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Two-State Model Based on Electron-Transfer Reactivity Changes to Quantify the Noncovalent Interaction between $Co(NH_3)_5Cl^{2+}$ and 18-Crown-6 Ether: The Effect of Second-Sphere Coordination on Electron-Transfer Processes

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The electron-transfer reaction between $[Fe(CN)_6]^{4-}$ and $[CoCl(NH_3)_5]^{2+}$ was studied in the presence of 18-crown-6 ether (18C6) in different reaction media constituted by water and acetonitrile as organic cosolvent at 298.2 K. The results corresponding to this reaction show a clear influence of 18C6 on the kinetics: a positive catalytic effect. Trends in the observed reactivity are explained by a change in the degree of association of one of the reactants (the cobalt complex) with the 18C6. This association is governed by an equilibrium constant that depends on the dielectric constant of the medium. The results show an increase of the rate constants for the electron-transfer process as the 18-crown-ether concentration increases and an increase of the binding free energy of the cobalt complex to the 18C6 when the electrostatic field of the medium becomes weaker. An analysis of the experimental data allows not only the reactivity changes associated with adducts formation processes for an electron-transfer reaction but also information on the binding free energy of the cobalt complex to the 18C6 to be obtained, which can be quantified by using a two-state model. We have found a good correlation between the energy of binding and the Kosower's Z-value. The influence of the 18C6 in the intramolecular electron transfer in the binuclear complex $[Fe(CN)_5pzCo(NH_3)_5]$ has been also investigated.

Introduction

Complexes of crown ethers have been widely recognized as models for molecular recognition.[1] 18-crown-6 ether (18C6) has been recently used for molecular recognition of the biologically important amino acid lysine in small peptides and proteins[2] due to its ability to complex with ammonium or alkylammonium ions.[3] In this sense, crown ethers can also be used as receptors capable to form hydrogen bonds with protic ligands such as NH_3 in the first coordination sphere of a complex.[4] Modifications of redox properties of some ruthenium complexes caused by 18C6 and involving ammines as a protic ligand have been described.[5] However, there are no systematic studies about reactivity changes in chemical processes as, for example, electron-transfer reactions between these ruthenium complexes bound to 18C6 and other metal complexes.

We have investigated the effect of second-sphere coordination on the electron-transfer process between a cobalt-ammine complex, $[CoCl(NH_3)_5]^{2+}$, and the $[Fe(CN)_6]^{4-}$ ion. The kinetic studies allow not only to quantify the reactivity changes associated with the adduct formation processes but also to obtain information about the noncovalent interaction (interactions between chemical species different from covalent bonds) of the reactant (the cobalt complex in this case) with the receptor (the 18C6 crown ether), that is, on binding free energy.

Generally speaking, noncovalent interactions between two species produce a change in their properties. So the union of a substrate, S, to a receptor, R, promotes a change in the free energy of the substrate given by[6]

$$\Delta G_S = RT \ln \gamma_S \tag{1a}$$

$$\gamma_S = \frac{1}{1 + K[R]} \tag{1b}$$

Here the activity coefficient of the substrate, γ_s, is defined with respect to a reference state in which [R] = 0. On the other hand, *K* in eq 1b represents the equilibrium constant for the process

$$\text{S(free)} + \text{R} \rightleftharpoons \text{S/R(substrate linked to the receptor)} \tag{2}$$

Measuring some properties at different receptor concentrations it is possible to obtain K and from this, the standard free energy corresponding to the union substrate/receptor. Following this approach, we have done a systematic study of the interaction between a cationic metal complex, $[CoCl(NH_3)_5]^{2+}$, and 18C6 crown ether. We have used an electron-transfer process as a probe, taking into account its apparent simplicity: in this kind of reaction an electron is transferred from a donor, D, to an acceptor, A, without breaking or forming new bonds, a fact which implies that the electron-transfer reaction is one of the simplest of chemical processes.

As it will be described, from kinetic data, a two state model allows the strength of the binding as function of the 18C6 concentration to be evaluated. Even more, taking into account that the strength (or energy) of the ligand/substrate interactions can be modulated through a change in the nature of the continuous pseudophase (the solvent), a systematic study of the binding in water−acetonitrile mixtures has been done. Also, the stoichiometry for adduct formation was examined by Job's continuous variation method. In this way, a complete picture of the binding can be obtained. In mixtures, the reactivity may

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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. Of course relaxation phenomena, affecting the dynamic solvent effects, are 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 change continuously the macroscopic properties of the reaction media. They are, therefore, a subject of both experimental and theoretical interest.[7]

Experimental Section

Materials. All of the chemicals were of analysis R grade and were used without further purification. Acetonitrile, tetrabutylammonium bromide and $Na_4[Fe(CN)_6]$ were purchased from Merck. 18C6 was purchased from Fluka and stored in a vacuum desiccator for several days before being used. $[CoCl(NH_3)_5]Cl_2$, $[Co(NH_3)_5pz](CF_3SO_3)_3$, and $[Fe(CN)_5NH_3]Na_3 \cdot 3H_2O$ were prepared and purified following the procedures described in refs 8−10. For the latter, as it is known,[11] a rapid hydrolysis of the ammonia complex produces the corresponding acuo complex. The water used in the preparation of the solutions had a conductivity of $\sim 10^{-6}$ Sm^{-1} and was deoxygenated before use.

Spectra. The spectra of the $[CoCl(NH_3)_5]^{2+}$ complex at different 18C6 concentrations were recorded with a Cary 500 scan UV−vis-NIR spectrophotometer at 298.2 K. Measurements were performed at 530 nm, corresponding to the maximum of $[CoCl(NH_3)_5]^{2+}$ absorbance.

Kinetic Measurements. Kinetic runs were carried out in a stopped-flow spectrophotometer from Applied Photophysics. The reaction was monitored by following the appearance of $[Fe^{III}(CN)_6]^{3-}$ at 420 nm for the outer sphere electron-transfer process.

All of the kinetic runs were carried out under first-order conditions using an excess of the reductant: $[Co^{III}Cl(NH_3)_5]^{2+} = 2 \times 10^{-5}$ mol dm^{-3} and $[Fe^{II}(CN)_6]^{4-} = 2.5 \times 10^{-4}$ mol dm^{-3} in the reaction mixture. First-order rate constants were obtained from the slopes of the linear plots of $\ln(A_\infty - A_t)$ vs time, where A_∞ and A_t were the absorbances when the reaction was finished and at time t, respectively. All of the experiments were repeated at least five times. These plots were good straight lines for at least three-half-lives. The estimated uncertainty in the rate constant was less than 5%. Experiments were carried out in the presence of $EDTAH_2Na_2$ in order to avoid the precipitation of the products of the reaction.[12] The temperature was maintained at 298.2 ± 0.1 K.

For the inner sphere electron-transfer reaction (see discussion), in order to follow the intramolecular electron-transfer process, the binuclear complex was prepared in situ using solutions of $[Fe^{II}(CN)_5H_2O]^{3-}$ and $[Co^{III}(NH_3)_5pz]^{3+}$

$$[Fe^{II}(CN)_5H_2O]^{3-} + [Co^{III}(NH_3)_5pz]^{3+} \rightarrow [Fe^{II}(CN)_5pzCo^{III}(NH_3)_5]$$

As this reaction is rapid in relation to the following electron-transfer reaction, their kinetics are well separated, in such a way that they can be followed without mutual interference. Kinetic runs were carried out in a stopped flow spectrophotometer from Applied Photophysics, monitoring the absorbance changes at 620 nm, which is the wavelength corresponding to the maximum absorbance of the binuclear complex. The concentration of the precursor reactants, $[Fe^{II}(CN)_5H_2O]^{3-}$ and $[Co^{III}(NH_3)_5pz]^{3+}$, after mixing, were 5×10^{-5} and 5×10^{-4} mol dm^{-3}, respectively. In preliminary experiments, we checked (using spectrophotometric UV−visible techniques in order to detect the $[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5]$) that these concentrations ensured a complete formation of the binuclear complex.

The water-cosolvent mixtures were prepared by weight. The bulk (static) dielectric constants (D_s) of these solutions, at 298.2 K, were 78.5 (pure water), 75.8, 70.5, 62.3, 58.8, 55.7, and 50.8, which correspond to the following mole fractions x_{ACN}: 0, 0.05, 0.1, 0.2, 0.25, 0.3, and 0.4

Electrochemistry. The standard formal potentials, $E^{0\prime}$

$$E^{0\prime} = E^0 + \frac{RT}{F} \ln \frac{\gamma_{ox}}{\gamma_{red}} \tag{3}$$

of the $[Fe(CN)_6]^{3-/4-}$ couple in $x_{ACN} = 0.4$ at different 18C6 concentrations were determined using a carbon working electrode, a saturated calomel electrode as reference, and an auxiliary platinum electrode. In eq 3, E^0 is the standard potential of the couple, $[Fe(CN)_6]^{3-/4-}$ in the present case, and γ_{ox} and γ_{red} are the activity coefficients of the oxidized and reduced components of this couple. The concentration of $[Fe(CN)_6]^{3-}$ in the experiments was 1×10^{-3} mol dm^{-3} and 0.1 mol dm^{-3} of tetrabutylammonium bromide was used as inert electrolyte. The apparatus and procedure employed have been previously described.[13]

Results

As for the electronic spectrum of the $[Fe(CN)_6]^{4-}$, no changes were observed for the standard formal redox potentials of the iron complex in the presence of 18C6: a value of $E^{0\prime} = 475$ mV (versus NHE) was measured in the absence of 18C6 and a value of $E^{0\prime} = 470$ mV was obtained in the presence of [18C6] = 0.1 mol dm^{-3}. The cobalt complex adduct formation could not be electrochemically investigated because the reduction of the cobalt complex is electrochemically irreversible.

LMCT band of the cobalt (III)-ammine complex does not show a blue shift by adding 18C6 in $x_{ACN} = 0.4$. However changes in the absorbance at 530 nm permit to determine the stoichiometry of the adduct formation by Job's continuous variation method. The absorbance increments of the complex solution in the presence of 18C6, ΔA, were plotted against the mole fraction of the complex in the sum of the complex and 18C6 molecules. The plot in Figure 1 clearly indicates that the cobalt (III) complex forms an 1:1 adduct by interaction with one molecule of 18C6.

The results of the kinetic runs are shown in Figures 2−7 as pseudo-first-order rate constants at different water−acetonitrile proportions and 18C6 concentrations. Due to solubility problems of the cobalt and iron complexes the maximum percentage of the ACN content corresponds to $x_{ACN} = 0.4$. These rate constants correspond to the electron transfer from the iron complex to the cobalt complex

$$[CoC1(NH_3)_5]^{2+} + [Fe(CN)_6]^{4-} \rightarrow [CoC1(NH_3)_5]^{+} + [Fe(CN)_6]^{3-} \tag{4}$$

Discussion

Data in Figures 2−7 show clearly the efficiency of the 18C6 crown ether in increasing the rate of the electron-transfer reaction. Taking into account that only the cobalt complex forms adducts through hydrogen linkage between the ammines coordinating to cobalt and the ether oxygens from crown ethers and that, with regard to the iron complex, $Fe(CN)_6{}^{4-}$, neither its

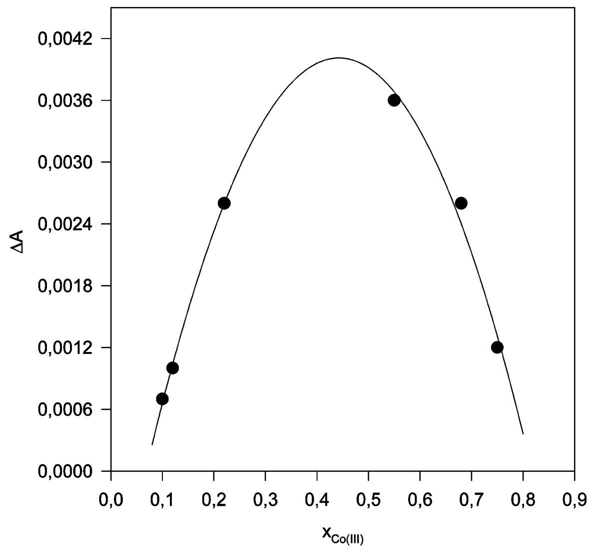

Figure 1. Plots of the absorbance increments of the complex solutions in the presence of 18C6, Δ*A*, against the mole fractions of the complex $[CoCl(NH_3)_5]^{2+}$ in $x_{ACN} = 0.4$.

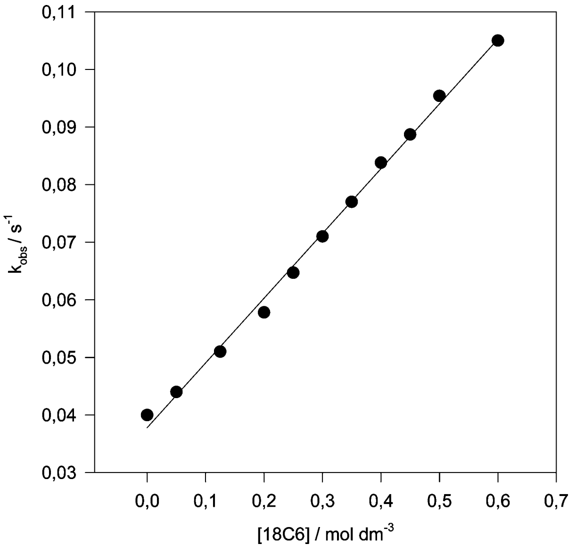

Figure 2. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in the absence of ACN. Symbols (●) are experimental data and lines are the best fit using eq 8 ($r = 0.993$).

electronic spectrum nor its redox potential changes in the presence of 18C6, we can consider that S corresponds to the cobalt complex in eq 2 and that the iron complex remains essentially in the bulk phase.

S is distributed between free and bound states that appear in eq 2. When applied to kinetics, two-state-models consider a rapid distribution (in relation to the kinetic events) of the reactants between two states, free and bound, to some supporting monodisperse materials, the 18C6 in this study. If the reactant is designed as Co, an equilibrium constant K can be defined as

$$K = \frac{[Co_B]}{[Co_F][18C6]} \tag{5}$$

where Co_F represents the free state of the cobalt complex, 18C6 is the dispersed material to which the solute binds (the crown ether in this study) and Co_B represents the bound state of the solute.

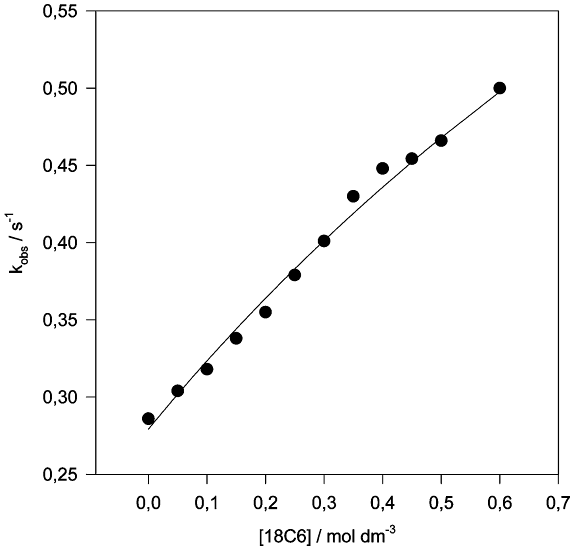

Figure 3. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in $x_{ACN} = 0.1$. Symbols (●) are experimental data and lines are the best fit using eq 7.

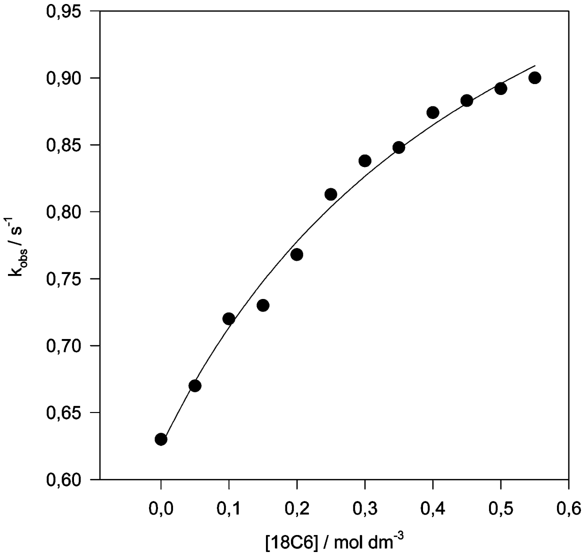

Figure 4. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in $x_{ACN} = 0.2$. Symbols (●) are experimental data and lines are the best fit using eq 7.

Generally speaking, as the properties of the local media, or phases, corresponding to the bound and free states are different, these states react at different rates

$$Co_F \xrightarrow{k_F} \text{products} \tag{6a}$$

$$Co_B \xrightarrow{k_B} \text{products} \tag{6b}$$

From eqs 5 and 6 it follows that the observed rate constant is given by[14]

$$k_{obs} = \frac{k_F + k_B K[18C6]}{1 + K[18C6]} \tag{7}$$

This equation (it is indeed the equation of the pseudophase model) opens the possibility to obtain free energies of binding by using specific reactions as probes.[15] This equation, in fact

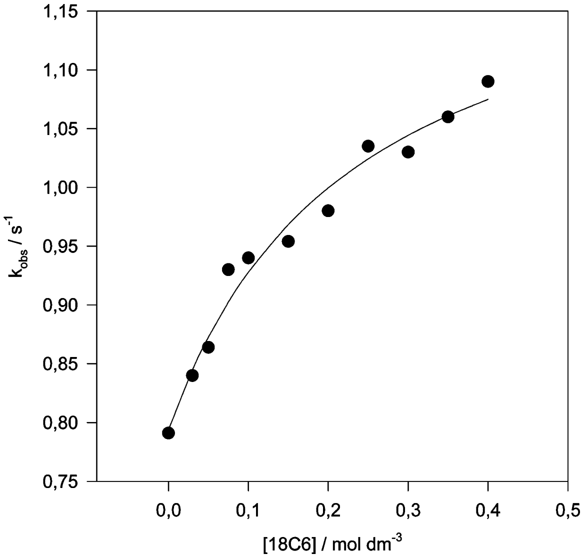

Figure 5. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in $x_{ACN} = 0.25$. Symbols (●) are experimental data and lines are the best fit using eq 7.

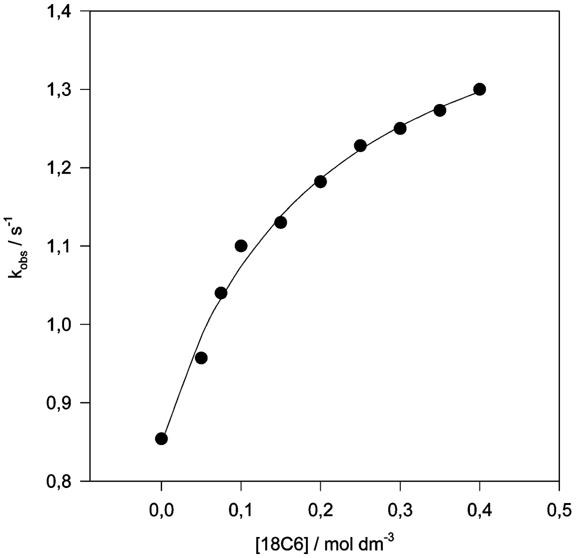

Figure 6. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in $x_{ACN} = 0.3$. Symbols (●) are experimental data and lines are the best fit using eq 7.

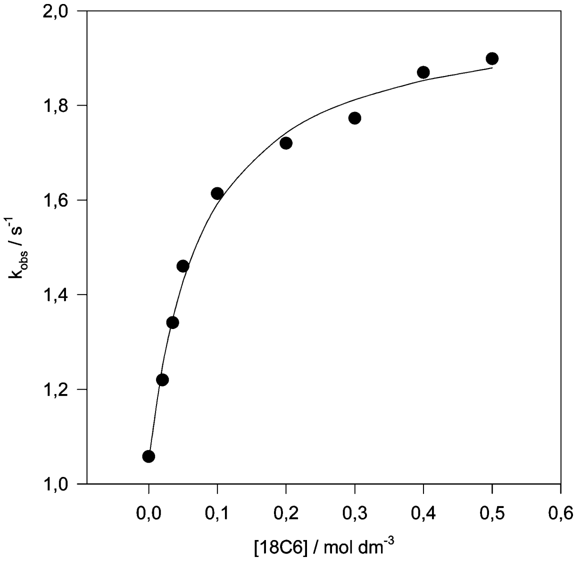

Figure 7. Plot of the experimental rate constants of the reaction $[Fe(CN)_6]^{4-} + [CoCl(NH_3)_5]^{2+}$ vs [18C6] concentration in $x_{ACN} = 0.4$. Symbols (●) are experimental data and lines are the best fit using eq 7.

the Olson−Simonson equation,[16] corresponds to the behavior expected for a two state reactive system. It is worth pointing out that, strictly speaking, eq 7 can be only applied in the case of unimolecular processes. However, as it has been shown in a previous paper,[17] eq 7 is still valid for a second-order process provided that only one of the reactants, the $[CoCl(NH_3)_5]^{2+}$ complex in the present case (given the capacity of the crown ether to form hydrogen bonds), is partitioned between the two states and the other ($[Fe(CN)_6]^{4-}$) remains essentially in the aqueous pseudophase. The total concentration of 18C6, $[18C6]_T$, can be used instead of [18C6] in eq 7 when 18C6 is added in large excess as it has been done in the present study. In this situation, the concentration of the partitioned substrate will be low enough in order to avoid saturation of the dispersed pseudophase (see ref 14). Indeed, even in this case, it is implicit that the presence of a substrate molecule in the dispersed pseudophase neither encourages nor discourages the union of a second molecule of substrate: in other words, binding of the substrate to the dispersed pseudophase is noncooperative in character. On the other hand, to consider the binding constant and the rate constant characterizing reactivity in the dispersed phase as true constants, that is, in order to use eq 7, one must assume that some characteristics of this phase (for example the shape, size or charge) must be concentration independent parameters. This situation holds for the present study using 18C6 as receptor but not in other cases where the characteristics of the phase of the receptor change with the receptor concentrations (for example when the receptor is charged and its surface potential is dependent on its concentration).

Figures 2−7 show a positive catalytic effect of the 18C6 in all mixtures studied. On the other hand, Figures 2−6 show that, as the acetonitrile content increases, a saturation behavior is observed as the [18C6] concentration increases too. However, as it can be seen, for example, in Figure 2, there is no sign of saturation in the case of pure water. The same behavior is found for $x_{ACN} = 0.05$ (data not shown). That is, the value of K (the equilibrium binding constant of the cobalt complex to the 18C6) is so small in these cases that experimental data can be fitted to eq 8 instead of eq 7 and so a linear dependence of k_{obs} with the [18C6] concentration is found

$$K_{obs} = K_F + k_B K[18C6] \tag{8}$$

Of course, in these two cases the values of K cannot be directly obtained, only the value of the product $k_B K$.

The shape for the fitted curve in Figures 2−7 explains itself that K increases as the acetonitrile content does the same. This result can be considered taking into account that the dielectric constant of the water−acetonitrile mixtures decreases as the concentration of the organic component increases, a fact which allows a stronger interaction between the $[CoCl(NH_3)_5]^{2+}$ and the 18C6. In the figures, the points are experimental data and the line is the best fit obtained by using eqs 7 and 8 (the difference between experimental and calculated rate constants is always less than 3%). The parameters resulting from the fit are given in Table 1. The values of these parameters deserve some comments. First of all, the values of k_F are almost the same as the values of k_{obs} in the absence of 18C6, a fact which confirms the quality of the fit. In relation to the effects of the

TABLE 1: Values of the Best Fit Parameters for eqs 7 and 8[a]

x_{ACN}	D_s[b]	Z[c]	Kk_B[d]	k_F	k_B[e]	K[e]
0	78.5	92.5	0.11	0.04	1.15(1.04)	0.097 (0.107)
0.05	75.8	91.8	0.30	0.12	1.74(1.70)	0.170 (0.174)
0.10	70.5	90.6		0.28 ± 0.005	1.31 ± 0.90	0.44 ± 0.20
0.20	62.3	89.1		0.62 ± 0.008	1.19 ± 0.06	1.9 ± 0.43
0.25	58.8	88.6		0.79 ± 0.014	1.24 ± 0.059	4.3 ± 1.3
0.30	55.8	87.8		0.85 ± 0.014	1.52 ± 0.044	5.0 ± 0.88
0.40	50.8	86.7		1.04 ± 0.027	1.97 ± 0.033	16.2 ± 1.9

[a] k_F, s^{-1}; k_B, s^{-1}; K, mol^{-1} $dm.^3$ [b] Static dielectric constant. [c] Kosower's *Z*-value. [d] Obtained from eq 8. [e] Values in parenthesis correspond to the correlation of ln *K* vs D_s.

cosolvent on k_F, it can be seen, from data in Table 1, that k_F increases as the dielectric constants of the medium decreases. This increase of the rate constant as the organic solvent increases has already been observed in other electron-transfer processes and is directly related with changes in the reaction free energy.[18] The increase in the rate constant is mainly due to the fact that the reaction becomes more favorable from a thermodynamic point of view when the proportion of cosolvent in the mixtures increases. This fact arises because the donor becomes more reductant and the acceptor more oxidant. This is the expected behavior: a decrease of the dielectric constant of the solutions produces a destabilization of the ions. This destabilization increases as the absolute value of the ionic charge does so. Thus, the oxidized form of the $[CoCl(NH_3)_5]^{2+}$ will be more destabilized than the reduced form of this couple. Consequently, according to eq 3, the standard formal potentials of the cationic couple will increase and those of the anionic couple will decrease, when the proportion of the organic component in the solvent increases. Although the redox potential cannot be measured for the cobalt complex, this behavior has been observed following different procedures[18] for similar complexes, as $[Co(NH_3)_5pz]^{3+}$.

In relation to k_B, taking into account the values from Table 1 it is clearly an alternative way (see eq 6b) for the reaction process between the iron complex and the cobalt bound to the 18C6 which promotes a positive catalytic effect. Data for k_B values indicate that this pathway is less influenced by changes of the medium, almost constant, but always higher than those of k_F.

Referring now to the equilibrium binding constant, the values of *K* indicate that the binding free energy decreases as the organic component increases, as a consequence of a more hydrophobic medium which favors the formation of adducts through hydrogen bonds between the ammines groups coordinating to the cobal complex and the crown ether. That is, the interaction between the complex and the 18C6 becomes stronger as the electrostatic field of the medium becomes weaker. In the case of water and $x_{ACN} = 0.05$, it is clear from eq 8 that the value of *K* cannot be obtained directly. From the slope of the plot of k_{obs} versus [18C6] only the values for the product Kk_B can be obtained. However, we found a good correlation between ln *K* (which represents energy of binding) and parameters such as the dielectric constant of the medium or the Kosower's *Z*-value of the water-cosolvent mixtures. One of these correlations appears in Figure 8 corresponding to the Kosower's *Z*-value. A similar behavior is found for the other parameter, the dielectric constant of the medium. From these correlations, *K* and k_B have been determined separately for the case of water and $x_{ACN} = 0.05$. As it can be seen in Table 1, the values obtained from these correlations are in good agreement with the others corresponding directly to the fitting of the data to eq 7. Values in parenthesis were obtained from the changes of ln *K* with D_s.

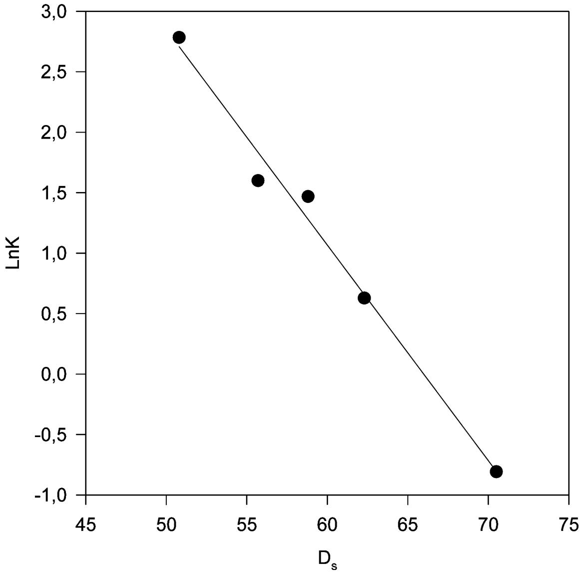

Figure 8. Plot of ln *K* vs Kosower's *Z*-values corresponding to different water−acetonitrile mixtures ($r = 0.998$).

It is now important to refer to the nature of the experimental rate constant, k_{obs}. The present discussion refers to k_{obs} which, a priori, do not have to correspond exactly to k_{et}, that is, to a true (unimolecular) rate constant for the electron-transfer reaction. Notice that k_{et} corresponds to the process

$$\text{precursor complex} \xrightarrow{K_{et}} \text{successor complex} \qquad (9)$$

and k_{obs} to the process

$$\text{reactants (separated)} \xrightarrow{K_{obs}} \text{products (separated)} \qquad (10)$$

Thus k_{obs}, the experimental rate constant, contains contributions from the diffusion processes corresponding to the formation of the precursor complex from the reactants, and/or the formation of the successor complex from the products. So, for bimolecular electron-transfer reactions, like the one studied here, k_{et} is not the datum obtained in a kinetic experiment, k_{obs}. This difference arises because, as in other solution processes, k_{obs} corresponds to a combination of different steps. One of these steps is the electron-transfer process, characterized by k_{et}. Thus, for a donor D and an acceptor A pair, the steps would be

$$A + D \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} A/D \qquad (11a)$$

$$A/D \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} A^-/D^+ \qquad (11b)$$

$$A^-/D^+ \underset{k'_{-D}}{\overset{k'_D}{\rightleftharpoons}} A^- + D^+ \qquad (11c)$$

Obviously, in this study A would be the cobalt complex and D the iron complex. The first step represents the formation of the precursor, or encounter complex, from the separate reactants and the second, the true electron-transfer reaction which produces the successor complex. Finally, step c represents the formation of the separate products from the successor complex. As k_{obs} corresponds to

$$A + D \xrightarrow{k_{obs}} A^- + D^+ \tag{12}$$

this rate constant contains contributions from the forward and reverse reactions in the above three steps mentioned. However, the factorization of k_{obs} into the different contributions can be done by selecting suitable systems, as it has been done in the present case.

Thus, if the reaction is accompanied by a major decrease in free energy, as it happens in the reaction studied here, k_{obs} does not contain contributions from the third step and from the reverse process of the second step. None the less, the observed rate constant, k_{obs}, still has contributions from the forward and backward processes of the first step, k_D and k_{-D}, and from the forward reaction of the second step, k_{et}. Equation 11a represents the formation of the precursor complex from the separate reactants. This step is usually a fast diffusion controlled process, in such a way that it can be considered at equilibrium ($K = k_D/k_{-D}$). On the other hand, in the present case, the backward process in eq 11b does not happen, because, once reduced, the cobalt complex decomposes rapidly (it is chemically and electrochemically irreversible). Consequently the backward process in eq 11b is impossible. Thus, it can be shown that in this case

$$k_{obs} = \frac{Kk_{et}[D]}{1 + K[D]} \tag{13}$$

if one works as we do here, in excess of the donor. Moreover, if [D] is big enough, in such a way that $K[D] \gg 1$, eq 13 results in

$$k_{obs} = k_{et} \tag{14}$$

In preliminary experiments, working with $[Fe(CN)_6]^{4-}$ concentrations higher than 2.5×10^{-4} mol dm^{-3} (see the Experimental Section), we checked that in our working conditions eq 14 holds; consequently, we have directly obtained k_{et} in the present discussion. In any case, the fact that the 18C6 crown ether involves a positive catalytic effect directly on a true unimolecular electron-transfer rate constant was also checked working with a binuclear complex.

As has been described, the most convenient procedure in order to directly measure k_{et} should be to study systems where $k_{exp} = k_{et}$. This is possible by studying reactions between complexes of high charge and opposite signs, as our study presented here. The other possibility is to study intramolecular electron transfers such as those occurring in the binuclear complex

$$[(CN)_5Fe^{II}(\mu{-}pz)Co^{III}(NH_3)_5] \tag{15}$$

For this reason we considered of interest the study of 18C6 effects on the kinetics of the intramolecular electron-transfer reaction

$$[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(NH_3)_5] \quad pz = \text{pyrazine} \tag{16}$$

in order to see if the positive catalytic effect found for the 18C6 corresponds, strictly speaking, to a true electron-transfer process and so the reactivity changes found for solutions containing 18C6 do not have contributions from the diffusion processes.

The Fe^{II}/Co^{III} binuclear complex described can be formed in situ from $[Fe^{II}(CN)_5H_2O]^{3-}$ and $[Co^{III}(NH_3)_5pz]^{3+}$ through a rapid reaction (because the coordinated water in the iron complex is rather labile and because the affinity of the $Fe(CN)_5^{3-}$ for nitrogen heterocycles is high[19]) which does not cause interference with the following electron-transfer process within the binuclear complex. Notice that in the binuclear complex the cobalt center also bears a pentaammine group, that is, it will present the same interaction with the 18C6 as the $CoCl(NH_3)_5^{2+}$ does. Due to stability problems of the iron complex (the molecules of acetonitrile can coordinate to the $Fe(CN)_5^{3-}$ complex) the kinetics corresponding to the intramolecular electron-transfer reaction in the binuclear complex were carried out in the presence of tert-butyl alcohol and not in the presence of acetonitrile. A mixture of water-tert-butyl alcohol was used in order to reach the same dielectric constant corresponding to $x_{ACN} = 0.1$, that is, $D_s = 70$ (solubility problems do not allow to work at lower D_s). Results appear in Table 2. As can be seen k_{et} (which corresponds directly to k_{obs}) also increases as the [18C6] increases. So it is confirmed that the positive catalytic effect of the 18C6 through the second coordination sphere of the cobalt center corresponds to a true unimolecular electron-transfer process.

TABLE 2: Rate Constants for the Reaction $[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(NH_3)_5]$ in the Mixture Water−*tert*-Butyl Alcohol Corresponding to $D_s = 70$

[18C6]/mol dm^{-3}	k/s^{-1}
0.00	$0.16 \pm 8 \times 10^{-3}$
0.15	$0.21 \pm 1 \times 10^{-2}$
0.25	$0.24 \pm 1.2 \times 10^{-2}$
0.35	$0.26 \pm 1.3 \times 10^{-2}$
0.5	$0.33 \pm 1.6 \times 10^{-2}$

In conclusion, the binding of the complex $[CoCl(NH_3)_5]^{2+}$ to 18C6 crown ether has been studied following a kinetic approach. A two-state model based on changes of the rate constants of an electron-transfer process as a probe has allowed to obtain the standard free energy corresponding to the interaction between the $[CoCl(NH_3)_5]^{2+}$ and the 18C6 crown ether. At the same time, this study allows to obtain information about the effect of second-sphere coordination on electron-transfer processes. A positive catalytic effect is found when the process takes place in the presence of 18C6, not only for intermolecular electron transfer but also for intramolecular electron-transfer reaction. On the other hand the binding free energy of the cobalt complex to the 18C6 increases as the Kosower's Z-value decreases, that is, the interaction between the complex and the 18C6 becomes stronger as the electrostatic field of the medium becomes weaker. The experimental correlation found between ln K and Z allows to quantify the equilibrium binding constant when this one is rather small, that is, in the absence and at the lower concentration of ACN. Given that electron-transfer processes are among the simplest of chemical processes, the kinetic approach described allows a complete picture of the binding when the substrate does not have measurable properties in order to obtain directly the equilibrium binding constant using different techniques: titration methods such as NMR, UV−visible spectroscopy, or cyclic voltammetry.

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(14) In order to obtain eq 7 from eq 5 and 6 an additional hypothesis is necessary on the equilibrium distribution described by eq 5: the concentration of the partitioned substrate must be low enough in order to avoid saturation of the dispersed pseudophase. Indeed, even in this case, it is implicit that the presence of a substrate molecule in the dispersed pseudophase neither encourages nor discourages the union of a second molecule of substrate: in other words, binding of the substrate to the dispersed pseudophase is non-cooperative in character.

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