ABNORMAL SALT EFFECTS ON A CATION/ANION REACTION. AN INTERPRETATION BASED ON THE ANALYSIS OF THE COMPONENTS OF THE EXPERIMENTAL RATE CONSTANT

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Salt effects ($NaNO_3$) on the kinetics of the reactions $[Fe(CN)_6]^{3-}$ + $[Ru(NH_3)_5(pyz)]^{2+}$ = $[Fe(CN)_6]^{4-}$ + $[Ru(NH_3)_5(pyz)]^{3+}$ (pyz = pyrazine) were studied through *T*-jump measurements. An abnormal (positive) salt effect on the forward reaction was observed and a normal (negative) effect on the reverse one. These facts imply an asymmetric behavior of anion/cation reactions depending on the charge sign of the oxidant and reductant. The results can be rationalized by using the Marcus–Hush treatment for electron-transfer reactions after decomposition of the experimental rate constants into their components.

Keywords: Electron transfer; *T*-Jump measurements; Kinetics; Abnormal salt effect; Marcus–Hush treatment; Ferricyanide oxidation; Ruthenium complexes; Thermodynamics.

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

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\neq}} . \qquad (1)$$

In this equation, k_0 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 ≠, corresponding to the reference state. According to the Brønsted equation, a negative salt effect is expected for anion/cation reactions and a positive salt effect is predicted for reactions of ions of the same charge sign. These predictions have been checked many times. In fact, Livingston's diagram[3] is a beautiful illustration of salt effects. All this is well known by chemists working in the field of chemical kinetics, up to such a point that

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salt effects are taken frequently as criteria for the 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].

To clarify these abnormal effects, a kinetic study of the reaction (*2*) has been carried out in $NaNO_3$ solutions of different concentrations (1–6 mol dm^{-3}).

$$[Fe(CN)_6]^{3-} + [Ru(NH_3)_5(pyz)]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + [Ru(NH_3)_5(pyz)]^{3+} \quad (2)$$

The result of this study reveals the existence of abnormal salt effects for the forward reaction. However, the reverse reaction shows normal behavior. These facts can be rationalized by using the Marcus–Hush[5] theory of electron-transfer processes, after decomposition of the experimental rate constant into its components. In particular, we have been able to obtain the main parameters that control the kinetics of the electron-transfer reactions, the reorganization, λ, and reaction, $\Delta G'$, Gibbs energies of the processes. The knowledge of these parameters and their variations on changing the reaction medium is important. In particular, in the case of reactions between transition metal complexes, this knowledge is of interest with regard to the implications of these electron-transfer processes for the design of novel systems of technological significance (e.g., molecular electronics or sensor devices)[6].

It is worth pointing out that this paper constitutes an extension of previous studies by our group[7] in this field. This extension regards the measurement of the equilibrium constant corresponding to the formation of the encounter complex (see hereinafter) and the introduction of the effective (dielectric) permittivity, when dealing with salt solutions. This has permitted us to obtain better values of electron-transfer rate constants.

EXPERIMENTAL

Materials

The complexes $[Ru(NH_3)_5(pyz)](ClO_4)_2$ (pyz = pyrazine) and $[Co(NH_3)_5(dmso)](ClO_4)_3$ (dmso = dimethylsulfoxide) were prepared and purified according to the procedure described in the literature[8]. The reagents $K_4[Ru(CN)_6]$, $Na_3[Fe(CN)_6]$ and $NaNO_3$ of AR grade were used as purchased. The water used as the solvent had conductivity < 10^{-6} S m^{-1}.

Equilibrium Measurements

The equilibrium constants, *Q*, for reaction (*2*) were obtained from spectrophotometric data.

$$Q = \frac{k_f}{k_r} = \frac{[Fe(CN)_6]^{4-}\,[Ru(NH_3)_5(pyz)]^{3+}}{[Fe(CN)_6]^{3-}\,[Ru(NH_3)_5(pyz)]^{2+}} \qquad (3)$$

Measurements were carried out at 472 nm, the wavelength of the maximum absorption of $[Ru(NH_3)_5(pyz)]^{2+}$ (ε_{max} = 1.3 × 10^4 mol^{-1} dm^3 cm^{-1}). A small correction for the absorption of $[Fe(CN)_6]^{3-}$ at 472 nm (ε = 14 mol^{-1} dm^3 cm^{-1}) was applied. The concentrations in the mixtures of $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_5(pyz)]^{2+}$ ranged from 1 × 10^{-4} to 5 × 10^{-4} mol dm^{-3}. All measurements were performed at 298.2 K.

Determination of the Equilibrium Constant *K* for the Formation of the Ion Pair $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$

A spectrophotometric method served for the determination of the equilibrium constant, *K*, for the formation of the ion pair $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$. Absorbance measurements were carried out with a Cary 500 Scan UV-Vis-NIR spectrophotometer. The solutions contained $[Co(NH_3)_5(dmso)]^{3+}$ and $[Ru(CN)_6]^{4-}$ at equimolar concentrations, ranging from 1 × 10^{-4} to 6 × 10^{-3} mol dm^{-3}.

The experiments were carried out at 298.2 K, employing a 1-cm path length cell. The monitoring wavelength was 352 nm, which corresponds to the maximum of the MMCT (metal-to-metal charge transfer) band of the ion pair. The molar absorption coefficient for this ion pair was determined from the slope of the Beer's plot at concentrations corresponding to the complete formation of the ion pair (Fig. 1). Having the molar absorption coefficient, it is simple to obtain the values of K corresponding to the formation of the ion pair[9].

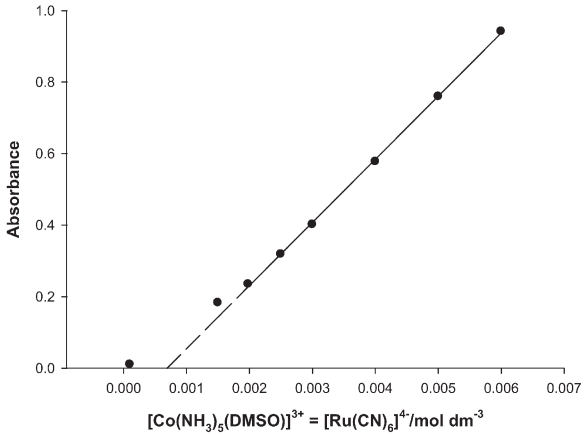

FIG. 1
The Beer's plot of the formation of the $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$ ion pair at 298.2 K and 0.1 M $NaNO_3$. Reactants at equimolar concentrations. The points are the experimental data and the line corresponds to the Beer's plot

Kinetic Measurements

Kinetics of the reactions (*2*) was studied by the *T*-jump technique, using a Hi-Tech SF-61 apparatus. The concentrations of the reactants $[Ru(NH_3)_5(pyz)]^{2+}$ and $[Fe(CN)_6]^{3-}$ in the mixture ranged from 5×10^{-5} to 1×10^{-4} mol dm^{-3}. The solutions also contained $NaNO_3$ at desired concentrations. The initial temperature and the voltage were adjusted according to the considerations of the apparatus in such a way that the final temperature of 298.2 K was reached (after the *T*-jump). After perturbation of the system, the absorbance was recorded up to the equilibrium (at 298.2 K).

Under the experimental conditions, the relaxation time, τ, is given by Eq. (*4*)

$$\frac{1}{\tau} = k_r\{Q([[Fe(CN)_6]^{3-}]_e + [[Ru(NH_3)_5(pyz)]^{2+}]_e) + [[Fe(CN)_6]^{4-}]_e + [[Ru(NH_3)_5(pyz)]^{3+}]_e\} . \quad (4)$$

In this equation, $[X]_e$ represent the equilibrium concentrations of the species X. The values of Q are given by $Q = k_f/k_r$. Both rate constants, k_f and k_r, can readily be obtained from Eq. (*4*) and the previously measured values Q.

RESULTS

Table I contains the values of Q and τ corresponding to the studied salt solutions. Each value of Q and τ was obtained in, at least, five independent experiments. The values of Q can be expressed by Eq. (*5*)

$$Q = Q^0 \frac{\gamma^{3-}\gamma^{2+}}{\gamma^{4-}\gamma^{3+}} \quad (5)$$

where γ are the activity coefficients of the ions with charges indicated, and $Q^0 = k_f^0/k_r^0$, i.e., the thermodynamic equilibrium constant. Taking the logarithm of Q in Eq. (*5*), and using the extended Debye–Hückel equation for the activity coefficients[10], the result is

$$\log Q = \log Q^0 + \frac{A\sqrt{I}}{1+\sqrt{I}} + BI . \quad (6)$$

The values of Q fit well to this equation (Fig. 2a). Thus, the values of Q in Table I are the data obtained from this fitting procedure. Analogously, the values of τ (Fig. 2b) in Table I have been obtained by following the same procedure.

Effective (Dielectric) Permittivity

Recently, reports on strategies to deal with solutions at high salt concentrations have appeared in the literature[11]. In these papers, effective ion-ion potentials are parametrized in order to include multibody effects at high ionic

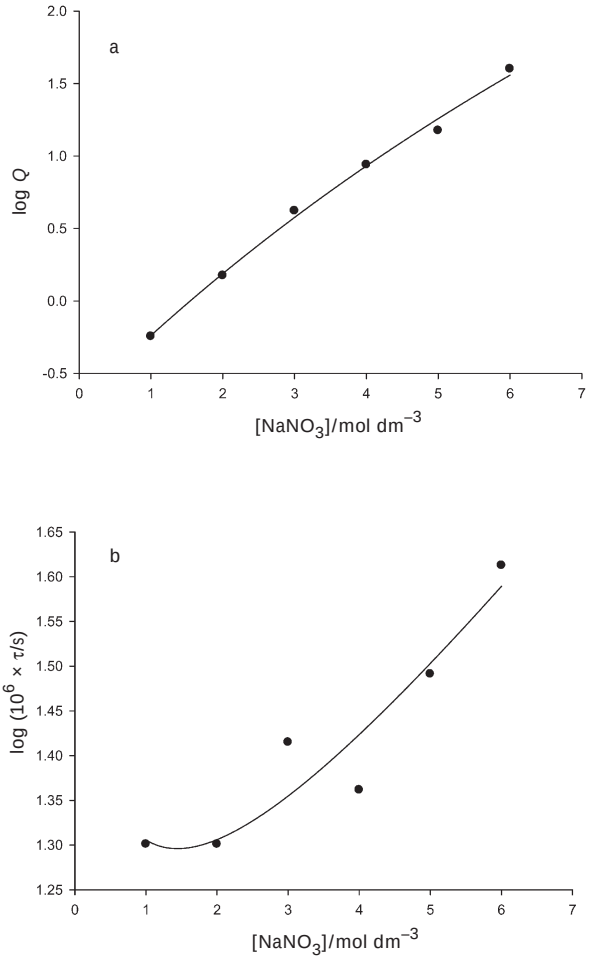

FIG. 2

a The plot of log Q vs concentration of $NaNO_3$. The points are the experimental data and the line is the best fit obtained using Eq. (*6*). b The plot of log ($10^6\tau$) vs concentration of $NaNO_3$. The points are the experimental data and the line is the best fit obtained using an equation analogous to Eq. (*6*)

concentrations. The purpose is to capture these effects by employing a concentration dependent (relative) permittivity. Using the same idea we have obtained concentration-dependent (relative) permittivity from the experimental values of the formation constant of the ion pair $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$.

Figure 3 gives the formation constant K of the $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$ ion pair, at different salt concentrations. Some data in Fig. 3

TABLE I

Equilibrium constant, Q, and relaxation time, τ, for the reaction $[Fe(CN)_6]^{3-} + [Ru(NH_3)_5(pyz)]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + [Ru(NH)_3)_5(pyz)]^{3+}$

$[NaNO_3]$, mol dm^{-3}	Q	$10^6\,\tau$, s
1.0	0.6	20
2.0	1.6	20
3.0	3.8	23
4.0	8.0	26
5.0	18	32
6.0	37	39

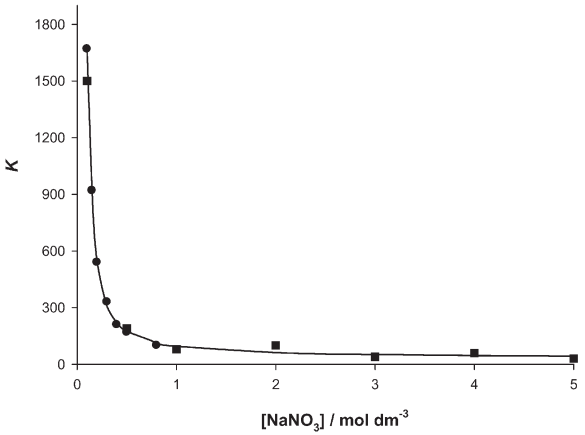

FIG. 3

Values of K (equilibrium constant corresponding to the formation of $[Co(NH_3)_5(dmso)]^{3+}/[Ru(CN)_6]^{4-}$ ion pair) obtained from spectroscopic (●) and kinetic (■) measurements at several $NaNO_3$ concentrations

correspond to the values of K for $[Co(NH_3)_5(H_2O)]^{3+}/[Fe(CN)_6]^{4-}$ ion pair[12]. These data were obtained following a kinetic procedure different from the one employed here. However, as can be seen from Fig. 3, there is a good match between the two data sets.

In order to show that the values of K, calculated from the effective (different) values of the (relative) permittivity, are independent of the model used in the calculations, we will consider two different approaches: the Eigen–Fuoss (EF)[13] and the exponential mean spherical approximation (emsa)[14]. According to these formulations, K is given by Eq. (*7*)

$$k = \frac{4\times 10^3 \pi N_A a^3}{3} \exp\left(-\frac{V_{AD}^{i}(a,I)}{k_B T}\right) \qquad (7)$$

where $V_{AD}^{i}(a,I)$ represents the mean force potential between the ions (A and D) forming the ion pair, at distance a and ionic strength I.

$$V_{AD}^{EF} = \frac{Z_A Z_D e^2}{4\pi\varepsilon_0\varepsilon_s a(1+\kappa a)} \qquad (8)$$

$$V_{AD}^{emsa} = \frac{Z_A Z_D e^2}{4\pi\varepsilon_0\varepsilon_s a(1+\Gamma\sigma_A)(1+\Gamma\sigma_D)} \qquad (9)$$

In Eqs (*7*)–(*9*), N_A represents the Avogadro number, Z_A and Z_D are the valences of the ions, e is the proton charge, ε_0 the vacuum permittivity, a the contact distance of the ions in the ion pair (taken as the sum of ionic radii), ε_s the (relative) permittivity of the solvent, κ the Debye screening parameter, Γ the mean spherical approximation (msa) screening parameter (the screening parameters are proportional to I), and σ_A and σ_D are the diameters of the ions. These radii (or diameters) have been calculated using Eq. (*10*)[15]

$$r = \tfrac{1}{2}(l_1 l_2 l_3)^{1/3} \qquad (10)$$

where l_i are the lengths of the three different L–M–L′ axes in the complexes[16]. The r values are given in Table II.

It is clear that from the data in Fig. 3 and Eqs (*7*)–(*10*) it is possible to get the effective solvent (relative) permittivity, ε_s^{eff}, corresponding to EF and

emsa approaches, once the radii have been calculated. The values of ε_s^{eff} for these approaches are given in Table III.

One can see that the effective values of the (relative) permittivity to be used in the application of the EF or emsa treatments are of the same order of magnitude as experimental values[17], but somewhat lower. This behavior of the (relative) permittivity is similar to the findings of other studies that employ concentration-dependent (relative) permittivity, calculated by simulation methods[11,18]. It is worth pointing out that in these papers, like

TABLE II
Radii of the complexes studied

Complex	*r*, Å
$[Fe(CN)_6]^{3-}$	4.6
$[Ru(NH_3)_5(pyz)]^{2+}$	4.3
$[Ru(CN)_6]^{4-}$	4.7
$[Co(NH)_3)_5(dmso)]^{3-}$	3.8

TABLE III
Dielectric permittivities, ε_s (experimental and effective values) at 298.2 K

$[NaNO_3]$, mol dm^{-3}	ε_{exp} [a]	ε_{EF}	ε_{emsa}
0.1	76.9	55.7	53.3
0.15	76.1	54.1	51.0
0.2	75.4	53.0	49.3
0.3	74.0	51.2	46.7
0.4	72.7	49.5	44.1
0.5	71.5	48.0	42.0
0.8	68.0	43.5	36.5
1.0	65.8	40.8	33.5
2.0	56.8	30.7	23.2
3.0	50.1	24.3	17.4
4.0	45.2	20.4	13.8
5.0	42.0	17.6	11.7

[a] From ref.[17]

here, the effective (relative) permittivity is dependent on the model type (of the potentials) employed in the simulations.

We employed the effective values of the solvent (relative) permittivity to calculate the formation constants of the encounter complex of the electron-transfer reactions, from separate donor and acceptor. These values are necessary in order to separate the true electron-transfer rate constant from k_f and k_r, the experimental rate constants (see below).

DISCUSSION

From the data in Table I, the values of k_r and k_f have been obtained. These values are given in Table IV. As mentioned hereinbefore, these rate constants show opposite trends when the salt concentration 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.

Under the conditions prevailing in this work, $K[R] << 1$, where K is the equilibrium constant corresponding to the formation of the encounter complex and [R] the concentration of the reactant (donor or acceptor) in excess, the values of k_f and k_r are given by Eqs (*11a*) and (*11b*), respectively

$$k_f = K_f k_{et}^f \qquad (11a)$$

and

$$k_r = K_r k_{et}^r . \qquad (11b)$$

TABLE IV
Rate constants for the forward and reverse reactions $[Fe(CN)_6]^{3-} + [Ru(NH_3)_5(pyz)]^{2+}$ $\underset{k_r}{\overset{k_f}{\rightleftharpoons}}$ $[Fe(CN)_6]^{4-} + [Ru(NH_3)_5(pyz)]^{3+}$

$[NaNO_3]$, mol dm^{-3}	10^{-8} k_f, mol^{-1} dm^{-3} s^{-1}	10^{-8} k_r, mol^{-1} dm^{-3} s^{-1}
1.0	4.8	7.5
2.0	5.2	3.6
3.0	5.8	1.8
4.0	6.3	0.8
5.0	6.9	0.4
6.0	7.6	0.2

The values of K_f and K_r were determined using EF and emsa approaches, and the effective (relative) permittivity. The values of K_f and K_r, as well those of k_{et}^f and k_{et}^r are presented in Table V. A good agreement is found for the values obtained following the two approaches.

Now, the reason for the normal behavior of k_r and the abnormal behavior of k_f are apparent: in the case of k_r, its components K_r and k_{et}^r decrease as the salt concentration is increased. In the case of k_f, K_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 true electron-transfer process, i.e., the electron transfer within the encounter complex

$$[Fe(CN)_6]^{3-}/[Ru(NH_3)_5(pyz)]^{2+} \xrightarrow{k_{et}^f} [Fe(CN)_6]^{4-}/[Ru(NH_3)_5(pyz)]^{3+} \quad (12)$$

shows a positive salt effect, which is more marked, and thus the negative salt effect on K_f. On the contrary, in the case of the components of k_r, both k_{et}^r and K_r show a negative salt effect.

To deeper insight into the different behavior of k_{et}^f and k_{et}^r with regard to salt effects, the Marcus–Hush theory for the electron-transfer processes was used. According to this treatment, the rate constant for processes of this kind is given[19] by Eq. (*13*)

$$k_{et} = \kappa_{el} \nu_n e^{-\Delta G^{\neq}/RT}. \quad (13)$$

TABLE V
Equilibrium constants of precursor complex formation, K (mol^{-1} dm^{-3}), and electron-transfer rate constants, k_{et} (s^{-1}), following EF and emsa approaches for forward, f, and reverse, r, reactions at 298.2 K

$[NaNO_3]^a$	K_f^{EF}	K_f^{emsa}	K_r^{EF}	K_r^{emsa}	$k_{et,f}^{EF}$ [b]	$k_{et,f}^{emsa}$ [b]	$k_{et,r}^{EF}$ [c]	$k_{et,r}^{emsa}$ [c]
1.0	11.1	10.7	69.1	64.2	4.3	4.5	10.9	11.7
2.0	8.9	8.6	45.0	41.1	5.9	6.1	8.0	8.8
3.0	8.3	7.9	38.5	34.8	7.0	7.3	4.5	5.0
4.0	7.8	7.5	34.6	31.9	8.1	8.4	2.4	2.6
5.0	7.6	7.2	32.2	29.1	9.1	9.6	1.3	1.4
6.0	6.9	6.4	26.9	22.9	11.0	11.9	0.7	0.8

[a] Concentration in mol dm^{-3}; [b] $k_{et,f} \times 10^{-7}$; [c] $k_{et,r} \times 10^{-6}$.

Here κ_{el}, ν_n and $\Delta G^{\neq}$ are the electronic transmission coefficient, nuclear frequency factor, and Gibbs energy of activation, respectively. The latter is given by Eq. (*14*)

$$\Delta G^{\neq} = \frac{(\lambda + \Delta G')^2}{4\lambda} . \qquad (14)$$

The parameter λ in Eq. (*14*) is the so-called Gibbs energy of reorganization for the electron-transfer process (Eq. (*12*)). This Gibbs energy consists of a solvent contribution, λ_s, an ionic atmosphere contribution, λ_{at}, and a contribution arising from the internal reorganization of the donor and the acceptor, λ_{in}. The latter is usually considered to be independent of the reaction media.

Except for strongly nonadiabatic processes, the pre-exponential term in k_{et} is of the order of the (average) vibrational 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 6.2×10^{12} s^{-1} was used. This value corresponds to that of the pre-exponential factor in the expression of the rate constant given by the classical transition state theory ($k_B T/h$) at our experimental temperature. In this way, $\Delta G^{\neq}$ can be obtained from k_{et} (Eq. (*15*))

$$\Delta G^{\neq} = -RT \ln \frac{k_{et}}{6.2 \times 10^{12}} . \qquad (15)$$

The parameter $\Delta G'$ in Eq. (*14*) is the (standard formal) Gibbs 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) Gibbs energy of the reaction, which produces the separate products from the separate reactants (Eq. (*2*)). The latter is, of course,

$$\Delta G = -RT \ln Q \qquad (16)$$

and can be calculated from the values of Q in Table I. The ΔG and $\Delta G'$ values are related, through,

$$\Delta G' = \Delta G + \omega_P - \omega_R . \qquad (17)$$

Here ω_R and ω_P are the Gibbs energies corresponding to the formation of the precursor complex from the separate reactants and the formation of the successor complex from the separate products.

For the forward reaction

$$\omega_R = -RT \ln K_f \qquad (18)$$

and

$$\omega_P = -RT \ln K_r . \qquad (19)$$

In this way, from Eqs (*16*)–(*19*), the values of $\Delta G_f'$ in Table VI can be calculated (clearly $\Delta G_r' = -\Delta G_f'$).

Finally, the values of λ_f and λ_r have been calculated from $\Delta G_f'$ and $\Delta G_r'$ using Eq. (*14*). These values are presented in Table VI. We have found that λ_f and λ_r are the same, in agreement with the Marcus–Hush theory.

Apparently, 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 consequences of the character (anion or cation) of the donor and acceptor in these reactions. Thus, in the case of the forward reaction, the donor is a cation and the acceptor an anion. For this reaction, the donor $[Fe(CN)_6]^{3-}$, becomes a more powerful oxidant and $[Ru(NH_3)_5(pyz)]^{2+}$ a more reductant species in the presence of the salts. This is clearly seen from Eq. (*20*) which gives the standard formal redox potential of a given ox/red couple

$$E^{0\prime} = E^0 + \frac{RT}{F} \ln \frac{\gamma_{ox}}{\gamma_{red}} . \qquad (20)$$

TABLE VI

Gibbs energy change, $\Delta G_r' = -\Delta G_f'$, and reorganization energy, λ, following EF and emsa approaches for forward, f, and reverse, r, reactions of electron transfer at 298.2 K[a]

$[NaNO_3]$, mol dm^{-3}	$\Delta G'_{f,EF}$	$\Delta G'_{f,emsa}$	λ_{EF}	λ_{emsa}
1.0	–3.1	–3.0	122.7	122.2
2.0	–5.2	–5.1	124.3	123.7
3.0	–7.1	–7.0	125.9	125.3
4.0	–9.0	–8.9	127.6	126.8
5.0	–10.7	–10.6	129.2	128.4
6.0	–12.3	–12.1	130.9	129.9

[a] All energies in kJ mol^{-1}.

For the $[Fe(CN)_6]^{3-/4-}$ pair, both γ_{ox} and γ_{red} decrease with increasing the salt concentration. However, the decrease in γ_{red} is more marked because of the higher absolute charge of the reduced form of this pair. Thus, $E^{0\prime}$ increases as the salt concentration increases. On the contrary, for the cationic pair ($[Ru(NH_3)_5(pyz)]^{3+/2+}$ herein), the effect of the salt is to decrease $E^{0\prime}$, because γ_{ox} decreases more than γ_{red}. Consequently, the forward reaction becomes more favorable from a thermodynamic point of view, and this produces the abnormal salt effect. For the reverse reaction, similar arguments help to explain that k_r decreases as the salt concentration increases.

A conclusion emerges from the previous discussion. In the anion/cation electron-transfer reactions, salt effects operate in opposite directions on K and k_{et}, when the oxidant is an anion. This is because K decreases as the salt concentration increases, and k_{et} increases because the true electron-transfer reaction becomes more favorable from a thermodynamic point of view. Therefore, the sign of the salt effect on an observed rate constant ($k = K k_{et}$) depends on the magnitude of these effects. If the increase in k_{et} is higher than the decrease in K, when the salt concentration increases, then a positive salt effect is observed (as reported herein). However, if the decrease in K is higher than the increase in 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 K go in the same direction. Consequently, in this case, a negative salt effect is always observed.

SYMBOLS

a	contact distance of the ions
E^0	standard redox potential
$E^{0\prime}$	standard formal redox potential
I	ionic strength
k_{et}	electron-transfer rate constant
k_f	forward rate constant
k_r	reverse rate constant
K	equilibrium constant for ion-pair formation
l_i	length of the ligand–metal–ligand axes
Q	apparent equilibrium constant
Q^0	thermodynamic equilibrium constant
V^i_{AD}	ionic mean force potential
$\Delta G^{\neq}$	Gibbs energy of activation
γ	activity coefficient
Γ	msa screening parameter
ε	molar absorption coefficient
ε_s	solvent (relative) permittivity

ε_s^{eff}	effective solvent (relative) permittivity
ε_0	vacuum permittivity
κ	Debye screening parameter
κ_{el}	electronic transmission coefficient
λ	reorganization energy
ν_n	nuclear frequency factor
σ	diameter of an ion
τ	relaxation time
ω_P	Gibbs energy for the formation of successor complex from the separate products
ω_R	Gibbs energy for the formation of precursor complex from the separate reactants

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16. To calculate l_i , van der Waals radii of the ligands have been used and metal–ligand distances have been obtained from Cambridge Structural Database (http://www.ccdc.cam.ac.uk/) and Inorganic Crystal Structural Database (ICSD) (http://icsdweb.fiz-karlsruhe.de/).
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