Influence of Changes in the Interfacial Electrical Potential on a Ligand Substitution Reaction in Aqueous Sodium Dodecyl Sulfate Micellar Solutions

5 AUTHORS, INCLUDING:

María Luisa Moyá
Universidad de Sevilla
130 PUBLICATIONS   **1,921** CITATIONS

Influence of Changes in the Interfacial Electrical Potential on a Ligand Substitution Reaction in Aqueous Sodium Dodecyl Sulfate Micellar Solutions

Gaspar Fernández,[†] María del Mar Graciani,[†] Amalia Rodríguez,[†] Francesco Ferranti,[‡] and María Luisa Moyá*,[†]

Departamento de Química Física, Universidad de Sevilla, C/Profesor García González s/n, 41012 Sevilla, Spain, and Dipartimento di Chimica Fisica ed Inorganica, Università degli Studi di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

The ligand substitution reaction between $Fe(CN)_5H_2O^{3-}$ and β-$Co(trien)_2(pzCO_2)^{2+}$ (trien = triethylenetetraammine; $pzCO_2$ = pyrazinecarboxylate) was studied in aqueous salt and sodium dodecyl sulfate micellar solutions. In homogeneus aqueous solutions, an increase in the concentration of the background electrolytes resulted in a decrease in the observed rate constant. This was explained by considering the influence of the salts on the activity coefficients of the participants in the reaction using a Guggenheim–Guntleberg-type equation. In sodium dodecyl sulfate micellar solutions, the effect of the variation of the surfactant concentration operated mainly through its influence on the approaching process between the two oppositely charged reactants. When the surfactant concentration is high enough to ensure the total incorporation of the Co(III) complex molecules into the micellar pseudophase, the decrease in the electrical component of the free energy of activation (controlled by changes in the interfacial electrical potential, $\Delta\Psi$) is responsible for the increase in the observed rate constant when [SDS] increases. The addition of salts and alcohols to the sodium dodecyl sulfate micellar reaction media provokes an increase in the observed rate constant, this increase being greater the higher the [additive]. This can be explained considering that the presence of these additives results in a diminution of the electric component of the free energy of activation due to a decrease in $|\Delta\Psi|$ of the negatively charged micelles.

Introduction

The effects of ionic micelles on the rates of the reactions can be discussed by considering that the free energy of activation, controlling the observed rate constant, has two components: an intrinsic one, independent of the influence of the interfacial electrical potential, and an electric component representing the contribution of the electrical potential. To investigate the influence of the electric component on the reaction rate, a suitable process has to be studied. In a previous work,[1] the ligand substitution reaction between $Fe(CN)_5H_2O^{3-}$ and $Co(en)_2(pzCO_2)^{2+}$ was studied in aqueous sodium dodecyl sulfate, SDS, micellar solutions. The experimental results showed that the presence of the negatively charged SDS micelles affected the reaction mainly through the reactants-approaching process and that changes in the interfacial electrical potential were important in controlling reactivity. However, this study was incomplete because solubility problems did not permit the reaction to be carried out in a reaction medium with [SDS] < 0.03 mol dm^{-3}. On the other hand, a quantitative relation between the observed rate constant, k_{obs}, and the electrical interfacial potential, $\Delta\Psi$, values was not done. With this in mind, the authors were looking for a process whose observed rate constant was expected to be controlled by the electric component of the free energy of activation, but without solubility problems that precluded the study of the reaction within the whole range of [SDS]. The ligand substitution reaction between $Fe(CN)_5H_2O^{3-}$ and β-$Co(trien)(pzCO_2)^{2+}$ seemed

to be a good candidate. The mechanism of this reaction is similar to that followed by the process studied in ref 1. Therefore, changes in the interfacial electrical potential are expected to determine the changes in k_{obs}. The reaction renders a binuclear complex characterized by a high molar extinction coefficient,[2] allowing the use of low reactants concentrations. Besides, the β-$Co(trien)(pzCO_2)^{2+}$ complex is more hydrophobic than the bis(ethylenediamine) one, and no solubility problems were found when the reaction was carried out in dilute aqueous SDS micellar solutions. Since this ligand substitution reaction was not studied previously, this work begins with the investigation of the process in homogeneus aqueous solutions, in the presence of various amounts of different electrolytes. After that, the reaction was carried out in the presence of SDS micelles in a wide surfactant concentration range. Finally, the effect of the addition of salts and alcohols to the micellar reaction media on the observed rate constant was investigated. All the experiments were done at 298.2 K.

Experimental Section

Materials. β-(Triethylenetetraammine)(pyrazinecarboxylato)cobalt(III) perchlorate, β-$[Co(trien)(pzCO_2)](ClO_4)_2$, and sodium amminopentacyanoferrato(II) trihydrate, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, were prepared by published methods[3,4] and characterized by visible absorption spectra and CHN microanalysis. The β-dimer of the cobalt(III) complex shows an absorption band at 467 nm, with $\epsilon = 130$ mol^{-1} dm^3 cm^{-1}. The amminopentacyanoferrato(II) complex shows an absorption band at 400 nm with $\epsilon = 450$ mol^{-1} dm^3 cm^{-1}. The IR spectrum of the cobalt(III) complex was also recorded.

* To whom all correspondence should be addressed. E-mail: moya@cica.es.
† Universidad de Sevilla.
‡ Universitá degli Studi di Bologna.

(1) Rodríguez, A.; Graciani, M. M.; Moyá, M. L. *Langmuir* **1996**, *12*, 4093.

(2) Toma, H. E. *Inorg. Nucl. Chem.* **1975**, *37*, 785.
(3) Sargeson, A. M. *Inorg. Chem.* **1967**, *6*, 787.
(4) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd. ed.; Academic Press: New York, 1965; Vol. 2, p 1511.

Sodium dodecyl sulfate was obtained from Aldrich and was used without further purification. Its critical micelle concentration (cmc) obtained by means of conductivity measurements was in agreement with that in the literature. All the alcohols used were obtained from Aldrich. NaNO$_3$, KNO$_3$, LiNO$_3$, Ca(NO$_3$)$_2$, Mg(NO$_3$)$_2$, Mg(NO$_3$)$_2$, NaCl, CsCl, LiCl, and NaClO$_4$ were obtained from Merck. Tetrabutylammonium bromide, But$_4$NBr, tetrapropylammonium bromide, Pr$_4$NBr, tetraethylammonium bromide, Et$_4$NBr, and tetramethylammonium bromide, Me$_4$NBr, were obtained from Aldrich. Water was obtained from a Millipore Milli-Q water system; its conductivity was less than 10^{-6} S cm^{-1}.

The amminopentacyanoferrate(II) gives the aqua complex Fe(CN)$_5$H$_2$O^{3-} instantly on dissolution (λ_{max} = 440 nm and $\epsilon \approx$ 700 mol^{-1} dm^3 cm^{-1} in pure water[5]). Therefore, our subsequent discussion will be based on the consideration that the reactant iron(II) species is the aquopentacyanoferrate(II) complex.

Conductivity Measurements. Conductivity was measured with a Crison MicroCM 2201 conductometer connected to a water flow thermostat maintained at 298.2 ± 0.1 K.

Kinetics. The rate measurements were performed using a Hi Tech stopped-flow and a Unicam UV-2000 spectrophotometer, depending on the reaction time. Kinetics were followed in all cases at the wavelength of the maximum absorbance in the binuclear complex. The spectra of this complex in the different reaction media were recorded in a Hewlett-Packard diode array. The thermostatic system maintained the temperature in a range ±0.1 K.

Thermal- and light-induced electron transfer are known to occur between iron(II) and cobalt(III) centers mediated by bridging pyrazines.[6] In this respect, the binuclear complex [(en)$_2$Co(μ-pzCO$_2$)Fe(CN)$_5$]$^-$ is much less reactive than the complex [(NH$_3$)$_4$Co(μ-pzCO$_2$)Fe(CN)$_5$]$^-$ ($k_{et} < 10^{-5}$ s^{-1} and $k_{et} =$ 1.3 × 10^{-2} s^{-1} for the former and the latter electron-transfer reactions, respectively[6]) because of a substantial decrease in the driving force compared to that of the tetraammine complex. In the case of the [β-(trien)Co(μ-pzCO$_2$)Fe(CN)$_5$]$^-$ binuclear species a greater decrease in the driving force is expected accompanying the electron-transfer reaction than that in the ethylenediamine complex. That is, a rate constant for the electron-transfer reaction between the cobalt(III) and the iron(II) centers smaller than 10^{-5} s^{-1} is expected, as was found. Therefore, no coupling between the binuclear complex formation and the subsequent electron-transfer reaction occurs.

Kinetic measurements were always taken in fresh solutions. N$_2$ was bubbled through the water before preparing the aqueous and micellar solutions to prevent oxidation of the iron(II) complex. All the media studied were unbuffered, since the reaction is pH-independent within the range 5 < pH < 9.

In all cases the cobalt(III) complex concentration was in large excess to work under pseudo-first-order conditions. The reactant concentrations used were [Fe(II)] = 4 × 10^{-5} mol dm^{-3} and [Co-(III)] = 8 × 10^{-4} mol dm^{-3} in aqueous solutions and [Fe(II)] = 4 × 10^{-5} mol dm^{-3} and [Co(III)] = 4 × 10^{-4} mol dm^{-3} in micellar solutions. The observed rate constants were obtained from the slopes of ln($A_\infty - A_t$) vs the time plots, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, respectively. Under these working conditions the first-order kinetic plots were linear over more than 3 half-lives. For the stopped-flow measurements no less than 15 determinations contribute to each k_{obs} value. For the slower reactions each k_{obs} value was obtained from 6 determinations. The rate constants were reproducible within a precision of 5% or better.

Results

The cmc of aqueous sodium dodecyl sulfate solutions could not be obtained in the presence of the cobalt(III) reactant because of solubility problems. The cmc of the SDS solutions in the presence of 4 × 10^{-5} mol dm^{-3} of aquopentacyanoferrato(II) ions was obtained from conductivity measurements and was equal to 8 × 10^{-3} mol dm^{-3}.

(5) Norris, P. R.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1995**, 3643.
(6) Malin, J.; Ryan, D.; O'Halloran, V. *J. Am. Chem. Soc.* **1978**, *100*, 2097.

Table 1. Observed Rate Constants for the Reaction Fe(CN)$_5$H$_2$O^{3-} + β-Co(trien)(pzCO$_2$)$^{2+}$ → [β-(trien)Co(μ-pzCO$_2$)Fe(CN)$_5$]$^-$ in Several Electrolyte Aqueous Solutions; T = 298.2 K[a]

[Salt]/mol dm^{-3}	k_{obs}/s^{-1}				
	NaNO$_3$	KNO$_3$	LiNO$_3$	NaCl	NaClO$_4$
10^{-3}	9.67	8.52	8.87	11.4	10.6
5×10^{-3}	8.74	7.78	8.33	10.1	10.1
10^{-2}	7.49	6.82	7.52	9.29	9.08
5×10^{-2}	4.92	4.44	4.69	5.56	5.43
10^{-1}	3.01	2.67	3.55	4.12	3.99
2×10^{-1}	1.75	1.68	2.24	2.47	2.49

[Salt]/mol dm^{-3}	k_{obs}/s^{-1}		
	Ca(NO$_3$)$_2$	Mg(NO$_3$)$_2$	Sr(NO$_3$)$_2$
5×10^{-4}	8.30	10.2	10.4
2.5×10^{-3}	6.63	7.98	8.17
5×10^{-3}	5.13	6.35	6.40
2.5×10^{-2}	3.33	3.32	3.36
5×10^{-2}	1.88	2.29	2.50
10^{-1}	1.38	1.33	1.35

[a] [Co(III)] = 8 × 10^{-4} mol dm^{-3}; [Fe(II)] = 4 × 10^{-5} mol dm^{-3}.
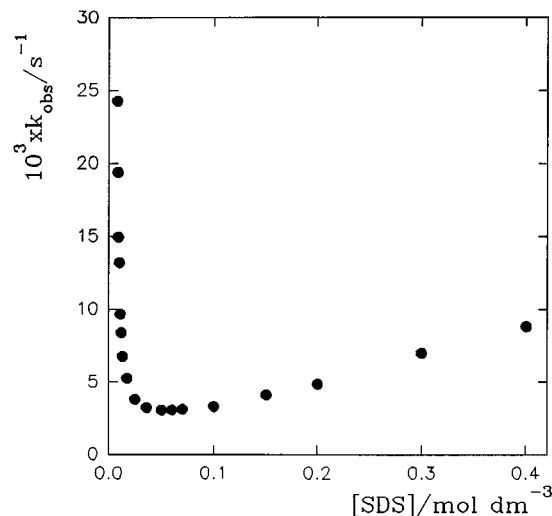
Figure 1. Dependence of k_{obs}/s^{-1} on the SDS concentration for the reaction Fe(CN)$_5$H$_2$O^{3-} + β-Co(trien)(pzCO$_2$)$^{2+}$ → [β-(trien)-Co(μ-pzCO$_2$)Fe(CN)$_5$]$^-$. T = 298.2 K.

The dependence of the pseudo-first-order rate constant on the Co(III) complex concentration was investigated in aqueous and SDS micellar solutions. In all cases a second-order rate law was found, first-order in respect to each of the reactants. The plots of k_{obs}/s^{-1} vs [Co(III)]/mol dm^{-3} are straight lines and do not exhibit meaningful intercepts.

Table 1 shows the kinetic data obtained in aqueous solutions in the presence of several background electrolytes. Figure 1 shows the dependence of k_{obs} on the SDS concentration. Figure 2 shows the influence of the addition of various background electrolytes on the observed rate constant in the presence of [SDS] = 0.1 mol dm^{-3}. Table 2 shows the kinetic data obtained for [SDS] = 0.1 mol dm^{-3} in the presence of various amounts of tretraalkyl-ammonium salts. Finally, Table 3 summarizes the kinetic data obtained in an anionic micellar solution with [SDS] = 0.1 mol dm^{-3}, when several amounts of various alcohols are added to the micellar reaction medium.

Discussion

Kinetic results and activation parameter values corresponding to the substitution reactions at pentacyano-ferrate(II) complexes show that these types of processes
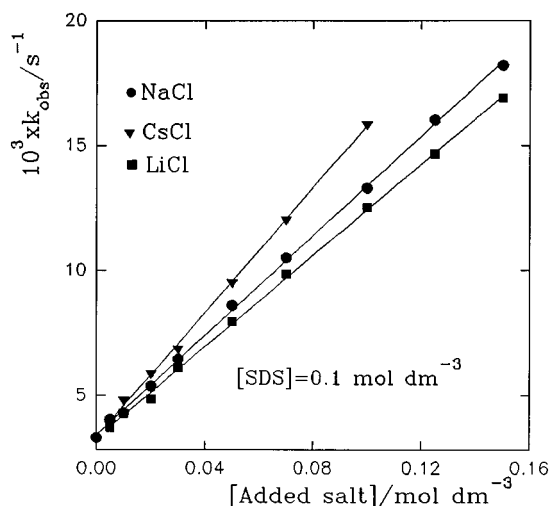
Figure 2. Plots of k_{obs}/s^{-1} for the reaction $Fe(CN)_5H_2O^{3-}$ + β-$Co(trien)(pzCO_2)^{2+} \rightarrow [\beta$-$(trien)Co(\mu$-$pzCO_2)Fe(CN)_5]^-$ vs added electrolyte concentration in aqueous SDS micellar solutions with [SDS] = 0.1 mol dm^{-3}. T = 298.2 K.

take place preferentially through a dissociative mechanism, D, because of the presence of the strong field cyanide ligands;[6-9] that is,

$$Fe(CN)_5H_2O^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_5^{3-} + H_2O \qquad (1)$$

$$Fe(CN)_5^{3-} + \beta\text{-}Co(trien)(pzCO_2)^{2+} \overset{k_2}{\rightarrow}$$
$$[\beta\text{-}(trien)Co(\mu\text{-}pzCO_2)Fe(CN)_5]^- \quad (2)$$
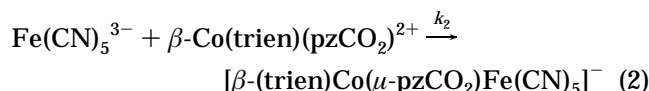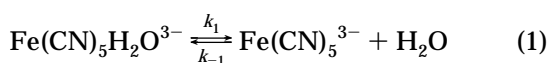
Applying the steady-state approximation, the rate law can be written

$$v = \frac{k_1 k_2}{k_{-1}} [Fe(II)][Co(III)] \qquad (3)$$

and the observed rate constant can be expressed as

$$k_{obs} = \frac{k_1 k_2}{k_{-1}} [Co(III)] \qquad (4)$$

In aqueous salt solutions it was found that k_{obs} decreases when the electrolyte concentration increases. Since the Co(III) concentration remains constant through all the experiments, the decrease in k_{obs} will be due to the influence of salt on $k_1 k_2/k_{-1}$. The reactants are ions of opposite signs, and therefore, on the basis of simple electrostatic interactions a decrease in the reaction rate is expected due to screening effects, which make the approaching process between the reactants less favorable. Table 1 shows that the negative salt effect is specific in the sense that it depends on the nature of the salt present in the reaction medium. The results can be explained by considering the following expression:

$$k_{obs} = k_{obs}^0 \frac{\gamma_A \gamma_B}{\gamma_{\neq}} \qquad (5)$$

In this equation k_{obs}^0 is the rate constant in the reference

(7) Guardado, P.; Van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3473.
(8) Tejera, I.; Rodríguez, A.; Sánchez, F.; Moyá, M. L.; Burgess, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2573.
(9) Abu-Gharib, E. A.; Ben Ali, R.; Blandamer, M. J.; Burgess, J. *Transition Met. Chem.* **1989**, *12*, 371.

Table 2. Observed Rate Constants for the Reaction
$Fe(CN)_5H_2O^{3-}$ + β-$Co(trien)(pzCO_2)^{2+} \rightarrow$
$[\beta$-$(trien)Co(\mu$-$pzCO_2)Fe(CN)_5]^-$ in [SDS] = 0.1 mol dm^{-3}
in the Presence of Various Tetraalkylammonium Electrolytes; T = 298.2 K[a]

	$10^3 \times k_{obs}/s^{-1}$			
[Salt]/mol dm^{-3}	But$_4$NBr	Pr$_4$NBr	Et$_4$NBr	Met$_4$NBr
0.005	3.20	4.59	4.89	4.27
0.010	4.43	5.33	5.80	5.88
0.020	6.21	8.82	11.3	13.2
0.030	8.48	13.2	17.0	17.9
0.035			24.2	28.7
0.040	11.5	22.3	31.5	36.2
0.050	13.8	27.5		
0.070		33.1		
0.100	25.4			

[a] [Co(III)] = 4×10^{-4} mol dm^{-3}; [Fe(II)] = 4×10^{-5} mol dm^{-3}.

Table 3. Observed Rate Constants for the Reaction
$Fe(CN)_5H_2O^{3-}$ + β-$Co(trien)(pzCO_2)^{2+} \rightarrow$
$[\beta$-$(trien)Co(\mu$-$pzCO_2)Fe(CN)_5]^-$ in [SDS] = 0.1 mol dm^{-3}
in the Presence of Various Alcohols; T = 298.2 K[a]

[Hexanol]/M	0.0125	0.0262	0.0322	0.0394	0.050
$10^3 \times k_{obs}/s^{-1}$	3.42	3.80	3.98	4.62	6.13
[Pentanol]/M	0.029	0.0453	0.0678	0.0830	0.103
$10^3 \times k_{obs}/s^{-1}$	3.62	4.46	5.64	7.10	8.74
[Butanol]/M	0.10	0.25	0.50	0.75	1.00
$10^3 \times k_{obs}/s^{-1}$	4.37	6.18	10.7	17.4	25.2
[Propanol]/M	0.103	0.198	0.296	0.328	0.465
$10^3 \times k_{obs}/s^{-1}$	4.57	9.73	16.8	18.5	25.9

[a] [Co(III)] = 4×10^{-4} mol dm^{-3}; [Fe(II)] = 4×10^{-5} mol dm^{-3}.

state, γ_A and γ_B are the activity coefficients of the reactants, and $\gamma_{\#}$ is the activity coefficient for the activated complex. Taking into account the salts concentration ranges used, a Guggenheim−Guntleberg-type equation was used to relate the activity coefficients of a given ionic solute to ionic strength.[10] Equation 5 takes the form

$$\log k_{obs} = \log k_{obs}^0 + \frac{A'I^{1/2}}{1 + I^{1/2}} + bI \qquad (6)$$

In this equation $A' = 2Az_Az_B$, A being the Debye constant, I the ionic strength present in the reaction medium, and b an adjustable parameter whose value depends on the nature of the salt. The second term on the right-hand side of eq 6 represents the Coulombic effects of added salt upon the participants in the reaction. The term bI accounts for the non-Coulombic effects of the salt. Kinetic data summarized in Table 1 were fitted by using eq 6, considering $A' = -6.108$. $\log k_{obs}^0$ and b were considered as adjustable parameters. The agreement between the calculated and the experimental data was good. Table 4 shows the values of the adjustable parameters obtained from the fittings for the different background electrolytes. It can be seen that for all the salts the same value for $\log k_{obs}^0$ was obtained (within experimental errors), as was expected.

Figure 1 shows the dependence of k_{obs} on the sodium dodecyl sulfate concentration. One can see that for low surfactant concentrations, an increase in [SDS] results in a decrease in the observed rate constant. At [SDS] $\approx$ 0.03 mol dm^{-3} k_{obs} reaches a minimum and, subsequently, k_{obs} increases as the surfactant concentration increases. Assuming that the mechanism of the process is the same in micellar solutions as in pure water, the dependence of

(10) Koryta, J.; Drovak, J.; Bohackova, V. *Electrochemistry*; Methuen: London, 1970; p 32.

**Table 4. Adjustable Parameters Obtained from the
Fitting of the Kinetic Data in Aqueous Electrolyte
Solutions by Using Equation 6**

salt	$\log(k_{obs}^0/s^{-1})$	$b/mol^{-1}\ dm^3$
NaNO$_3$	1.26 ± 0.06	4.4 ± 0.8
KNO$_3$	1.20 ± 0.06	4.6 ± 0.8
LiNO$_3$	1.21 ± 0.05	5.6 ± 0.9
Ca(NO$_3$)$_2$	1.10 ± 0.07	4.7 ± 0.9
Mg(NO$_3$)$_2$	1.17 ± 0.07	4.3 ± 0.9
Sr(NO$_3$)$_2$	1.18 ± 0.08	4.4 ± 0.8
NaCl	1.31 ± 0.05	5.0 ± 0.8
NaClO$_4$	1.29 ± 0.05	5.2 ± 0.8

k_{obs} on [SDS] is expected to respond mainly to variations in k_2 provoked by alterations in the surfactant concentration.[1] Path 2 is an approaching process between two species of opposite charge. The iron(II) complex will remain in the bulk aqueous phase, but the positively charged Co-(III) complex will have a strong affinity for the negatively charged micellar surface. The initial decrease in k_{obs} when [SDS] increases can be the consequence of the incorporation of the Co(III) complex into the micellar pseudophase. The cmc of the system could not be obtained in the presence of the cobalt(III) complex concentration used in the kinetics because of solubility problems. Therefore, the authors will consider a value of 8×10^{-3} mol dm^{-3} as an upper limit (one would expect the cmc to decrease because of the presence of the positively charged Co(III) complex). For SDS concentrations close to 8×10^{-3} mol dm^{-3}, the concentration of micelles in the reaction medium is low and the β-Co(trien)(pzCO$_2$)$^{2+}$ molecules will distribute between the aqueous and micellar phases. When [SDS] increases, the concentration of the micelles also increases and the incorporation of the Co(III) complex into the micellar pseudophase will be favored. The Fe(CN)$_5$$^{3-}$ species are in the aqueous phase and the approaching process between these molecules and the β-Co(trien)-(pzCO$_2$)$^{2+}$ molecules residing in the aqueous phase will be easier to incorporate than the approaching process when the β-Co(trien)(pzCO$_2$)$^{2+}$ molecules are incorporated into the negatively charged micelles. For this reason, k_{obs} is expected to decrease as [SDS] increases until all the cobalt(III) complex molecules were incorporated into the SDS micelles. A subsequent increase in the surfactant concentration would not provoke a decrease in k_{obs}. However, it was found that, after a minimum, k_{obs} increases as [SDS] increases. This can be explained by considering that an increase in the surfactant concentration results in a decrease in the interfacial electrical potential, $\Delta\Psi$.[11] This decrease in $\Delta\Psi$ of the negatively charged SDS micelles will favor the approaching process between the negatively charged Fe(CN)$_5$$^{3-}$ molecules and the β-(trien)Co(pzCO$_2$)$^{2+}$ complex molecules residing in the negatively charged micellar surface and will, therefore, increase the reaction rate. In this regard, it was found that the plot of ln k_{obs} vs $\Delta\Psi$, for [SDS] ≥ 0.06 mol dm^{-3}, is a good straight line. The assumption that within this surfactant concentration range all of the Co(III) complex is incorporated into the micellar pseudophase (that is, the reaction will take place in the Stern layer) indicates that the changes in the electrical component of the free energy of activation, representing the contribution of the electrical potential, is the main factor controlling reactivity. Of course, other factors influencing reactivity can be operative, such as

possible structural changes when [SDS] changes[12,13] and the influence of changes in the surfactant concentration on path 1.

Now, it is interesting to compare the results obtained in ref 1 with those obtained in this work. Given the similarity between the two reactions, like variations in k_{obs} by changing [SDS] were expected. In the case of the process Fe(CN)$_5$H$_2$O^{3-} + Co(en)$_2$(pzCO$_2$)$^{2+}$, the initial decrease in k_{obs} by increasing [SDS] was not observed because solubility problems precluded the experiments with dilute [SDS]. For [SDS] ≥ 0.03 mol dm^{-3}, an initial increase in k_{obs} is found when [SDS] increases but, at [SDS] ≈ 0.2 mol dm^{-3}, k_{obs} reached a plateau and a subsequent increase in the surfactant concentration did not result in k_{obs} changes. For the reaction under study in this work, no plateau was found for the dependence of k_{obs} on [SDS] for surfactant concentrations up to 0.4 mol dm^{-3}. The authors tried to carry out the reaction in the presence of [SDS] > 0.4 mol dm^{-3}. Experimental data seemed to indicate that the reaction rate leveled off at high [SDS]. However, in the presence of these high surfactant concentrations, the kinetics were not reproducible and the final absorbance was smaller than that expected. This did not permit the obtainment of reliable rate constant values and no conclusions could be drawn. So far, the authors have not found a plausible explanation for the difference observed for the two ligand substitution processes.

To investigate the importance of the electrical component in k_{obs}, the effects of added electrolytes and added alcohols to the micellar reaction media on the reaction rate were studied. Figure 2 and Tables 2 and 3 show the changes in k_{obs} provoked by the addition of different amounts of various background electrolytes and alcohols, in the presence of [SDS] = 0.1 mol dm^{-3}. This surfactant concentration was chosen to ensure that all the Co(III) complex molecules were incorporated into the micellar pseudophase. In both cases, an increase in the amount of additive present in the micellar medium results in an increase in k_{obs}. Figure 2 also shows that, for a given electrolyte concentration, $k_{obs}(Li^+) < k_{obs}(Na^+) < k_{obs}(Cs^+)$. It is known that the addition of this type of electrolytes to an SDS micellar solution results in a decrease in the $\Delta\Psi$ values, this decrease being greater the higher the added salt concentration is.[14,15] The observed decrease in $\Delta\Psi$, at a given electrolyte concentration, depends on the nature of the salt. This lowering is higher when the hydrated counterion radius is smaller, following the sequence $\Delta\Psi(Cs^+) < \Delta\Psi(Na^+) < \Delta\Psi(Li^+)$.[16] Therefore, considering that for [SDS] = 0.1 mol dm^{-3} the Co(III) complex is totally bound to the anionic micelles, and assuming that the influence of added salts on k_{obs} works mainly through their influence on path 2, the expected trend would be $k_{obs}(Li^+) < k_{obs}(Na^+) < k_{obs}(Cs^+)$, as in fact was found. This indicates that the main factor influencing reactivity is the variation in $\Delta\Psi$ by changing the added salt concentration. The authors found $\Delta\Psi$ values for SDS micellar solutions in the presence of some of the added electrolytes studied in the literature.[15,16] However, these data do not correspond to [SDS] = 0.1 mol dm^{-3}, but to much more dilute surfactant concentrations, and they could not be used. In the Bernas et al. paper[17] a few $\Delta\Psi$

(11) Charbit, G.; Dorion, F.; Gaboriaud, R. *J. Chim. Phys.* **1984**, *81*, 187.
(12) Bezzobotnov, V. Yu.; Borbely, S.; Cser, L.; Faragó, B.; Gladkih, I. A.; Ostanevich, Yu. M.; Vass, Sz. *J. Phys. Chem.* **1988**, *92*, 5738.
(13) Bales, B. L.; Almgrem, M. *J. Phys. Chem.* **1995**, *99*, 2498.

(14) Hartland, G. V.; Grieser, F.; White, L. R. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 591.
(15) Frahm, J.; Dieckmann, S.; Haase, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 566.
(16) Fernández, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 566.
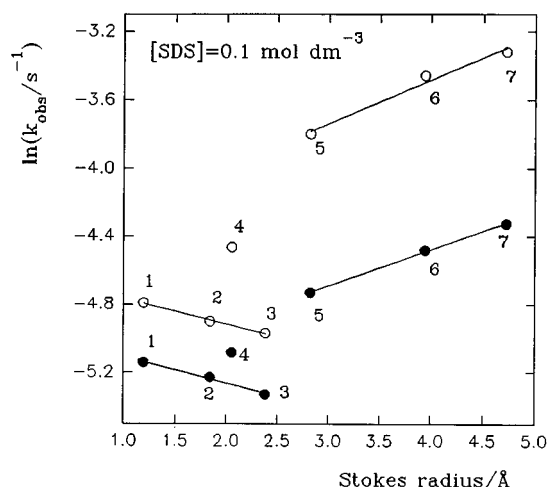(17) Bernas, A.; Grand, D.; Hasutecloque, S.; Giannotti, C. *J. Phys. Chem.* **1986**, *90*, 6189.

Figure 3. Plot of $\ln(k_{obs}/s^{-1})$ vs the hydrated Stokes radius for the reaction $Fe(CN)_5H_2O^{3-} + \beta\text{-Co(trien)}(pzCO_2)^{2+} \rightarrow [\beta\text{-(trien)-}Co(\mu\text{-}pzCO_2)Fe(CN)_5]^-$ in aqueous SDS micellar solutions, with [SDS] = 0.1 mol dm^{-3}, in the presence of various added electrolytes. [Salt] = 0.02 mol dm^{-3}; [Salt] = 0.04 mol dm^{-3}. T = 298.2 K. Numbers represent: 1, NCsCl; 2, NaCl; 3, LiCl; 4, Me$_4$NBr; 5, Et$_4$NBr; 6, Pr$_4$NBr; 7, But$_4$NBr.

values for various salts, at [salt] = 0.1 mol dm^{-3}, in the presence of [SDS] = 0.1 mol dm^{-3} are reported. The plot of ln k_{obs} vs $\Delta\Psi$ is a good straight line, although only three points are present in the figure.

Table 2 shows that k_{obs} increases by increasing the tretraalkylammonium salts concentrations. This decrease depends on the nature of the salt. In the case of quaternary salts it seems that a hydrophobic bonding with the exposed hydrocarbon on the micelle surface overcomes the electrostatic contribution of the cation–headgroup interactions.[18] One can consider that the trend in the interfacial potential may be $\Delta\Psi(Bu_4NBr) < \Delta\Psi(Pr_4NBr) < \Delta\Psi(Et_4NBr)$, which could explain the experimental trend observed in k_{obs}. In the case of the tetramethylammonium salt, it is not clear if the hydrophobic interactions overcome the electrostatic ones, and in fact the behavior of this salt is different from that shown by other tetraalkylammonium salts.[19] The authors have not found $\Delta\Psi$ values for SDS micellar solutions in the presence of tetraalkylammonium salts. However, in the case of the other electrolytes studied, it was found that, at least for [SDS] = 0.1 mol dm^{-3}, the lowering in $\Delta\Psi$ originated by the presence of LiCl, NaCl, and CsCl is nearly proportional to the hydrated Stokes radii of the cations.[11,17] Assuming a similar relation between the $\Delta\Psi$ values and the hydrated Stokes radii of the cations for the tetraalkylammonium salts, Figure 3 was plotted. This figure shows the plot of ln k_{obs} vs the Stokes radius of the different cations of the salts used as backgound electrolytes for [SDS] = 0.1 mol dm^{-3} and two salt concentrations. One can see that a linear dependence is found for the two sets of salts used, in agreement with the expected control of the reaction rate by changes in the interfacial electrical potential. At this point it is worth noting that the addition of salts changes the structural

characteristics of the SDS micelles (changes in the cmc, in the aggregation number, in the dissociation degree, etc.).[19–25] Of course, these changes can affect the observed rate constant value. Nonetheless, the experimental results seem to indicate that the changes in the interfacial electrical potential is the more important factor controlling reactivity.

Table 3 shows the kinetic data obtained when various alcohols were added to a micellar solution with [SDS] = 0.1 mol dm^{-3}. In all cases an increase in k_{obs}, by increasing [alcohol], was found. In a recent work[26] the localization of n-alcohols and their structural effects in aqueous solutions of sodium dodecyl sulfate were studied. On one hand, their results showed that short-chain alcohols tend to remain in the aqueous phase and, by altering the solvent properties, induce a decrease in the aggregation number of the micelles. On the other hand, alcohols with longer hydrocarbon chains were found to be present in both phases; their presence in the micellar phase being more important the longer the alkyl chain and the larger the concentration. This was rationalized by assuming that the insertion of alcohol molecules in the micelle produces weaker repulsive interactions between the charged head-groups of the surfactant molecules. In the case of the alcohols used in this work, within the concentration ranges studied, an increase in the dissociation degree of the SDS micelles and a decrease in the aggregation number are found when the amount of alcohol increases.[27] However, it seems that the surface charge density decreases. Hartland et al.[14] measured the surface potential of sodium dodecyl sulfate micelles in pentanol–SDS systems, with [SDS] = 0.05 mol dm^{-3}, by using a micelle-solubilizing acid–base indicator. They found that $\Delta\Psi$ decreases as the amount of alcohol increases. To use these data, and given that 0.05 mol dm^{-3} can be assumed to be a high enough surfactant concentration to ensure that all the Co(III) complex molecules were localized into the micellar pseudophase, the reaction was followed in the presence of this surfactant concentration and at the same pentanol concentrations shown in Table 3. The plot of the logarithm of these kinetic data vs the corresponding $\Delta\Psi$ values is a good straight line, showing the importance of the electrical contribution to k_{obs}. The influence of the nature of the alcohol could be explained by considering that the experimental trends observed show the effectiveness of the different alcohols in lowering $\Delta\Psi$.

Summarizing, in dilute and moderately concentrated salt solutions kinetic salt effects on the binuclear complex formation between $Fe(CN)_5H_2O^{3-}$ and β-Co(trien)(pz-CO$_2$)$^{2+}$ have been explained by considering the influence of the salts on the activity coefficients of the participants in the reaction, using a Guggenheim–Guntlenberg-type equation. In the case of the SDS micellar solutions, the SDS concentration influences the reaction rate mainly through the approaching process of the reagents (it is assumed that the formation of the species $Fe(CN)_5^{3-}$ is not influenced much by changes in [SDS]). At a high enough [SDS] to incorporate all the Co(III) complex molecules into the micellar pseudophase, changes in $\Delta\Psi$, by changing [SDS], seem to be the dominant factor controlling reactivity. Under these [SDS] conditions, added

(18) Almgrem, M.; Swarup, S. *J. Phys. Chem.* **1983**, *87*, 872.

(19) Mukerjee, P.; Mysels, K.; Kapanan, P. *J. Phys. Chem.* **1966**, *71*, 4166.

(20) Llanos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.

(21) Quina, F. H.; Nassar, P. M.; Bonilha, J. B. S.; Bales, B. L. *J. Phys. Chem.* **1995**, *99*, 17028.

(22) Dutt, G. B.; van Stam, J.; De Schryver, F. C. *Langmuir* **1997**, *13*, 1957.

(23) Siemiarczuk, A.; Ware, W. R.; Liu, Y. S. *J. Phys. Chem.* **1993**, *97*, 8082.

(24) Kuman, S.; Aswal, V. K.; Goyal, P. S.; Kabir-ud-Din *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 761.

(25) Kuman, S.; David, S. L.; Aswal, V. K.; Goyal, P. S.; Kabir-ud-Din *Langmuir* **1997**, *13*, 6461.

(26) Caponnetti, E.; Martino, D. Ch.; Floriano, A. M.; Triolo, R. *Langmuuir* **1997**, *13*, 3277.

(27) Zana, R. *Adv. Colloid Interface Sci.* **1995**, *57*, 1.

electrolytes and added alcohols influence the reaction rate principally through the changes in $\Delta\Psi$ provoked by their presence in the micellar reaction medium. That is, in aqueous SDS micellar solutions, in the presence and absence of added salts and added alcohols, changes in k_{obs} are governed by variations in the $\Delta\Psi$.