the error inherent in this approximation depends on the donor number of the solvent. Such an error is a minimum for solvents whose donor numbers are about 15. In view of the donor number of water, which is 14 [53], and taking into account that the solvents used were rich in water, the donor number of those solvents must be close to 15. So the error in the estimation of $\Delta G^{\circ\prime}$, if any, must be small in the present case.

A consideration of Tables 5–7 makes clear the following fact: the excess of reorganization free energy appears in all the cases. However, the sizes of this contribution are quite different in the case of peroxidisulfate oxidation and in the intramolecular electron transfer in the binuclear complex. As this is also the order of decreasing internal free energy of reorganization, this fact could cast some doubt

Table 7
Experimental and calculated solvent reorganization free energies, $(\lambda_{\mathrm{out}})_{\mathrm{exp}}$ and $(\lambda_{\mathrm{out}})_{\mathrm{calc}}$, respectively, and excess reorganization free energies, λ^{exc}, for the MMCT band within the $[(\mathrm{NH_3})_5\mathrm{Ru^{III}}$–NC–$\mathrm{Ru^{II}(CN)_5}]^-$ complex in different water–cosolvent mixtures at 298.2 K

%W [a]	Xs [b]	$(\lambda_{\mathrm{out}})_{\mathrm{exp}}$ (kJ mol^{-1})	$(\lambda_{\mathrm{out}})_{\mathrm{calc}}$ (kJ mol^{-1}) [c]	λ^{exc} (kJ mol^{-1}) [d]
Water–methanol				
0	0	24.6	24.6	0
5.7	0.033	24.4	24.5	0
10.2	0.060	24.8	24.4	0.4
18.4	0.112	25.5	24.3	1.2
26.5	0.169	25.9	24.2	1.7
30.6	0.200	25.9	24.1	1.8
39.2	0.265	26.0	24.0	2.0

[a] Percent of organic cosolvent weight in the mixtures.

[b] Molar fractions of cosolvent in the mixtures.

[c] Calculated by using Eq. (20).

[d] Obtained by using Eq. (24).

in relation to our interpretation. It could be considered that λ^{exc} reflects some kind of interplay between solvent and internal modes participating in the reorganization or, in other words, that λ_{in} and λ_{out} are not independent parameters as we have assumed. In fact, although this approximation is generally accepted, it is not, strictly speaking, valid. That is, inner sphere reorganization should depend somewhat on the solvent, although this possibility is not usually taken into account. As an example in which the dependence of λ_{in} on the solvent is easily seen, one can cite an electron transfer process between bare ions, when the inner solvation sphere consists of solvent molecules. In this case, a change in the solvent implies a change in the nature of the ligands and therefore in λ_{in}. Nevertheless, there are other factors, such as hydrogen bond formation, which can influence λ_{in} through changes in the metal–ligand bond lengths and force constants, as well as through the conformation of the ligands [54]. In this sense, λ_{in} can be modified when the ability of the solvent to form hydrogen bonds changes. Consequently, in order to validate the previous interpretation of λ^{exc}, we have performed some simulations described below.

3.2. Simulations

In our simulations we have considered two kind of solvents: pure solvents and binary mixtures. In both cases we modeled the solvent molecules as dipolar nonpolarizable hard spheres. The solute (precursor and successor complexes) consisted of two hard spheres at fixed distance, in such a way that no contribution arising from internal reorganization is present in our simulations. In other words $\lambda_{\mathrm{in}} = 0$, so that, obviously, the possibility of a coupling between solvent and internal vibrations is ruled out. One of solute spheres bears a unit charge while the other is neutral (actually, this situation corresponds to the simple electron transfer process depicted in Fig. 4). Namely, we model a charge shift process. As the solvent molecules are considered nonpolarizable, the optical dielectric constant, $n^2 = 1$, for all the solvents, and Pekar's factor is then given simply by $(1 - 1/D_{\mathrm{S}})$. The D_{S} values were also obtained through simulations. The details of the calculations have been given elsewhere [55]. Fig. 7 shows the results of the simulations. The upper curve shows the reorganization free energy in solvent mixtures and the lower one shows the same parameter for pure solvents. The vertical distance between both curves represents λ^{exc} at the given value of the Pekar's factor. It is clear from the figure that the reorganization free energy is always higher for the mixture than for a pure solvent with the same Pekar's factor. It is also seen in the figure that λ^{exc} increases as the concentration of the less polar component increases, in the region rich in the more polar component in the mixture, as experimentally observed (see Tables 5–7). It is also important that, given the types of molecules used in the simulation, our results show that the existence of λ^{exc} does not arise either from any kind of specific solvent effects, which of course, are absent in our simulations, nor from a coupling of internal and external (solvent) vibrations. This does not imply that, in the case of real systems, these effects are not operative, but rather that, even in their absence, the excess of reorganization free energy would appear in solvent mixtures.

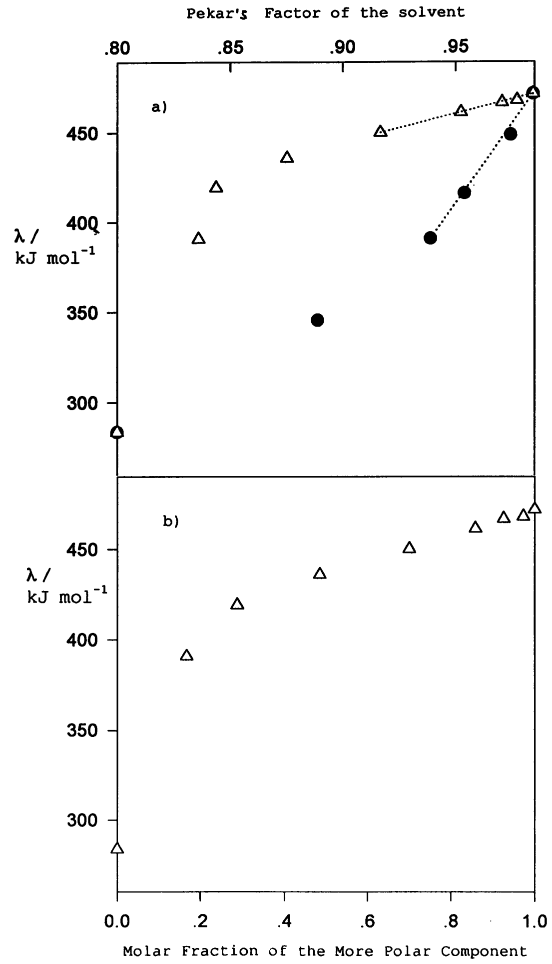

Fig. 7. (a) Plot of reorganization free energy vs. Pekar's factor for pure (circles) and mixed solvents (triangles) for a charge shift process obtained from Monte Carlo simulations. (b) Plot of reorganization free energy vs. the molar fraction of the more polar component in the mixture.

The results of the simulations also give support to our approach of using a fitted value for the parameter B (see Eqs. (20)–(23)). As seen in Fig. 7, in the region rich in the more polar component, the reorganization free energy (in the case of simulation the solvent reorganization free energy) is linear with Pekar's factor.

Finally, it is of interest to compare the solute–solvent radial distribution function, $g(r)$, around the solute particle, for both components in the mixture, for different values of the solute charge. In Fig. 8 (a and b) we show $g(r)$ for three different solute charges corresponding to the initial, intermediate [56] and final states. Fig. 8a corresponds to the radial distribution function of the less polar component around a solute charge, while Fig. 8b corresponds to the more polar solvent. As can be seen, the composition around the solute is richer in the less polar component when its charge is lower; just the opposite occurs with the more polar component. This means that some molecules of one of the component in the mixture must go away from the vicinity of the solute particle, while the molecules of the other solvent component should move into the neighborhood of the solute.

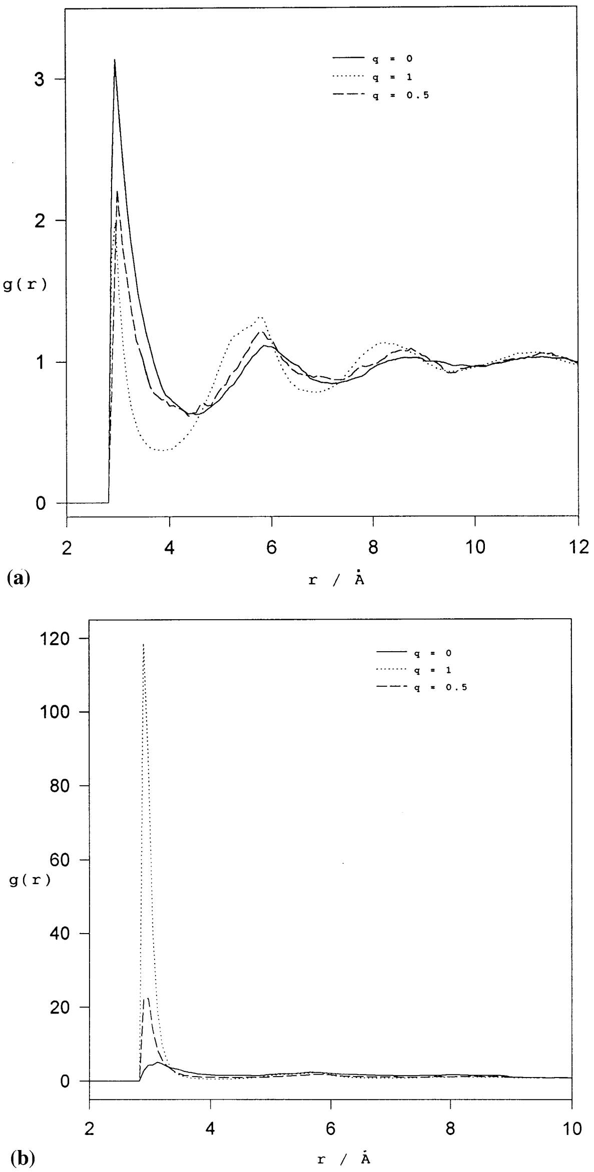

Fig. 8. Radial distribution function for the less polar component (a) and the more polar component (b) of the solvent mixture, around a solute particle at several charge states.

In this way, the molar composition of the solvent around a solute is quite distinct from that of its nominal bulk molar fraction. This modification in the solute local solvation produces an extra solvent reorganization free energy. This extra energy cannot show up, obviously, in pure solvents, because no change in the local composition of the solvent around the solute exists.

4. Conclusions

From previous results, it is clear that in the case of solvent mixtures, the dielectric properties of the solvent, are not enough alone to quantitatively characterize the activation process in electron transfer reactions, even in the absence of specific solvent effects. This is a consequence of the existence of an extra component of the solvent reorganization caused by changes of preferential solvation accompanying the electron transfer in the mixtures. This implies not only a change in the solvent orientation, but also changes in local compositions around the reactants in the activation process. Of course this component of the reorganization free energy is absent in pure solvents.

Acknowledgements

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