"Abnormal" Salt and Solvent Effects on Anion/Cation Electron-Transfer Reactions: An Interpretation Based on Marcus−Hush Treatment

E. Garcia-Fernandez, R. Prado-Gotor, and F. Sanchez*

Department of Physical Chemistry, Faculty of Chemistry. University of Sevilla, C/Profesor García González S/N, 41012 Sevilla, Spain

Salt and solvent effects on the kinetics of the reactions $[Fe(CN)_6]^{3-} + [Ru(NH_3)_5pz]^{2+} \rightleftarrows [Fe(CN)_6]^{4-} + [Ru(NH_3)_5pz]^{3+}$ (pz = pyrazine) have been studied through T-jump measurements. The forward and reverse reactions show different behaviors: "abnormal" salt and solvent effects in the first case and normal effects in the second one. These facts imply an asymmetric behavior of anion/cation reactions depending on the charge of the oxidant. The results can be rationalized by using the Marcus−Hush treatment for electron-transfer reactions.

Introduction

Classical theory of kinetic salt and solvent effects on anion/cation reactions, as given in current textbooks,[1] is based on the Brönsted equation[2]

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_{\neq}} \quad (1)$$

In this equation, k_o is the rate constant in a given reference state and γ_A, γ_B, and $\gamma_{\neq}$ are the activity coefficients of the reactants, A, B, and the transition state $\neq$. A negative salt effect is expected for anion/cation reactions according to the Brönsted equation. As to the solvent effects, this equation predicts an increase of the rate of the reaction when the dielectric constant of the reaction medium decreases. These predictions have been checked many times. In fact, the famous Livingston diagram[3] is a beautiful illustration for these predictions, in the case of salt effects. All this is well-known by scientists working in the field of chemical kinetics, up to such a point that salt and solvent effects are taken frequently as a criteria for mechanism diagnosis. It is less known that in the field of electron-transfer reactions there are cases in which a *positive* salt effect is found for anion/cation reactions.[4] Also, "abnormal" solvent effects for this kind of reaction (a decrease in the rate constant when the dielectric constant of the reaction medium decreases) have been found.[5]

To clarify these "abnormal" effects, we have carried out a kinetic study of the reactions

$$[Fe(CN)_6]^{3-} + [Ru(NH_3)_5pz]^{2+} \underset{k_f}{\overset{k_r}{\rightleftarrows}}$$

$$[Fe(CN)_6]^{4-} + [Ru(NH_3)_5pz]^{3+} \quad (2)$$
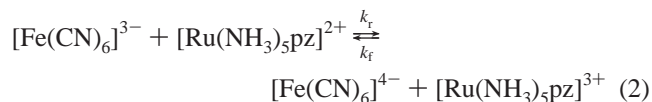
in different salt solutions. Also a study of the solvent effects (water + cosolvent mixtures) on these reactions is presented here. The results of these studies reveal the existence of "abnormal" salt and solvent effects for the forward reaction. However the reverse reaction shows a normal behavior. These

facts can be rationalized by using the Marcus−Hush[6] theory of electron-transfer processes.

Indeed, it is shown that the study of reversible electron-transfer reactions permits us to obtain the main parameters which control the kinetics of the electron-transfer reactions, the reorganization, λ, and reaction, $\Delta G'$, free energies. Knowledge of these parameters and their variations, when the reaction medium changes, is relevant. In particular, in the case of reactions between coordination complexes, this knowledge is of interest in relation to the implications of these electron-transfer processes in the design of novel systems of technological significance (e.g., molecular electronics or sensor devices).[7]

Experimental Section

Materials. The complex $[Ru(NH_3)_5pz]^{2+}$ (pz = pyrazine) has been prepared and purified according to the procedure described in the literature.[8] The other reagents, $LiNO_3$ and ethyleneglycol (used as a cosolvent), were all Anala.R grade and used as purchased. The water used in the preparation of solutions had a conductivity of less than 10^{-6} S m^{-1}.

Equilibrium Measurements. The equilibrium constants, Q, for reaction 2

$$Q = \frac{[Fe(CN)_6^{4-}][Ru(NH_3)_5pz^{3+}]}{[Fe(CN)_6^{3-}][Ru(NH_3)_5pz^{2+}]} \quad (3)$$

were obtained from spectrophotometric data. Measurements were performed at 472 nm, corresponding to the maximum of $[Ru(NH_3)_5pz]^{2+}$ absorbance, employing a Cary 500 Scan UV−vis−NIR spectrophotometer. At this wavelength, the molar absorption coefficient of this complex is 12 956 mol^{-1} dm^3 cm^{-1}. A small correction for the absorbance of $[Fe(CN)_6]^{3-}$ ($\epsilon_{472} = 14$ mol^{-1} dm^3 cm^{-1}) was applied. The *initial* concentrations of the reactants in these experiments were $[Ru(NH_3)_5pz^{2+}] = 10^{-4}$ mol dm^{-3} and $[Fe(CN)_6^{3-}] = 4 \times 10^{-4}$ mol dm^{-3}, in water + cosolvent mixtures. These mixtures contained NaClO$_4$ at a 0.3 mol dm^{-3} concentration in order to work in the same conditions as in the kinetic experiments (see below). In salt solutions, $[Fe(CN)_6^{3-}]$ and $[Ru(NH_3)_5pz^{2+}]$ ranged from 1.03 × 10^{-4} to 4.5 × 10^{-4} mol dm^{-3}.

* To whom correspondence should be addressed. Tel: +34-954557175. Fax: +34-954557174. E-mail: gcjrv@us.es.

Kinetic Measurements. The kinetics of the reactions in eq 2 were studied by the T-jump technique using a Hi-Tech model SF-61 apparatus. The concentrations of the reactants ranged from 5.16×10^{-5} to 2.25×10^{-4} mol dm^{-3} for $[Ru(NH_3)_5pz]^{2+}$ and $[Fe(CN)_6]^{3-}$, in the case of salt solutions. In water−cosolvent mixtures, $[Ru(NH_3)_5pz^{2+}] = 5 \times 10^{-5}$ mol dm^{-3} and $[Fe(CN)_6^{3-}] = 2 \times 10^{-4}$ mol dm^{-3}. As in our apparatus the T-jump is the consequence of the discharge of a capacitor, $NaClO_4$ at concentration 0.3 mol dm^{-3} was added to water + cosolvent mixtures in order to permit the discharge. The initial temperature and the voltage were adjusted according to the instructions of the apparatus in such a way that a final temperature (after the T-jump) of 298.2 K was reached. After the perturbation of the system, the absorbance was recorded up to equilibrium (at 298.2 K).

Under our working conditions, relaxation time is given by[9]

$$\frac{1}{\tau} = k_r\{Q([Fe(CN)_6^{3-}]_{eq} + [Ru(NH_3)_5pz^{2+}]_{eq}) + [Fe(CN)_6^{4-}]_{eq} + [Ru(NH_3)_5pz^{3+}]_{eq}\} \quad (4)$$

From this equation and from the values of $Q = k_f/k_r$ both rate constants can be obtained easily.

Results

Tables 1 and 2 contain the values of Q and τ corresponding to salt solutions and water cosolvent mixtures, respectively. These values have been obtained as follows: each experimental value is the average of, at least, three independent experiments. For salt solutions (see eq 3)

$$Q = K\frac{\gamma_3 - \gamma_{2+}}{\gamma_4 - \gamma_{3+}} + BI \quad (5)$$

where γ_i is the activity coefficient of the ion of the charge indicated and K the *thermodynamic* equilibrium constant. Taking the logarithm in eq 6, and using an extended Debye−Hückel equation for the activity coefficients,[10] the result is

$$\log Q = \log K + \frac{A\sqrt{I}}{1 + \sqrt{I}} \quad (6)$$

The values of Q fit well to this equation (see Figure 1). Thus, the values of Q appearing in Table 1 are the values resulting from this fitting procedure. Analogously, the values of τ appearing in this table have been obtained following the same procedure.

The values of Q and τ for water + cosolvent mixtures appearing in Table 2 are, as those in Table 1, the values resulting from the fit of the experimental values of these parameters to eq 7 (see Figure 2)

$$P = \frac{P_w + MxP_c}{1 + MxP_c} \quad (7)$$

In this equation, P is the value of the parameter (Q or τ) in the water cosolvent mixture, P_w is the value in water and P_c is the value in the cosolvent, M is an adjustable parameter, and $x = x_c/x_w$, that is, the ratio between the mole fractions of the cosolvent and water.[11]

Discussion

(a) Salt Solutions. From data in Tables 1 and 2, the values of k_f and k_r have been obtained. These values are given in Table
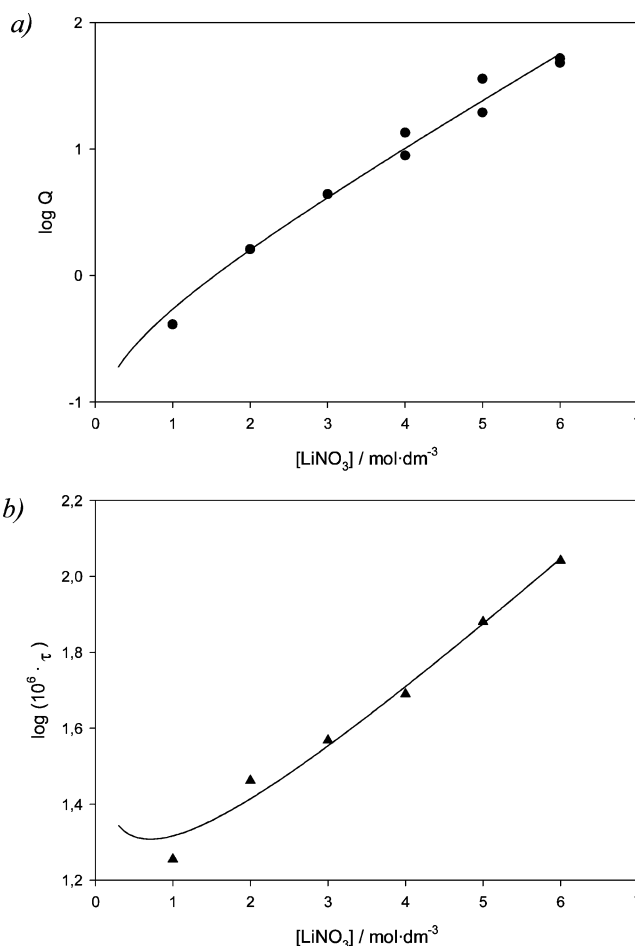

Figure 1. (a) Plot of log Q vs $[LiNO_3]$/mol dm^{-3} and (b) plot of log($10^6\tau$) vs $[LiNO_3]$/mol dm^{-3}. In both cases, the dots are the experimental data and the lines are the best fit obtained by using eq 6.

TABLE 1: Values of the Equilibrium Constant, Q,[a] and Relaxation Time, τ,[b] Corresponding to Salt Solutions

$[LiNO_3]$/mol dm^{-3}	Q	$10^6\tau$/s	$[LiNO_3]$/mol dm^{-3}	Q	$10^6\tau$/s
1	0.5	20.7	4	10.1	51.3
2	1.6	26.0	5	24.1	75.0
3	4.1	35.8	6	56.4	111.3

[a] See eq 3. [b] See eq 4.

TABLE 2: Values of the Equilibrium Constant, Q, and Relaxation Time, τ, Corresponding to Water + Co-solvent Mixtures

% cosolvent	Q	$10^6\tau$/s	% cosolvent	Q	$10^6\tau$/s
0	0.09	23.3	15	0.04	32.0
5	0.06	25.9	20	0.03	35.6
10	0.05	28.8	25	0.03	39.8

[a] See eq 3. [b] See eq 4.

3. As mentioned in the introductory section, these rate constants, *although both of them* correspond to anion/cation reactions, show opposite trends when the concentration of the salt is varied. The trend of k_r can be considered normal, according to the classical theory of salt effects. On the contrary, the trend of k_f can be considered abnormal according to this theory. It is interesting to note that variations in k_r are much greater than those of k_f. This suggests that these variations are the consequence of two factors. These two factors would act in an opposite sense in the case of k_f and in the same sense in the case of k_r.
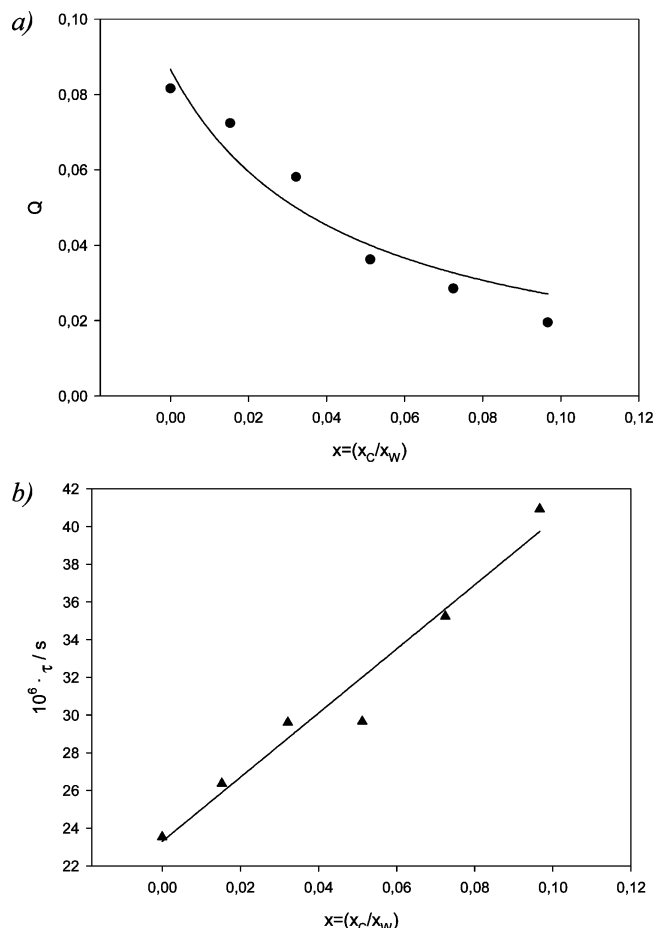
Anion/Cation Electron-Transfer Reactions

J. Phys. Chem. B, Vol. 109, No. 31, 2005 **15089**

Figure 2. (a) Plot of the equilibrium constant, Q, vs x (see text) and (b) plot of the relaxation time ($10^6\tau$)/s vs x (see text) for water + cosolvent mixtures. In both cases, the dots are the experimental data and the lines are the best fit obtained by using eq 7.

TABLE 3: Values of Observed Rate Constants, k_f/mol^{-1} dm^3 s^{-1}, k_r/mol^{-1} dm^3 s^{-1}, $(Q_{ip})_f$/mol^{-1} dm^3, $(Q_{ip})_r$/mol^{-1} dm^3, $(k_{et})_f$/s^{-1}, and $(k_{et})_r$/s^{-1} Corresponding to Salt Solutions

[LiNO$_3$]/ mol dm^{-3}	$10^{-8} k_f$	$10^{-8} k_r$	$(Q_{ip})_f$	$(Q_{ip})_r$	$10^{-8} (k_{et})_f$	$10^{-7} (k_{et})_r$
1	3.3	6.2	3.6	12.8	0.9	4.8
2	4.7	3.0	3.3	11.1	1.4	2.7
3	5.4	1.3	3.2	10.4	1.7	1.3
4	5.8	0.6	3.2	10.0	1.8	0.6
5	6.3	0.3	3.1	9.9	2.0	0.3
6	6.5	0.1	3.1	9.6	2.1	0.1

Under conditions prevailing in this work, that is

$$Q_{ip}[R] \ll 1 \tag{8}$$

where Q_{ip} is the equilibrium constant corresponding to the formation of the encounter complex from the separate donor and acceptor, and [R] is the concentration of the reactant (donor
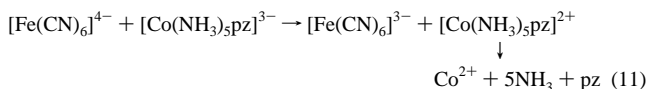
$$A + D \overset{Q_{ip}}{\rightleftharpoons} A/D \tag{9}$$

or acceptor) in excess, k_f and k_r are given by[12]

$$k_r = (Q_{ip})_r (k_{et})_f \tag{10a}$$

$$k_r = (Q_{ip})_r (k_{et})_r \tag{10b}$$

The values of Q_{ip} (f and r) have been obtained from the *experimental* values of this parameter appearing in ref 13. The

values in this reference correspond, in fact, to a closely related electron-transfer reaction

$$[Fe(CN)_6]^{4-} + [Co(NH_3)_5pz]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Co(NH_3)_5pz]^{2+}$$
$$\downarrow$$
$$Co^{2+} + 5NH_3 + pz \tag{11}$$

Thus, Q_{ip} for the reactions presented here can be obtained from those of eq 11, after correction of the distance of the ions in the encounter complex for the reverse reaction and, in the case of the forward reaction, after an additional correction of the charges. In this way, the values of $(Q_{ip})_f$ and $(Q_{ip})_r$ appearing in Table 3 have been obtained. Finally, using eq 10, the values of $(k_{et})_f$ and $(k_{et})_r$ have been calculated. These values are given in Table 3.

Now the cause of the normal behavior of k_r and the abnormal behavior of k_f are clearly seen: In the case of k_r, both $(Q_{ip})_r$ and $(k_{et})_r$ decrease as the salt concentration is increased. In the case of k_f, $(Q_{ip})_f$ decreases, but $(k_{et})_f$ increases as the salt concentration is increased. Thus, the abnormal behavior of k_f is due to the fact that the electron-transfer process (that is, the electron transfer at the encounter) shows a *positive* salt effect,

$$[Fe(CN)_6]^{3-}/[Ru(NH_3)_5pz]^{2+} \xrightarrow{(k_{et})_f}$$
$$[Fe(CN)_6]^{4-}/[Ru(NH_3)_5pz]^{3+} \tag{12}$$
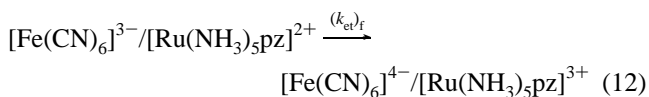
which is more marked than the negative salt effect on $(Q_{ip})_f$. In the case of k_r, both $(Q_{ip})_r$ and $(k_{et})_r$ show a negative salt effect.

To gain a deeper insight into the different behavior of $(k_{et})_f$ and $(k_{et})_r$ in regard to salt effects, the Marcus–Hush formulation for the electron-transfer processes will be used. According to this treatment, the rate constant for processes of this kind is given by[14]

$$k_{et} = \kappa_{el} \nu_n e^{-\Delta G^{\ddagger}/RT} \tag{13}$$

Here κ_{el}, ν_n, and $\Delta G^{\ddagger}$ are the electronic transmission coefficient, the nuclear frequency factor, and the (Gibbs) free energy of activation, respectively. The latter is given by

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G')^2}{4\lambda} \tag{14}$$

The λ parameter appearing in this equation is the so-called (free) energy of reorganization for the electron-transfer process (eq 12). This free energy is constituted by a solvent contribution, λ_s, an ionic atmosphere contribution, λ_{at}, and a contribution, λ_i, arising from the internal reorganization of the donor and the acceptor. The latter is usually considered as independent of the reaction media.

Except for strongly nonadiabatic processes, the preexponential term in k_{et} is of the order of the (average) vibratory frequency promoting the activation of the precursor complex. Thus, a value of $10^{12}-10^{13}$ s^{-1} seems reasonable. In the following calculations, a value of 6.62×10^{12} s^{-1} was used. This value corresponds to the value of the preexponential factor in the expression of the rate constant given by the classical transition state theory (k_BT/h) at our working temperature. In this way, $\Delta G^{\ddagger}$ can be obtained from k_{et}

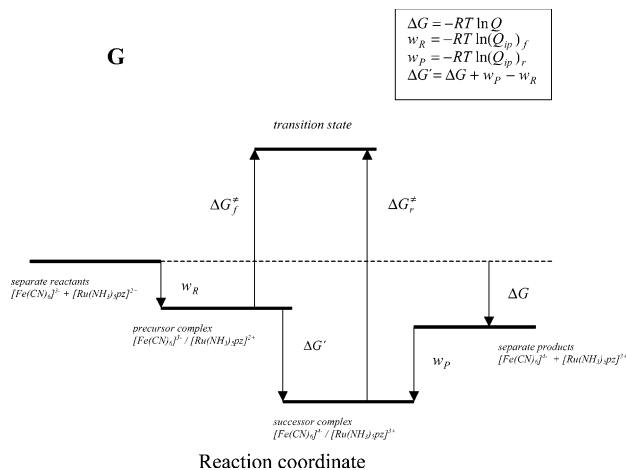$$\Delta G' = -RT \ln \frac{k_{et}}{6.62 \times 10^{12}} \tag{15}$$

G

$$\begin{aligned} \Delta G &= -RT \ln Q \\ w_R &= -RT \ln(Q_{ip})_f \\ w_P &= -RT \ln(Q_{ip})_r \\ \Delta G' &= \Delta G + w_P - w_R \end{aligned}$$

Figure 3. Reaction diagram showing the relationship between different relevant free energies (see text) in salt solutions.

G

$$\begin{aligned} \Delta G &= -RT \ln Q \\ w_R &= -RT \ln(Q_{ip})_f \\ w_P &= -RT \ln(Q_{ip})_r \\ \Delta G' &= \Delta G + w_P - w_R \end{aligned}$$
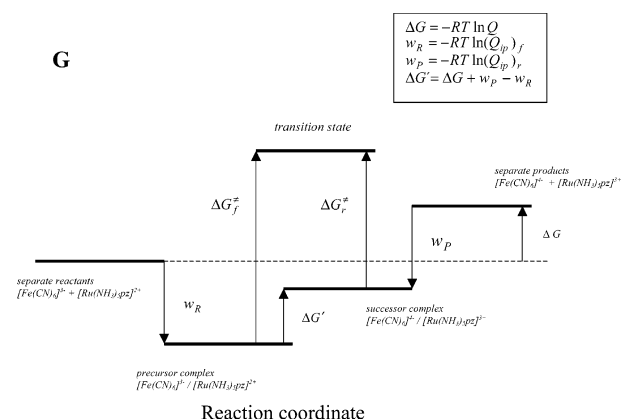

Figure 4. Reaction diagram showing the relationship between different relevant free energies (see text) in water + cosolvent mixtures.

The parameter $\Delta G'$ in eq 14 is the (standard formal) free energy corresponding to the electron-transfer process (eq 12) which produces the successor complex from the precursor complex. This parameter is different from ΔG, the (standard formal) free energy of reaction which produces the separate products from the separate reactants (eq 2). This latter is, of course

$$\Delta G = -RT \ln Q \tag{16}$$

and can be calculated from the values of Q appearing in Table 1. The ΔG and $\Delta G'$ values are related through (see Figures 3 and 4)

$$\Delta G' = \Delta G + w_p - w_R \tag{17}$$

Here w_R and w_P are the free energies corresponding to the formation of the precursor complex from the separate reactant and the formation of the successor complex from the separate products.

For the forward reaction

$$w_R = -RT \ln(Q_{ip})_f$$

$$w_p = -RT \ln(Q_{ip})_r \tag{18}$$

In this way, $(\Delta G')_f$ appearing in Table 4 can be calculated (it is clear that $(\Delta G')_r = -(\Delta G')_f$).

Finally, the values of λ_f, which also appear in Table 4, have been calculated from $(\Delta G^{\ddagger})_f$ and $(\Delta G')_f$ using eq 14. In the table, λ_r also appears, calculated from $(\Delta G^{\ddagger})_r$ and $(\Delta G')_r$. It is

TABLE 4: Values of $(\Delta G')_f$/kJ mol^{-1}, λ_f/kJ mol^{-1}, and λ_r/kJ mol^{-1} Corresponding to Salt Solutions

[LiNO$_3$]/ mol dm^{-3}	$(\Delta G')_f$	λ_f	λ_r	[LiNO$_3$]/ mol dm^{-3}	$(\Delta G')_f$	λ_f	λ_r
1	−1.6	113.3	113.3	4	−8.6	119.9	119.9
2	−4.1	114.0	114.0	5	−10.7	123.0	123.0
3	−6.4	116.6	116.6	6	−12.8	126.2	126.3

interesting to note that λ_f and λ_r are the same, in agreement with the Marcus–Hush theory.

Now it is clearly seen that the different salt effects on $(k_{et})_f$ and $(k_{et})_r$ are due to the differences in $\Delta G'$. That is, the forward reaction becomes more favorable when the salt concentration increases, and (obviously) the opposite is true for the reverse reaction. These facts are the consequence of the character (anion or cation) of the donor and the acceptor in these reactions. Thus, in the case of the forward reaction, the donor is a cation and the acceptor an anion. In this way, the $[Fe(CN)_6]^{3-}$ species becomes a more powerful oxidant and the $[Ru(NH_3)_5pz]^{2+}$ a more reductant species in the presence of the salts. This is clearly seen from the equation

$$E^{\circ\prime} = E^{\circ} + \frac{RT}{F} \ln \frac{\gamma_{ox}}{\gamma_{red}} \tag{19}$$

which gives the standard formal redox potential of a given ox/red couple. For the $[Fe(CN)_6]^{3-/4-}$ couple, both γ_{ox} and γ_{red} decrease with increasing salt concentration. But the decrease in γ_{red} is more marked because of the higher absolute charge of the reduced form of this couple. Thus, $E^{\circ\prime}$ increases as the salt concentration increases. The opposite is true for the cationic $[Ru(NH_3)_5pz]^{3+/2+}$ couple. Consequently, the reaction becomes more favorable from a thermodynamic point of view.

A conclusion emerges from the previous discussion: In the anion/cation electron-transfer reactions, salt effects operate in opposite directions on Q_{ip} and k_{et} when the oxidant is an anion, because Q_{ip} decreases as the salt concentration increases and k_{et} increases because the reaction becomes more favorable from a thermodynamic point of view. Therefore, the sign of the salt effect on the observed rate constant ($k = Q_{ip}k_{et}$) will depend on the magnitude of these effects: If the increase of k_{et} is higher than the decrease of Q_{ip}, when the salt concentration increases, then a positive salt effect will be seen (as here). However, if the decrease of Q_{ip} is higher than the increase of k_{et}, then a negative salt effect will be observed.

For anion/cation electron-transfer reactions in which the oxidant is the cation, salt effects on k_{et} and Q_{ip} will go in the same direction. Consequently, in this case, a negative salt effect will *always* be seen.

(b) Solvent Effects. Now the data corresponding to the water + cosolvent mixtures will be considered. These mixtures have a lower dielectric constant than that of water. Consequently, according to the classical theory of solvent effects, an increase in rate should be expected, when the amount of cosolvent in the reaction media increases. This prediction, according to data in Table 5, is accomplished by k_r but not by k_f. This table also contains $(Q_{ip})_f$ and $(Q_{ip})_r$ values, calculated as indicated in the case of salt effects, as well as the value of $(k_{et})_f$ and $(k_{et})_r$.

It is clear that failure of the classical theory for k_f arises from the fact that $(k_{et})_f$ decreases as the amount of cosolvent increases. The cause of this decrease is clearly seen if one considers the data in Table 6. These data have been obtained following the same procedure employed in the case of salt effects. It is seen that the different behavior of $(k_{et})_f$ and $(k_{et})_r$ comes, in this case, from the fact that the forward reaction becomes less favorable

Anion/Cation Electron-Transfer Reactions

J. Phys. Chem. B, Vol. 109, No. 31, 2005 **15091**

TABLE 5: Values of Observed Rate Constants k_f/mol^{-1} dm^3 s^{-1}, k_r/mol^{-1} dm^3 s^{-1}, $(Q_{ip})_f$/mol^{-1} dm^3, $(Q_{ip})_r$/mol^{-1} dm^3, $(k_{et})_f$/s^{-1}, and $(k_{et})_r$/s^{-1} Corresponding to Water + Cosolvent Mixtures

% cosolvent	$10^{-7}k_f$	$10^{-8}k_r$	$(Q_{ip})_f$	$(Q_{ip})_r$	$10^{-7}(k_{et})_f$	$10^{-7}(k_{et})_r$
0	6.1	7.1	4.3	18.5	1.4	3.8
5	4.8	7.4	4.3	18.8	1.1	3.9
10	3.8	7.6	4.4	19.2	0.9	4.0
15	3.1	7.7	4.5	20.0	0.7	3.8
20	2.5	7.6	4.5	20.1	0.6	3.8
25	1.8	8.4	4.6	21.2	0.4	4.0

TABLE 6: Values of $(\Delta G')_f$/kJ mol^{-1}, λ_f/kJ mol^{-1}, and λ_r/kJ mol^{-1} Corresponding to Water + Cosolvent Mixtures

% cosolvent	$(\Delta G')_f$	λ_f	λ_r	% cosolvent	$(\Delta G')_f$	λ_f	λ_r
0	2.5	123.6	123.6	15	4.3	127.2	127.2
5	3.2	124.8	124.8	20	4.7	128.3	128.3
10	3.8	125.9	125.9	25	5.2	130.8	128.5

when the proportion of cosolvent increases. Again eq 19 can be used in order to explain this. A decrease of the dielectric constant of the solvent will produce a destabilization of ions. Thus, γ_{ox} and γ_{red} will increase. For the forward reaction, γ_{red} will increase more than γ_{ox} in the case of the $[Fe(CN)_6]^{3-/4-}$ couple, in such a way that the $[Fe(CN)_6]^{3-}$ will become less of an oxidant. On the contrary, $[Ru(NH_3)_5pz]^{2+}$ will be less of a reductant since for the couple, $[Ru(NH_3)_5pz]^{3+/2+}$, γ_{ox} will increase more than γ_{red}.

Thus, the forward electron-transfer reactions becomes less favorable when the proportion of cosolvent increases. As the diminution of $(k_{et})_f$ (as a consequence of the fact that this reaction is becoming less favorable thermodynamically) is larger than the increase of $(Q_{ip})_f$ (caused by the diminution of the dielectric constant of the reaction media) an "anomalous" solvent effect appears. Of course, in the case of the reverse reaction, the effect of the solvent on both $(k_{et})_r$ and $(Q_{ip})_r$ go in the same direction and then a normal solvent effect is observed. In this regard, it is interesting to note that the solvent effect on $(k_{et})_r$ is small. This is a consequence of the fact that, although this reaction is becoming more favorable thermodynamically, when the amount of cosolvent increases, the reorganization energy also increases (see Table 6).

This increase of the reorganization energy in water cosolvent mixtures deserves some comment. As mentioned previously, the reorganization energy has three components: an internal contribution, λ_i, independent of the reaction media, a solvent contribution, λ_s, and an ionic atmosphere contribution, λ_{at}. The two latter contributions depend on the reaction media, λ_s through Pekar's factor, where $\gamma = (1/n^2) - (1/D)$. In this factor, n^2 is the square of the refraction index, that is, the optical dielectric constant of the solvent, and D is the static dielectric constant. Thus[6]

$$\lambda_s = N_A e^2 \left(\frac{1}{2r_A} + \frac{1}{2r_D} - \frac{1}{d_{AD}} \right) \gamma \tag{20}$$

where r_A, r_D, and d_{AD}, respectively, are the radii of A and D and the distance between their centers at the encounter.

As Pekar's factor decreases in the water−cosolvent mixtures used here, a decrease of λ_s should be expected, when the proportion of the cosolvent in these mixtures is increased. On the other hand, λ_{at} is given by

$$\lambda_{at} = \frac{N_A e^2}{\epsilon_s d_{AD}} \left(\frac{\kappa a - 1 + \exp(-\kappa a)}{\kappa a + 1} \right) \tag{21a}$$

$$\kappa = \left[\frac{8\pi N_A e^2 I}{1000 D k_B T} \right]^{1/2} \tag{21b}$$

So, it depends somewhat on the solvent because parameter κ, which represents the inverse Debye length, depends on the (static) dielectric constant of the mixture. At constant ionic strength, as in our experiments in water + cosolvent mixtures, an increase of λ_{at} is expected when the proportion of the cosolvent grows. However, this contribution is small: from water to the more rich (in cosolvent) mixture the contribution of λ_{at} is calculated to be 35 J/mol. Consequently, the observed increase in the reorganization energy cannot be accounted for from the λ_{at} contribution.

To explain the increase in λ, it is important to realize that our data correspond to solvent mixtures, instead of neat solvents. In these mixtures, when the electron transfer happens, both reactants change their charges and, consequently, a modification of the *composition* of their solvations shells is expected (this modification, of course, is absent in neat solvents). This change in the composition of the solvation shells 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 (not only the solvent polarization) must be intermediate between the positions corresponding to the (preferential) solvation of the precursor and successor complexes (eq 12). It is important to see 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 the activation step. This extra component to the reorganization energy would have the same origin as λ_{at}, but in this case, it is the reorganization of the solvent, instead of the reorganization of the ions, which produces it.

It is worth pointing out that this component of the reorganization energy has been observed by some of the present authors in previous works[15] as well as by other authors. Thus, Curtis et al.[16] suggested this extra contribution from the results obtained through thermodynamic (redox) measurements corresponded to some inorganic complexes in solvent mixtures. A similar conclusion was reached by Hupp et al.[17] from the study of the spectra of some complexes in solvent mixtures. Moreover, the existence of this extra component of the solvent reorganization energy in solvent mixtures has been predicted theoretically by Matyushov[18] and corroborated through simulations.[19] Consequently, the increase in λ observed here for water−cosolvent mixtures is an expected result.[20]

In conclusion, it has been shown that anion/cation electron-transfer reactions behave differently when the oxidant is an anion or a cation. In the latter case (back process here), salt and solvent effects on Q_{ip} and k_{et} go in the same direction in such a way that the observed total effect is the one predicted by the classical theory of medium effects. On the contrary, when the oxidant is an anion, salt and solvent effects on Q_{ip} and k_{et} go in the opposite direction in such a way that effects contrary to the predictions of the classical theory *may* appear. This will happen if the effects on k_{et} are more marked than the effects on Q_{ip}, as is the case here. It has also been shown that the Marcus−Hush treatment on electron-transfer reactions gives a clear picture of the cause of the "abnormal" medium effects: These "abnormal" effects appear in the case of salt effects when the free energy of reaction becomes more favorable with the increase in salt concentration (forward reaction here). Solvent effects appear as "abnormal" when the diminution of the dielectric constant of the mixtures

implies a less favorable free energy of reaction (forward reaction here). Finally, it is also of interest to point out that this interpretation has been facilitated by the simultaneous study of the forward and reverse electron-transfer reactions of two redox couples, which permits us to get λ and $\Delta G'$ without calculations based on models but directly from experimental data.

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(20) Preferential solvation phenomena that produce the increase of λ in solvent mixtures can give rise to a deviation of the linear response theory, in which the Marcus theory, and thus our analysis, is based. However, the deviation from the linear response, if important, would be noted by the fact that λ would be different for the forward and reverse processes. Here, the reorganization free energies for these processes are the same, and thus the Marcus theory seems applicable. This point has been discussed in detail by one of the present authors (F.S.) in ref 19.