Medium effects on the electron transfer transition within the binuclear complex $[(NH_3)_5Ru^{III}{-}NC{-}Ru^{II}(CN)_5]^-$

Francisco Sánchez-Burgos, Manuel Galán, Manuel Domínguez and Pilar Pérez-Tejeda*

Departamento de Química Física, Facultad de Química, C/Prof. García González s/n, E-41012 Sevilla, Spain

The metal-to-metal charge transfer band within the binuclear complex pentaammineruthenium(III) (μ-cyano) pentacyanoruthenium(II) was studied in several media (water–methanol, water–glycerol, and lithium nitrate solutions) at 298.2 K. The Gibbs reorganization free energy was determined by combining the spectroscopic band maximum and electrochemical data. The solvent reorganization free energies obtained from this method agree quite well with those calculated by using the Marcus model, although the trend in changes of the calculated magnitude of this parameter is opposite to that found experimentally for water–methanol mixtures and lithium nitrate solutions. This effect can be explained by considering an additional component of the solvent reorganization free energy, caused by changes of the solvation shell of the complex as a consequence of electron transfer.

In the last few years we have been interested in the study of solvent effects in electron transfer reactions.[1]

The main conclusions from these works are the following. (*i*) The Marcus treatment for the calculation of the outer-sphere reorganization free energy, λ_{out}, works quite well if the *geometric factor* appearing in the λ_{out} formula is adjusted in order to fit the experimental datum corresponding to a given solvent (see Discussion). This procedure for obtaining λ_{out} has recently been suggested by Hupp and coworkers[2] and it is based on the idea that the relevant distance parameter used in the calculations of λ_{out} must be the *effective* electron transfer distance, instead of the *geometric* distance between the reactant centers. This suggestion has recently received theoretical support from the work of Jeon and King,[3] which suggests that the results of quantum-mechanical calculations of the reorganization free energy can be reproduced by using an *effective* cavity size in the calculations performed with the Marcus formula. (*ii*) In solvent mixtures, according to our data,[1b–d] the Marcus treatment still gives a good estimation of λ_{out}, but cannot reproduce the *fine structure* of this parameter. We have hypothesized that in these mixtures a new component of the reorganization free energy appears. This new component may arise from a translational movement of solvent molecules during the preferential solvation of the sites, as consequences of electron transfer.

Since the conclusion concerning solvent mixtures has been extracted from kinetic data by using some hypotheses in obtaining the reorganization free energy, a study where this parameter could be *directly* obtained from experimental non-kinetic data seemed pertinent. For this reason, we have studied the intervalence band in the mixed valence complex $[(NH_3)_5Ru^{III}{-}NC{-}Ru^{II}(CN)_5]^-$, in different water–cosolvent mixtures and in solutions of a supporting electrolyte. This compound was chosen because it shows a clear metal-to-metal charge transfer (MMCT) band in water[4,5] and because this binuclear complex belongs to class II in the Robin–Day classification,[6] which is essential to the purpose of this work. The selected system also permits the experimental estimation of the free energy change, $\Delta G^{\circ\prime}$, for the intervalence transition:

$$[(NH_3)_5Ru^{III}{-}NC{-}Ru^{II}(CN)_5]^- \xrightarrow{h\nu}$$
$$[(NH_3)_5Ru^{II}{-}NC{-}Ru^{III}(CN)_5]^-$$
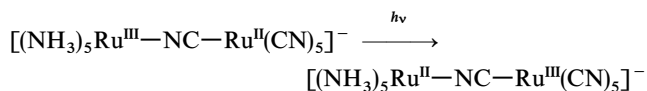
since both ruthenium centers exhibit reversible behaviour from an electrochemical point of view.

Results

Electrochemistry

In order to obtain experimental Gibbs energy changes, $\Delta G^{\circ\prime}$, corresponding to the above-mentioned electron transfer process, the formal standard redox potentials of the two centers in the binuclear complex were determined by electrochemical measurements (see Experimental). In Fig. 1 a typical differential pulse voltammogram is shown. The results are given in Table 1. From these redox potentials the free energy change, $\Delta G^{\circ\prime}$, corresponding to electron transfer can be calculated from

$$\Delta G^{\circ\prime} = -nF\,\Delta E^{\circ\prime} \qquad (1)$$

$\Delta E^{\circ\prime}$ being determined as $E_{1/2}(Ru_a^{III}) - E_{1/2}(Ru_b^{II})$. The values of $\Delta G^{\circ\prime}$ are also collected in Table 1.
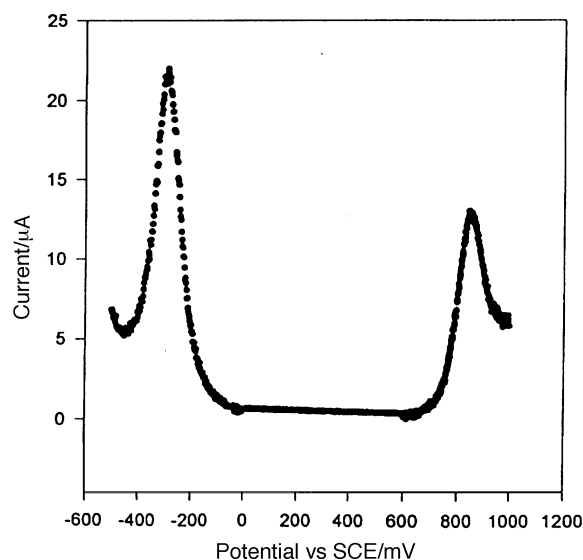
Fig. 1 Differential pulse voltammogram for the binuclear complex $[(NH_3)_5Ru^{III}{-}CN{-}Ru^{II}(CN)_5]^-$, in a methanol–water mixture (mole fraction = 0.033) at 298.2 K

Table 1 Redox potentials *vs.* NHE, $E_{1/2}$ and free energy change, $\Delta G^{\circ\prime}$ for the $[(NH_3)_5Ru_a^{III}\!-\!NC\!-\!Ru_b^{II}(CN)_5]^-$ complex in several media at 298.2 K

x_{org}	$E_{1/2}(Ru_a)$/V	$E_{1/2}(Ru_b)$/V	$\Delta G^{\circ\prime}$/kJ mol^{-1}
Methanol–water[a]			
0.033	−0.060	1.087	110.7
0.060	−0.055	1.080	109.5
0.112	−0.054	1.059	107.4
0.169	−0.054	1.047	106.2
0.200	−0.056	1.036	105.4
0.265	−0.045	1.027	103.4
Glycerol–water[a]			
0.020	−0.053	1.096	110.3
0.036	−0.050	1.098	109.1
0.077	−0.050	1.097	110.7
0.131	−0.058	1.094	111.1
0.165	−0.056	1.090	110.9
0.233	−0.065	1.078	110.3
[Salt]/mol dm^{-3}	$E_{1/2}(Ru_a)$/V	$E_{1/2}(Ru_b)$/V	$\Delta G^{\circ\prime}$/kJ mol^{-1}
LiNO$_3$			
0.2	−0.068	1.088	111.5
0.6	−0.053	1.105	111.7
1.0	−0.053	1.113	112.5
2.0	−0.052	1.117	112.8
3.0	−0.047	1.127	113.3
4.0	−0.038	1.145	114.1
5.0	−0.037	1.149	114.4

[a] In the water–cosolvent mixtures a 0.2 mol dm^{-3} concentration of LiNO$_3$ was always added.

It is worth pointing out that the redox potential obtained for the Ru^{III} center corresponds to the process:

$$[(NH_3)_5Ru^{III}\!-\!NC\!-\!Ru^{II}(CN)_5]^- + e^- \rightleftharpoons$$
$$[(NH_3)_5Ru^{II}\!-\!NC\!-\!Ru^{II}(CN)_5]^{2-}$$

and for the Ru^{II} center to:

$$[(NH_3)_5Ru^{III}\!-\!NC\!-\!Ru^{II}(CN)_5]^- \rightleftharpoons$$
$$[(NH_3)_5Ru^{III}\!-\!NC\!-\!Ru^{III}(CN)_5] + e^-$$
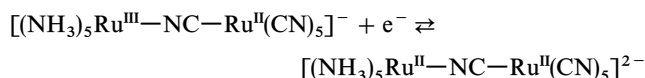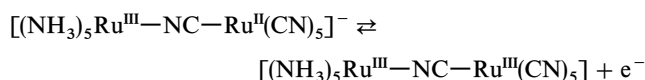
Therefore, the determination of $\Delta G^{\circ\prime}$ by the preceding method involves implicitly the following assumption: the redox potential of each ruthenium center is not affected by the oxidation state of the other. Recently, some authors[7] have stated that the error inherent in this approximation depends on the donor number of the solvents. Such an error is at a minimum for solvents whose donor numbers are about 15.[7] In view of the donor number of water, which is 14,[8] and taking into account that the media considered are rich in water, the donor number of our mixtures will be similar. Thus the error in $\Delta G^{\circ\prime}$ in our case, if any, should be small.

Spectroscopy

The binuclear complex $[(NH_3)_5Ru^{III}\!-\!NC\!-\!Ru^{II}(CN)_5]^-$ exhibits an MMCT band as mentioned above (this band is shown in Fig. 2 for a 0.2 mol dm^{-3} LiNO$_3$ solution). Table 2 summarizes the values of $E_{op} = h\upsilon_{max}$, the energy corresponding to the absorption maximum, and $\Delta\upsilon_{1/2}$, the full-width at half-height, obtained in the different media. In this table the refractive index values in the same media are also included. It can be observed that E_{op} decreases upon increasing the proportion of organic solvent in methanol–water and glycerol–water mixtures, while the E_{op} values increase with the concentration of the LiNO$_3$ solutions. These trends show typical behaviour corresponding to the MMCT band for a mixed valence compound belonging to class II in the Robin–Day classification.[10] That is, the maximum band energy is shifted to a lower value as the medium becomes less polar for
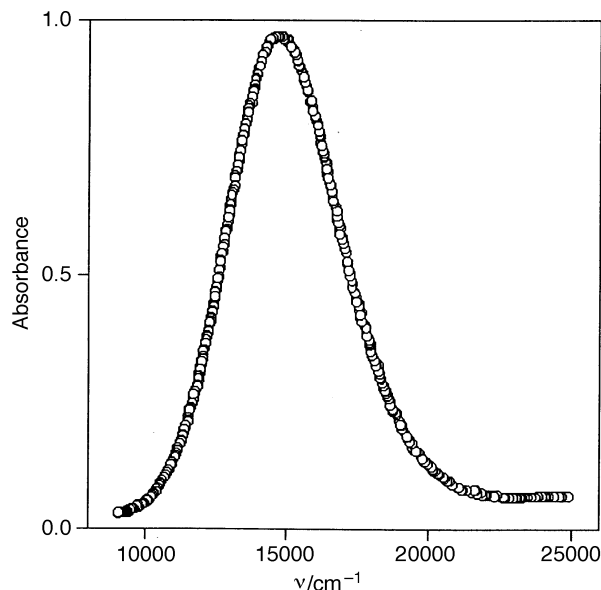

Fig. 2 Experimental spectrum of the MMCT band of the binuclear complex $[(NH_3)_5Ru^{III}\!-\!CN\!-\!Ru^{II}(CN)_5]^-$ in LiNO$_3$ solution (0.2 mol dm^{-3}) at 298.2 K

water–methanol and water–glycerol mixtures.[5,10] In the case of electrolyte solutions the trend of E_{op} values reflects the ionic strength influence, in agreement with other results.[11]

It can also be seen in Table 2 that the addition of electrolyte or organic solvent to pure water causes a small broadening in the intervalence band, the difference in $\Delta\upsilon_{1/2}$ being about 200 cm^{-1} for electrolyte solutions and 300–600 cm^{-1} for organic solvent mixtures. This kind of solvent effect is usually found in other mixed valence compounds.[12,13]

Table 2 Experimental values of E_{op} and $\Delta\upsilon_{1/2}$ for the MMCT band within the $[(NH_3)_5Ru^{III}\!-\!NC\!-\!Ru^{II}(CN)_5]^-$ complex and refractive index at 298.2 K for the different media

x_{org}	E_{op}/kJ mol^{-1}	$\Delta\upsilon_{1/2}{}^a$/cm^{-1}	n^b
Methanol–water[c]			
0.033	175.4	4985	1.3343
0.060	174.6	4996	1.3354
0.112	173.2	4942	1.3377
0.169	172.5	4944	1.3398
0.200	171.6	4995	1.3408
0.265	169.8	5172	1.342
Glycerol–water[c]			
0.020	175.9	4892	1.3441
0.036	175.4	5045	1.3523
0.077	174.9	4947	1.3703
0.131	173.8	4912	1.3891
0.165	173.3	5009	1.3985
0.233	172.8	4913	1.4141
[Salt]/mol dm^{-3}	E_{op}/kJ mol^{-1}	$\Delta\upsilon_{1/2}{}^a$/cm^{-1}	n^d
LiNO$_3$			
0.0	175.2	4600	1.3325
0.2	176.4	4776	1.3342
0.6	176.7	4811	1.3371
1.0	177.5	4600	1.3406
2.0	178.8	4776	1.3468
3.0	179.3	4779	1.3538
4.0	180.1	4799	1.3622
5.0	180.7	4779	1.3698

[a] $\Delta\upsilon_{1/2}$ values were calculated from the experimental spectra by taking the difference of the υ values for the high- and low-energy sides of the band at which $A/A_{max} = 1/2$. [b] Data taken from ref. 9. [c] In the cosolvent–water mixtures a 0.2 mol dm^{-3} concentration of LiNO$_3$ was always added. [d] This work (see Experimental).
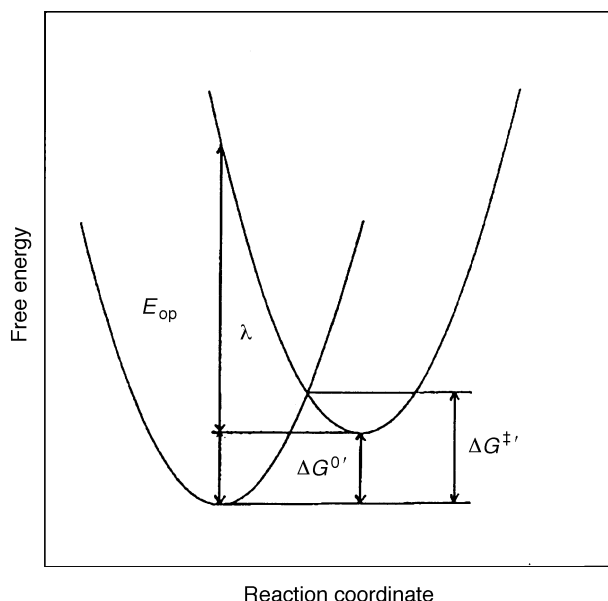
Fig. 3 Free energy surfaces (FES) showing the chacteristic magnitudes for the optical and thermal electron transfer processes

From the $\Delta G^{\circ\prime}$ and E_{op} data it is possible to calculate the reorganization energy, λ, by the equation:

$$E_{op} - \delta = \lambda + \Delta G^{\circ\prime} = \lambda_{in} + \lambda_{out} + \Delta G^{\circ\prime} \qquad (2)$$

where λ_{in} and λ_{out} are the intramolecular and solvent reorganization energies, respectively. The δ parameter in this equation represents a correction for the spin–orbit coupling of the excited state of the Ru^{II} center: in the octahedral symmetry the d^5T state of the metal is split by spin–orbit coupling into a higher degenerate E state and a lower A state. The energy separation of these states is $3\delta/2$, where δ is the spin–orbit coupling parameter.[12,14] Because of the existence of two

Table 3 Reorganization free energy values for the MMCT band within the $[(NH_3)_5Ru^{III}—NC—Ru^{II}(CN)_5]^-$ complex at 298.2 K

x_{org}	γ^a	λ_{exp}	$(\lambda_{out})_{calc}$	$(\lambda_{out})_{exp}$
Methanol–water^b				
0.000	0.5500	50.52	24.57	24.57
0.033	0.5486	50.35	24.51	24.41
0.060	0.5472	50.73	24.45	24.79
0.112	0.5445	51.46	24.31	25.52
0.169	0.5419	51.87	24.21	25.93
0.200	0.5406	51.88	24.15	25.94
0.265	0.5383	51.99	24.04	26.04
Glycerol–water^b				
0.020	0.5403	50.67	24.14	24.73
0.036	0.5333	50.26	23.82	24.31
0.077	0.5182	49.84	23.14	23.90
0.131	0.5031	48.33	22.47	22.39
0.165	0.4956	48.12	22.14	22.17
0.233	0.4834	48.20	21.56	22.26
[Salt]/mol dm^{-3}	γ^a	λ_{exp}	$(\lambda_{out})_{calc}$	$(\lambda_{out})_{exp}$
LiNO$_3$				
0.6	0.5438	50.58	24.29	24.64
1.0	0.5402	50.51	24.12	24.65
2.0	0.5319	51.63	23.75	25.69
3.0	0.5214	51.68	23.29	25.74
4.0	0.5069	51.63	22.64	25.69
5.0	0.4858	51.89	21.70	25.69

^{a} $\gamma = 1/n^2 - 1/D_S$; n and D_S values were taken from refs. 9 and 17, respectively, for aquo-organic mixtures; in LiNO$_3$ n values were taken from Table 2 of this work and D_S values were calculated according to ref. 18. All energies are in kJ mol^{-1}.

excited states, the experimental charge transfer band is the sum of two bands. The bands corresponding to the E and A states are at $\delta/2$ higher and δ lower energy, respectively, than the maximum absorption observed in the composite band. A value of 1200 cm^{-1} for δ was used in this work.[14]

The calculation of λ is based on eqn. (2), which is always true (see Fig. 3) provided that the interaction with the solvent is strong enough to ensure a structureless band.[2b] However, there has been some controversy over this equation, because it is written in terms of energy (E_{op}) and free energy ($\Delta G^{\circ\prime}$ and λ). For this reason it has been pointed out that in the second term of eqn. (2), instead of λ and $\Delta G^{\circ\prime}$ the corresponding energetic magnitudes should appear. Nevertheless, Marcus and Sutin[15] have convincingly argued that the parameters λ and $\Delta G^{\circ\prime}$, appearing on the right-hand side of eqn. (2), are better viewed as free energies. It can also be argued that λ depends on the optical and static dielectric constants of the solvent while $\Delta G^{\circ\prime}$ depends mainly on the static dielectric constant. For water, the temperature coefficients of these dielectric constants are small, so that the entropic terms must be small and they thus compensate to some extent.[16] Indeed, for an optical electron transfer the nuclei are frozen, so that the corresponding electronic entropy change would be:

$$\Delta S = R \ln \frac{\Omega^{exc}}{\Omega^g} \qquad (3)$$

where the Ω are the spin multiplicity of the corresponding excited or ground states. Thus, the corresponding free energy term should be $\simeq RT$, which is small in comparison to the E_{op} values. Consequently, we can take, in agreement with Marcus and Sutin,[15] λ and $\Delta G^{\circ\prime}$ as free energies. In fact, this is the approach that was used in order to interpret data concerning the same binuclear complex, $[(NH_3)_5Ru^{III}—NC—Ru^{II}(CN)_5]^{-}$,[5] and another closely related binuclear complex, $[(NH_3)_5Ru^{III}—NC—Fe^{II}(CN)_5]^{-}$,[2b] in water.

It is interesting to note in relation to the following discussion that the intramolecular reorganization energy, λ_{in}, appearing in eqn. (2), was determined from resonance Raman spectroscopy measurements for the complex used in this work.[5] Its value is 2169 cm^{-1}. On the other hand, the value of the solvent reorganization energy, λ_{out}, in water was established as 2400 cm^{-1} for the binuclear complex $[(NH_3)_5Ru^{III}—NC—Fe^{II}(CN)_5]^{-}$.[2b] Taking into account that the λ_{out} parameter will be similar for the $[(NH_3)_5Ru^{III}—NC—Fe^{II}(CN)_5]^{-}$ complex and the complex studied in this work, the total reorganization free energy, $\lambda = \lambda_{in} + \lambda_{out}$, in water can be estimated as 4569 cm^{-1} = 54.65 kJ mol^{-1}, which in reasonable agreement with the value obtained for this parameter, $\lambda_{exp} = 4223$ cm^{-1} = 50.51 kJ mol^{-1}, from eqn. (2) (see Table 3). The λ_{exp} values corresponding to other media used are also included in this table.

Discussion

As indicated at the beginning of this paper, the purpose of this work was to check the existence of an additional component in the reorganization free energy in solvent mixtures. This subject can be approached by a comparison between the reorganization free energy values obtained from eqn. (2), λ_{exp}, and those calculated by using Marcus' equation, λ_{calc} (see Table 3). The total reorganization free energy, λ_{calc}, was obtained from the sum of intramolecular, λ_{in}, and outer-sphere, λ_{out}, components.

The outer-sphere or solvent reorganization free energy is usually calculated by:

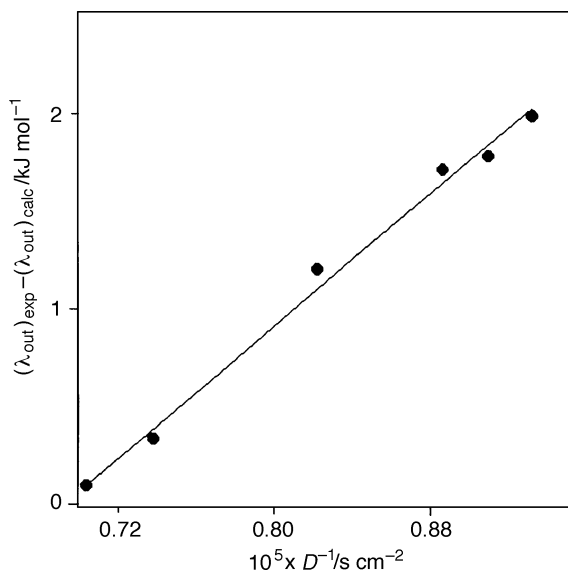$$(\lambda_{out})_{calc} = N_A e^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \gamma \qquad (4)$$

Fig. 4 Plot of $(\lambda_{out})_{exp} - (\lambda_{out})_{calc}$ *versus* diffusion coefficients for methanol–water mixtures at 298.2 K

$$\gamma = \frac{1}{n^2} - \frac{1}{D_S} \quad \text{(Pekar factor)} \quad (5)$$

where n and D_S are the refractive index and the static bulk dielectric constant of the medium, a_1 and a_2 are the acceptor and donor radii and R is the donor–acceptor distance, which must be considered as the *effective* distance of the electron transfer[2] and not as the geometric distance between the centers. For this reason, λ_{out} is better calculated by using an alternative method,[2] that is, as:

$$(\lambda_{out})_{calc} = A\gamma \quad (6)$$

where A represents an energetic factor, which involves the effective radii and the effective donor–acceptor distance for the electron transfer. A can be determined from:

$$A = \frac{(\lambda_{out})_{water}}{\gamma_{water}} = \frac{(\lambda_{exp})_{water} - \lambda_{in}}{\gamma_{water}} \quad (7)$$

With $\lambda_{in} = 1269$ cm^{-1}, as taken from ref. 5, a value for A of 44.67 kJ mol^{-1} results. Table 3 gives the calculated and experimental values for the solvent reorganization free energy, $(\lambda_{out})_{calc}$ and $(\lambda_{out})_{exp}$, respectively. The latter values were obtained from the difference between λ_{exp} for each medium and λ_{in} (it was assumed that this parameter is the same for every medium). This table also includes Pekar's factors for the different media.

As can be seen, the values of both $(\lambda_{out})_{calc}$ and $(\lambda_{out})_{exp}$ are close, the largest difference being about 15.5% for the LiNO$_3$ solution at a 5 mol dm^{-3} concentration. Thus, one can conclude that electrolyte solutions and mixed solvents are acceptably described by the dielectric properties appearing in Pekar's factor. However, as can be observed in Table 3, $(\lambda_{out})_{exp}$ and $(\lambda_{out})_{calc}$ for methanol–water mixtures and LiNO$_3$ solutions show opposite trends: for both media $(\lambda_{out})_{exp}$ increases on decreasing the water content, while Pekar's factor, and thus $(\lambda_{out})_{calc}$, decrease.

In the case of electrolyte solutions, the experimental trend of λ_{out} can be explained by considering an additional term, λ_{atm}, which takes into account the ionic atmosphere reorganization.[19] This contribution to the solvent reorganization energy comes from a different charge distribution in the ionic clouds before and after the electron transfer occurs. This contribution, of course, is not included in Pekar's factor. By way

of analogy, it is possible to explain the experimental trend of λ_{out} values for the methanol–water mixtures by considering an extra contribution to the solvent reorganization, which does not depend on Pekar's factor, as in electrolyte solutions. 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, which implies a movement of the solvent molecules before the electron transfer event.

In this regard it is worth pointing out that the importance of the changes in preferential solvation in mixed solvents in relation to electron transfer processes has been suggested by Curtis *et al.*[20] from thermodynamic (emf) measurements and by Hupp and Weydert[21] from the study of the metal-to-ligand charge transfer spectra of some complexes. Also, Piotrowiak *et al.*[22] and others[23] have explained some 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 metal-to-metal charge transfer processes in mixed solvents. However, related effects in the kinetics of the electron transfer processes have been pointed out by Nielsen *et al.*[24] in relation to primitive recognition effects in electron transfer reactions, and by the present authors[1c,1d] in order to rationalize kinetic results corresponding to thermal electron transfer processes in mixed solvents, as mentioned at the beginning of this paper.

Our interpretation of the extra component of λ in solvent mixtures receives further support from the following argument: the translational diffusion coefficient of methanol in water–methanol mixtures behaves anomalously, reaching a minimum at a methanol mole fraction ≈ 0.5.[25] If the diffusion coefficient D is considered as a measure of the translational mobility of solvent molecules, a correlation should be expected between the extra contribution of the reorganization free energy that depends on the movement of solvent molecules and the reciprocal of D. Fig. 4 exhibits such a correlation (the values of D were taken from ref. 26). It seems interesting to point out that in water–glycerol mixtures $(\lambda_{out})_{exp}$ is also somewhat higher than $(\lambda_{out})_{calc}$, which indicates that the extra solvent reorganization energy mentioned above must also exist in these types of mixtures, although it is not high enough to invert the trend in $(\lambda_{out})_{exp}$ as happens for methanol–water mixtures.

In conclusion, we have shown that dielectric properties of solvents, alone, cannot describe the reorganization process in the optical electron transfers when the solvent is a mixture, because 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 of the polarization, but also movement of some solvent molecules in the reorganization process accompanying the electron transfer. Of course this component is absent in pure solvents.

Experimental

Materials

The mixed valence compound Na[(NH$_3$)$_5$Ru^{III}—NC—Ru^{II}(CN)$_5$]·3H$_2$O was prepared and purified according to literature procedures.[4] The visible spectrum shows an MMCT band with an absorption maximum at 683 nm ($\varepsilon_{max} = 2850 \pm 50$ cm^{-1} mol^{-1} dm^3) in water.

Methanol, glycerol and lithium nitrate were purchased from Merck (quality p.a.) and used without further purification. Throughout the study, deionized water, obtained from a Millipore Milli-Q system, was used with a conductivity lower than 10^{-6} S m^{-1}.

The water–cosolvent mixtures were prepared by weight. The mole fractions (x_{org}) of the organic solvents (see Table 1) were chosen in order to achieve the following dielectric constants, D_S, in the media: 78.5 (pure water), 76, 74, 70, 66, 64, 60. The required weight percentages were taken from the literature.[17]

Different lithium nitrate solutions were also employed with concentrations ranging from 0.2 to 5 mol dm^{-3}. The dielectric constants for these electrolyte solutions were calculated according to the formula for the dielectric decrease given by Robinson and Stokes.[18]

Electrochemistry

The redox potentials of two centers in the binuclear complex were measured by a differential pulse voltammetry (DPV) technique. As the working electrode, a carbon paste electrode was used and the potential was measured against a saturated calomel electrode (SCE). The three-electrode assembly was completed with a platinum auxiliary electrode. The temperature was kept constant at 298.2 $\pm$ 0.1 K.

The system was calibrated by measuring the voltammogram of $K_4Ru(CN)_6$ in water with a 0.1 mol dm^{-3} concentration of sodium chloride as the supporting electrolyte. The peak potential vs. NHE was 0.927 V, somewhat higher than a previously published value (0.902 V).[27] For the mixed valence compound $[(NH_3)_5Ru^{III}—NC—Ru^{II}(CN)_5]^-$ the peak potentials vs. NHE in the presence of a 0.1 mol dm^{-3} concentration of NaCl were -0.058 V for the Ru^{III} and 1.082 V for the Ru^{II} centers, respectively. In the binuclear complex the rutheniumcyanide couple is shifted anodically 0.155 V from the potential of the free monomeric ion, while the ruthenium-ammine couple is cathodically shifted to a value of -0.058 V, to be compared with the 0.10 V of the $[Ru(NH_3)_6]^{3+/2+}$ couple.[28] These shifts can be explained on the basis of a substantial degree of electron donation through the cyanide bridge from the Ru^{II} to the Ru^{III} centers in the binuclear complex.[12]

The concentration of the mixed valence compound was 5×10^{-4} mol dm^{-3} for measurements in glycerol–water and lithium nitrate solutions. In methanol–water solutions the concentration was 1×10^{-4} mol dm^{-3} for solubility reasons. As the supporting electrolyte, lithium nitrate (0.2 mol dm^{-3}) was used for the mixtures containing organic solvents.

The relationship between the peak and the half-wave potentials for a reversible system is given by:[29]

$$E_{peak} = E_{1/2} + \Delta E/2 \qquad (8)$$

where ΔE is the voltage amplitude of the pulse (2 mV in our experiments), thus $E_{peak} \simeq E_{1/2}$. The uncertainty in the redox potentials is about ± 2 mV.

Spectroscopy

The spectra in the different media were recorded in a Hitachi 150-20 UV/VIS spectrophotometer at 298.2 K.

The concentration of the mixed-valence compound in the solutions varied from $1–5 \times 10^{-4}$ mol dm^{-3} depending on the solubility of the complex in the mixtures employed as solvents.

In order to check the possible influence of the concentration of the complex on the full-width at half-height and absorption maximum, different spectra were recorded in pure water with different concentrations of the binuclear complex in the range of $0.5–5 \times 10^{-4}$ mol dm^{-3}. Both the band maximum and the full-width were independent of the concentration in the above mentioned range: constant values of $\lambda_{max} = 682 \pm 1$ nm and $\Delta v_{1/2} = 4600 \pm 50$ cm^{-1} were found. In order to connect strictly the electrochemical with the spectroscopic data, the spectra were performed in the presence of LiNO$_3$ (0.2 mol dm^{-3}) for the media containing methanol and glycerol.

Refractive index measurements

The refractive indices of the lithium nitrate solutions were measured with an ATAGO Abbé Refractometer at 298.2 K. For the aquo-organic media the data were found in the literature.[9]

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