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Use of the Pseudophase Model in the Interpretation of Reactivity under Restricted Geometry Conditions. An Application to the Study of the $[Ru(NH_3)_5pz]^{2+} + S_2O_8{}^{2-}$ Electron-Transfer Reaction in Different Microheterogeneous Systems

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Abstract: The title reaction has been studied under restricted geometry conditions, comprising aqueous solutions of a polymer (DNA), cyclodextrins, and dendrimers as well as (CTA)Cl micellar solutions and sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/water/oil microemulsions. The results are interpreted by taking as a general basis the pseudophase model, modified in some cases in order to take into account the specificity of the reaction medium. These modifications describe the anti-cooperative character of the binding of the substrates to the surfaces and the changes of the electric potential at the surfaces. The conclusion is that the pseudophase model is a powerful tool for the interpretation of kinetic data in the reaction media considered in this work, provided that the specificity of these media were incorporated into the model.

Introduction

Recently there has been a growing interest in the study of electron-transfer reactions under conditions globally referred to as restricted geometry conditions,[1] that is, under conditions in which one or both reactants are forced to remain at the surface of micelles[1a−l] or in the cavity of cyclodextrins and related compounds[1m] or at the surface of DNA,[1n−w] etc. These studies are of interest for several reasons: (i) According to the charges of the reactants, their local concentrations can increase or decrease in relation to their bulk concentrations, thus allowing the tunning of reaction rates. (ii) Generally speaking, the properties of local reaction media are quite different from the properties of the bulk of the solutions as a consequence of the intense local electric fields. These fields affect all the relevant parameters that modulate the rate of electron-transfer processes. So, the solvent reorganization energy depends on the dielectric characteristics of the surrounding medium,[2] and these characteristics are modified by the field through solvent saturation effects.[3] On the other hand, the free energy of the reaction is dependent on the field, because the free energies of the reactant and product states also depend on the dielectric constant of the medium. Moreover, the field may change the adiabaticity of the reaction through the polarization of the orbitals of the reactants involved in the electron transfer.[4] The dynamics of the solvent, and thus the preexponential term in the rate constant, are also changed by the field.[5] Indeed, the diffusion coefficients of the intervening species, corresponding to the nonhomogeneous state (in the presence of the field), are quite different from those of the homogeneous state (without the field).[6] Therefore, the equilibrium correlations, such as the direct correlation functions, in the presence of a field may also be

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(6) The dynamics of water relaxation in, for example, reverse micelles is retarded in relation to pure water (see: Harza, P.; Sarkar, N. *Chem. Phys. Lett*. **2001**, *342*, 303, and references therein. A treatment of the retardation of the dynamics of water under restricted condition has been proposed. See: Bagchi, B.; Chandra, A. *Adv. Chem. Phys*. **1991**, *80*, 1.

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rather different from those in the absence of the field.[6] Finally, it has been suggested that the fluctuation dissipation theorem and other important theorems of statistical mechanics may no longer be valid in the presence of a strong field.[6] Thus, in the presence of micelles of hexadecyltrimethylammonium chloride ((CTA)Cl), the Franck−Condon factor for the intermolecular electron-transfer process within the binuclear complex pentaammineruthenium(III)(μ-cyano)pentacyanoruthenium(II)[7] increases by a factor of 10.[8]

For the above-mentioned reasons, there has been a huge amount of study done on electron-transfer processes (and other types of reations[8]) in the systems considered here. However, works are scarce in which a systematic study of a given reaction in different media was considered.[9] For this reason, we thought the study of the kinetics of the electron-transfer reaction between pentaammine(pyrazine)ruthenium(II) and peroxodisulfate in a series of reaction media constituted by aqueous solutions of cyclodextrins, DNA, and dendrimers as well as in (CTA)Cl micellar solutions and sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/oil/water microemulsions to be of interest. It should be mentioned that a previous study of this reaction in SDS micellar solutions was carried out by the present authors.[10]

As will be seen below, these reaction media present common as well as different characteristics. The similarities permit the interpretation of all the results, taking as a general starting point the pseudophase model.[11] However, in some cases, the model needs to be modified in order to take into account the particular characteristic of the given reaction medium. These modifications describe the anti-cooperative character of the binding of the substrates to the surfaces and the influence of the changes of the electrical potential at these surfaces. The pseudophase model, as will be seen below, permits a rationalization of ligand binding to the different systems considered in this work. This process of ligand binding is a key element in virtually all biological processes.[12]

Experimental Section

Materials. The complex $[Ru(NH_3)_5pz]^{2+}$ (pz = pyrazine), as perchlorate salt, was prepared and purified according to published procedures.[13] Sodium peroxodisulfate, sodium bis(2-ethylhexyl)sulfosuccinate (AOT), and hexadecyltrimethylammonium chloride ((CTA)Cl) were obtained from Fluka. AOT was stored in a vacuum desiccator over P_2O_5 for several days before use. The solutions of (CTA)Cl were titrated by a standard procedure.[14] The organic solvents used were obtained from Merck and dried over a 4 Å type molecular sieve. This molecular sieve was activated by heating it at 200 °C under reduced pressure for several hours and then cooled in vacuo over silica gel. Calf thymus DNA was purchased from Pharmacia and used without further purifications, because in preliminary experiments it was determined that purification does not introduce any change in the observed kinetics. Neither buffer solutions nor background electrolytes were added to the DNA solutions. Thus, as in the case of purification, it was found in preliminary experiments that the addition of buffer ($[Na(CH_3)_2AsO_2{\cdot}3H_2O] = 3 \times 10^{-3}$ mol dm^{-3} and $[HCl] = 3.8 \times 10^{-4}$ mol dm^{-3}, pH ≈ 7) does not modify the kinetic results (as long as the ionic strength of the solutions was kept constant). There was no need for a background electrolyte in order to maintain a constant ionic strength in the aqueous phase in contact with DNA. This was checked by carrying out a study of the kinetics of the $[IrCl_6]^{2-} + I^-$ reaction.[15] The results of this study showed there are no changes in the rate of the reaction when the DNA concentration changes. Since this reaction is sensitive to the changes of ionic strength in the aqueous phase, the results obtained imply that there is no change in the ionic strength in the aqueous phase. Polynucleotide concentrations were determined spectrophotometrically from the molar absorptivity (6600 mol^{-1} dm^3 cm^{-1} at 258 nm).[16] The α- and β-cyclodextrins (Merck) were dried at 80 °C for at least 12 h prior to use. The commercial starburst dendrimer (SB4.5G) was from Aldrich and used as received. The probes 4-heptadecylumbelliferone (Biochemika Fluka for fluorescence) and pyrene-1-carboxaldehyde (pyCHO), from Aldrich, were used without further purification. The Na_2SO_4 anhydro salt used was from Merck. The water used in preparation of the solutions has a conductivity $\approx 10^{-6}$ S m^{-1} and was deoxygenated before use.

Kinetic Measurements. Kinetic runs were carried out in a stopped-flow spectrophotometer from Hi-Tech or in a manual mixing system from Hi-Tech coupled to a Hitachi 150-20 UV−vis spectrophotometer. The reaction was monitored by following the changes in absorbance of the $[Ru(NH_3)_5pz]^{2+}$ at 472 nm. This wavelength corresponds to the maximum of the absorbance of the complex in all the reaction media studied here, except in the case of cyclodextrin solutions where the maximum of absorbance of the ruthenium complex depends on the concentration of the cyclodextrin. However, no changes in the molar extintion coefficient of the ruthenium complex were observed in these solutions.

All the kinetic runs were carried out under pseudo-first-order conditions using an excess of the oxidant. The concentrations of reactants were changed to look for the best working conditions in each reaction medium. These concentrations were the following:

(i) In α- and β-cyclodextrin solutions $[Ru(NH_3)_5pz^{2+}] = 2.0 \times 10^{-5}$ mol dm^{-3} and $[S_2O_8{}^{2-}] = 2.0 \times 10^{-4}$ mol dm^{-3}.

(ii) In the dendrimer solutions the concentrations were the same as in the cyclodextrin solutions.

(iii) In DNA solutions $[Ru(NH_3)_5pz^{2+}] = 2.0 \times 10^{-5}$ mol dm^{-3} and $[S_2O_8{}^{2-}] = 1.5 \times 10^{-4}$ mol dm^{-3}.

(iv) In (CTA)Cl solutions $[Ru(NH_3)_5pz^{2+}] = 4.0 \times 10^{-5}$ mol dm^{-3} and $[S_2O_8{}^{2-}] = 3.5 \times 10^{-4}$ mol dm^{-3}.

(v) In microemulsions (referred to the aqueous phase) $[Ru(NH_3)_5pz^{2+}] = 8.0 \times 10^{-5}$ mol dm^{-3} and $[S_2O_8{}^{2-}] = 3.5 \times 10^{-3}$ mol dm^{-3}.

(vi) In Na_2SO_4 solutions $[Ru(NH_3)_5pz^{2+}] = 8.0 \times 10^{-5}$ mol dm^{-3} and $[S_2O_8{}^{2-}] = 3.5 \times 10^{-3}$ mol dm^{-3}.

The temperature was always maintained at 298.1 ± 0.1 K. Kinetic complications were not observed.

Pseudo-first-order rate constants were obtained from the slopes of the plots of $\ln(A_{t} - A_\infty)$ vs time, where A_t and A_∞ were the absorbances at times t and when the reaction was finished. These plots were good straight lines for at least four half-lives. All the experiments were repeated at least five times. The estimated uncertainty in the rate constant was less than 5%.

Determination of the Critical Micellar Concentration. The critical micellar concentration (cmc) corresponding to the (CTA)Cl surfactant was obtained in the presence of the anionic reactant, that is, the reactant of opposite charge sign of the micelles, because, as is known, the cmc depends on the nature and concentration of the counterions (the small influence of the $ClO_4{}^-$ ions coming from the solutions of the ruthenium

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complex was ignored, taking into account the complex concentration is 1 order of magnitude smaller than the concentration of the oxidant). This cmc was obtained from conductivity measurements, carried out with a Crisson 522 conductimeter connected to a water-flow thermostat in such a way that the temperature was maintained at 298.1 ± 0.1 K. The cmc was obtained from the intersection point of the two linear plots corresponding to the representation of conductivity vs the logarithm of the surfactant concentration. A value of 4.8×10^{-5} mol dm^{-3} was obtained following this procedure.

Surface Potential Determinations. As is known, there is a difference of electric potential, Ψ, between the surface of a micelle (direct or reverse) and the aqueous phase in contact with the micelle. These potentials can be relevant in relation to the kinetic effects of micelles. For this reason, the potential drops in the micelles (direct or reverse) studied in this work were determined. In both cases the determination of surface potentials take as a starting point the measurement of the fluorescence of a suitable probe.

Emission intensity measurements were carried out in a Perkin-Elmer 650-40 spectrofluorimeter, interfaced to a PC for the recording and handling of the spectra, at 298.1 ± 0.1 K. Oxygen was removed from the solutions by fluxing them with argon for at least 30 min prior to excitation. From the emission intensities the values of the surface potentials were obtained as follows:

(a) Surface Potentials at the Aqueous Interface in AOT/Decane/Water Microemulsions. These surface potentials were obtained from the fluorescence of PyCHO. This compound is practically nonfluorescent in apolar organic solvents but shows a strong luminiscence when it is located at the micellar surface. The wavelength corresponding to the maximum of the fluorescence band depends on the dielectric constant of the medium in contact with the probe. This circumstance permits the determination of the surface potential in the aqueous interface of the microemulsions, according to the method of Grand et al.[17]

(b) Surface Potential at the Aqueous Interface in (CTA)Cl Micelles. These surface potentials were obtained from the changes in the pK of a suitable indicator.

The protonation equilibrium of an indicator bound to the surface of a micelle may be affected not only by the electrostatic potential but also by the different local environment (as compared with the bulk of the solution). Accordingly, the apparent shift of the pK of the indicator at the interfaces (in relation to the pK in water) includes contributions from both the local environment and the electric potential different at the interface. If the pK of the indicator at the interface, in the absence of the electric potential, pK^{i}, were known, this potential could be obtained from the value of the actual pK of the indicator at the interface, pK^{a}, according to[18]

$$\mathrm{p}K^{\mathrm{a}} - \mathrm{p}K^{\mathrm{i}} = -\frac{F\Psi}{2.3RT} \qquad (1)$$

Obviously, pK^{i} cannot be obtained from an experiment. However, it can be considered to be the same as the value of the pK of the indicator in contact with a neutral interface, pK_{o}^{a}. With this assumption, which implies that the enviromental effect is not very different for a neutral and a charged interface, the surface potential at the charged interface can be obtained from:[19,20]

$$\mathrm{p}K^{\mathrm{a}} - \mathrm{p}K_{\mathrm{o}}^{\mathrm{a}} = -\frac{F\Psi}{2.3RT} \qquad (2)$$

In the present work, the neutral interface was that corresponding to the micelles of the (neutral) surfactant Triton X-100 (p$K_{o}^{a} = 8.85$).[20] As indicator, we used heptadecylumbelliferone. This indicator achieves a strong binding to both charged and neutral micelles in such a way that it is possible to avoid any interference from a binding equilibrium (between the micellar and aqueous pseudophases).

Table 1. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8^{2-}$ in α-Cyclodextrin Solutions

10^2[α-CD]/(mol dm^{-3})	k_{obs}/s^{-1}	10^2[α-CD]/(mol dm^{-3})	k_{obs}/s^{-1}
0	7.7	1.75	5.6
0.0100	7.6	3.00	5.4
0.0501	7.2	4.00	5.3
0.270	6.6	6.00	5.2
0.501	6.3	7.50	5.1
0.60	6.2	9.00	5.1
1.00	5.9	10.0	5.1

Table 2. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8^{2-}$ in β-Cyclodextrin Solutions

10^3[β-CD]/(mol dm^{-3})	k_{obs}/s^{-1}	10^3[β-CD]/(mol dm^{-3})	k_{obs}/s^{-1}
0	7.7	7.60	6.2
0.0804	7.6	8.72	6.1
0.403	7.4	10.0	6.0
1.25	7.2	12.5	5.8
2.50	6.9	15.0	5.6
3.60	6.7	17.5	5.5
5.00	6.5	20.0	5.4

Table 3. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8^{2-}$ in SB4.5G Dendrimer Solutions

10^6[D]/(mol dm^{-3})	k_{obs}/s^{-1}	10^6[D]/(mol dm^{-3})	k_{obs}/s^{-1}
0	7.7	9.00	0.36
0.18	5.6	10.3	0.30
0.36	4.5	12.0	0.23
0.45	4.1	36.0	0.053
0.60	3.6	60.0	0.030
0.90	2.7	90.0	0.014
0.96	2.5	200	0.0067
3.6	0.90	300	0.0039
4.80	0.72	450	0.0028
6.00	0.52		

Table 4. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8^{2-}$ in DNA Solutions

10^3[DNA]/ (mol dm^{-3})	k_{obs}/s^{-1}	10^3[DNA]/(mol dm^{-3})	k_{obs}/s^{-1}
0	7.0	0.197	0.060
0.0249	6.6	0.244	0.036
0.0444	5.5	0.256	0.032
0.0588	4.8	0.360	0.023
0.0771	3.5	0.504	0.017
0.0923	1.8	0.718	0.012
0.102	1.6	0.890	0.011
0.121	1.3	1.30	0.010
0.131	0.21	1.81	0.0098
0.152	0.11	2.13	0.0095
0.168	0.074	2.49	0.0093
0.180	0.066		

The ratios between the acid and basic forms were obtained from fluorescence measurements, according to the procedure given in ref 21.

Results

The results obtained in this work are given in Tables 1−6, which contain the results of kinetic measurements as pseudo-first-order rate constants.[22] These results, k_{obs}, correspond to the

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Table 5. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8{}^{2-}$ in (CTA)Cl Micellar Solutions

10^3[(CTA)Cl]/ (mol dm^{-3})	10^3k_{obs}/s^{-1}	10^3[(CTA)Cl]/(mol dm^{-3})	10^3k_{obs}/s^{-1}
5.34	0.97	26.7	0.51
5.87	0.87	32.0	0.52
6.41	0.81	42.7	0.59
6.94	0.77	53.4	0.65
7.15	0.74	64.1	0.79
7.48	0.71	74.8	0.90
8.01	0.69	78.0	0.98
8.54	0.64	90.8	1.2
9.07	0.62	107	1.5
9.60	0.59	125	1.6
10.7	0.57	145	1.8
12.8	0.54	165	2.0
14.9	0.53	192	2.3
17.1	0.52	203	2.4
21.4	0.50		

Table 6. Rate Constant for the Reaction between $[Ru(NH_3)_5pz]^{2+}$ and $S_2O_8{}^{2-}$ in AOT/Decane/Water Microemulsions at [AOT] = 0.2 mol kg^{-1}

W	k_{obs}/s^{-1}	W	k_{obs}/s^{-1}
12.2	3.6	26	1.3
13	3.4	28	1.2
15	2.9	30	1.1
16	2.7	32	1.0
18	2.3	34	0.98
20	1.9	38	0.94
22	1.7	40	0.92
25	1.4	45	0.90

Table 7. Surface Potential (Ψ) Values at Different (CTA)Cl Concentrations

10^3[(CTA)Cl]/(mol dm^{-3})	Ψ/mV	10^3[(CTA)Cl]/(mol dm^{-3})	Ψ/mV
10.7	183	74.8	148
12.8	182	78.0	147
14.9	181	90.8	143
17.1	180	107	138
21.4	177	125	134
26.7	175	145	131
32.0	170	165	127
42.7	163	192	123
53.4	157	203	122
64.1	152		

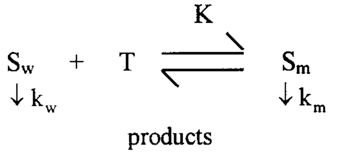
experimental kinetic measurements. Thus, the values of k_{obs} in the tables are independent of any interpretation (see below).

As to the values corresponding to the surface potentials (Tables 7 and 8), they are the results of the elaboration of the primary data, which, according to the methods referred to in the Experimental Section, do not give directly these potentials. A few words seem pertinent in relation to the potential values appearing in the tables. First of all, these potentials are estimated under some assumptions/simplifications. Between them, the most important is that the presence of a probe in the interfacial region does not seriously perturb the structure of the systems. It is clear that this assumption is common to any determination of a microscopic property of a system, based on the use of some kind of probe. On the other hand, it is clear that, even in this case, the property measured (in this case the surface potential) corresponds to the location of the probe. This location is not necessarily the same for all the substrates. According to this, the values of the surface potentials given in the tables must be considered as some sort of indicative values. In fact, in the opinion of the present authors, the variations (with the concentration of the surfactant or with the (water/AOT) molar ratio *W*—see below) are more significant than their absolute values. Fortunately, these variations are precisely the needed data for the discussion.

Table 8. Surface Potential (Ψ) Values in AOT/Decane/Water Microemulsions at [AOT] = 0.2 mol kg^{-1} and Different *W* Values

W	k_{obs}/s^{-1}	W	k_{obs}/s^{-1}
12.2	11	26	68
13	17	28	70
15	31	30	71
16	37	32	72
18	46	34	72
20	53	38	73
22	59	40	74
25	64	45	74

Scheme 1



Discussion

As is well-known, the pseudophase model was proposed by Menger and Portnoy in order to rationalize kinetic data in micellar systems.[11] On the basis of this model, a reaction can take place in one (or both) of the two pseudophases present in the micellar system, the aqueous pseudophase and the micellar pseudophase. This double possibility arises from the distribution of the solutes between the two pseudophases, according to Scheme 1, in which the subscripts w and m denote the aqueous and micellar pseudophases, respectively, and S denotes the solute. k_w and k_m are the rate constants of the processes taking place in the different pseudophases. *K* is the equilibrium constant for the binding of the species S to the micelles and can be expressed as

$$K = \frac{[S_m]}{[S_w][T]} \tag{3}$$

Here [T] is the micellized surfactant concentration. Following Scheme 1, the observed rate constant, k_{obs}, can be written as follows:

$$k_{obs} = \frac{k_w + k_m K[T]}{1 + K[T]} \tag{4}$$

For a true first-order process, all the parameters in this equation are unambiguously defined.[23] However, it is important to realize that eq 3, and thus eq 4, is based on an additional hypothesis: the concentration of S in the solution must be low enough in order to avoid saturation of the micellar pseudophase. Indeed, even in this case, it is implicit in the equations that the presence of a substrate species in a given micelle neither encourages nor discourages the union of another substrate: in

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(22) Rate constants correspond to the first electron transfer to $S_2O_8{}^{2-}$ from the ruthenium complex, which is the rate determining step. This step is slower than the second one ($SO_4{}^{\bullet -} + Ru(NH_3)_5pz^{2+} \rightarrow SO_4{}^{2-} + Ru(NH_3)_5pz^{3+}$) because the redox potential of $S_2O_8{}^{2-}$ is slower than those of the $SO_4{}^{\bullet -}$ and the reorganization energy of $S_2O_8{}^{2-}$ is greater than those of $SO_4{}^{\bullet -}$. See: Fürholz, U.; Haim, A. *Inorg. Chem.* **1987**, *26*, 3243. See also: Eberson, L. *Electron-Transfer Reaction in Organic Chemistry*; Springer-Verlag: New York, 1987; p 88.

other words, that the interaction micelle−substrate is noncooperative in character. Moreover, to consider K a true constant, it must be assumed that structural parameters of the micelle, such as shape, size, and the structure of the micellar pseudophase, do not change when the surfactant concentration is changed. Obviously, eqs 3 and 4 are representative of the pseudophase model only under the circumstances previously discussed. When these circumstances do not hold, modifications of these equations are in order. Thus, for high enough concentrations of S it is better to use, instead of eq 3, a Langmuir type equation:[24]

$$K = \frac{[S_m]}{[S_w]\{[T] - [S_m]\}} \tag{5}$$

and eq 4 must be properly modified.

For second-order reactions, eq 4 (or eq 5) cannot be applied, generally speaking. However, these equations are still valid, under the same assumptions considered for a first-order reaction, provided that only one of the reactants, R_1, is partitioned between the aqueous and micellar pseudophases and the other, R_2, remains in the aqueous pseudophase.

But now, the meanings of k_w and k_m are not as straightforward as in the case of first-order reactions. This is so because the concentrations of the reactants refer to the *total* volume of the solution. Given that this situation corresponds to the working conditions in this study, this question will be considered in some detail.

Since R_2, by hypothesis, remains in the aqueous phase only, for this reactant, taking into account that the volume of the system has practically the same value as that for the aqueous pseudophase, one can write

$$[R_2]_T = [R_2]_w \approx [R_2]^w \tag{6}$$

where

$$[R_2]_T = \frac{\text{moles of } R_2 \text{ in the solution}}{\text{volume of the solution}} \tag{7a}$$

$$[R_2]_w = \frac{\text{moles of } R_2 \text{ in the aqueous pseudophase}}{\text{volume of the solution}} \tag{7b}$$

$$[R_2]^w = \frac{\text{moles of } R_2 \text{ in the aqueous pseudophase}}{\text{volume of the aqueous pseudophase}} \tag{7c}$$

In this way, $k_w \approx k^w$ (k^w is the rate constant in the aqueous pseudophase corresponding to the concentration of R_2 in this pseudophase given by eq 7c).

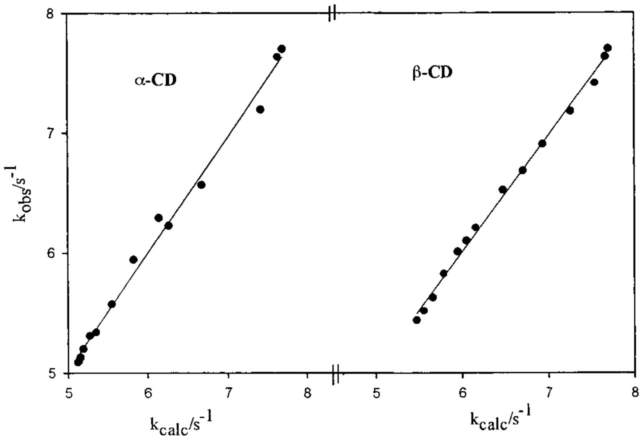

Figure 1. Plot of k_{obs}/s^{-1} (experimental) vs k_{calc}/s^{-1} (calculated from eq 4) for the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8^{2-}$ in α- and β-cyclodrextrin solutions.

The situation is different for k_m. In this case, k_m is related to the true rate constant in the micellar pseudophase, k^m, by

$$k_m = k^m \frac{[R_2]^m}{[R_2]_T} \approx k^m \frac{[R_2]^m}{[R_2]^w} = k^m \kappa_{R_2} \tag{8}$$

with

$$\kappa_{R_2} = \frac{[R_2]^m}{[R_2]^w} \tag{9}$$

Notice that parameter κ in eq 9 has a different meaning than that of parameter K in the pseudophase model (see eq 3). However, both parameters are related through eq 10:

$$K_i[T] = \kappa_i \varphi \tag{10}$$

where

$$\varphi = \frac{\text{volume of the aqueous pseudophase}}{\text{volume of the micellar pseudophase}} \tag{11}$$

Once we have established the circumstances in which eq 4 holds for a second-order reaction, and the meaning of the parameters in this case (in fact only the meaning of k_m is changed), we will consider the application of the pseudophase model to the different cases considered in this work.

(a) Cyclodextrin Solutions. Data in Tables 1 and 2 can be fitted to eq 4 (see Figure 1) with the following values of the parameters:

$k_w^\alpha = 7.7$ s^{-1}, $k_w^\beta = 7.7$ s^{-1}, $k_m^\alpha = 5.0$ s^{-1}, $k_m^\beta = 4.6$ s^{-1}, $K^\alpha = 227$ mol^{-1} dm^3, $K^\beta = 133$ mol^{-1} dm^3, where superscripts α and β refer to α- and β-cyclodextrin solutions.

It is clear, according to the previous discussion, that only one of the reactants interacts significantly with cylodextrins. In the authors' opinion, this reactant is the ruthenium complex because, as indicated in the Experimental Section, a shift of the wavelength corresponding to the maximum of the spectra of this complex was observed and this shift increases when the cyclodextrin concentration increases. On the contrary, no changes in the spectra of $S_2O_8^{2-}$ were observed in these solutions.

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(23) Strictly speaking, this is not true for k_m, because the pseudophase model considers aqueous and micellar pseudophases as distinct regions where the substrate concentration is well-defined. This description is unrealistic because the substrate concentration and the local properties will change smoothly with the distance from the micellar pseudophase, toward the concentration, and local properties of the bulk solvent (see: Bonan, C.; Germani, R.; Ponti, P. P.; Savelli, G.; Cerichelli, G.; Bacaloglu, R.; Bunton, C. A. *J. Phys. Chem.* **1990**, *94*, 5331). Changes in local properties obviously can change k_m (this is particularly true for electron-transfer processes; see Introduction). Thus, even for true first-order processes, k_m represents some class of average value.

(24) (a) Bunton, C. A.; Gan, L. H.; Moffat, J. R.; Romsted, L. S.; Savelli, S. G. *J. Chem. Phys.* **1985**, *85*, 4118. (b) Bacaloglu, R.; Bunton, C. A.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1497. (c) Staedler, E.; Zanette, D.; Rezende, M.; Nome, F. *J. Phys. Chem.* **1984**, *88*, 1892. (d) Rodenas, E.; Vera, S. *J. Phys. Chem.* **1985**, *89*, 513; **1986**, *90*, 3414.

The results in cyclodextrin solutions can also be rationalized taking as a starting point the Brönsted equation:[25]

$$k_{\mathrm{obs}} = k_{\mathrm{o}} \frac{\gamma_{\mathrm{R}_1}\gamma_{\mathrm{R}_2}}{\gamma_{\neq}} \tag{12}$$

In this equation, k_o is the rate constant in a given reference state and γ_{R_1}, γ_{R_2}, and $\gamma_{\neq}$ are the activity coefficients of the reactants and transition state, respectively. If the aqueous pseudophase is taken as the reference state, k_o becomes identical to k_w (strictly speaking to k^w). Indeed, since one of the reactants, the $S_2O_8^{2-}$, remains mostly in the aqueous pseudophase, $\gamma_{S_2O_8^{2-}} \approx 1$, in such a way that

$$k_{\mathrm{obs}} = k_{\mathrm{w}} \frac{\gamma_{[\mathrm{Ru(NH_3)_5pz}]^{2+}}}{\gamma_{\neq}} \tag{13}$$

We have shown in a previous paper[26] that, in general,

$$\gamma_i = \frac{1}{1 + K_i[\mathrm{T}]} \tag{14}$$

(in this case [T] = [CD] = [cyclodextrin]). Consequently,

$$k_{\mathrm{obs}} = k_{\mathrm{w}} \frac{1 + K_{\neq}[\mathrm{CD}]}{1 + K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}}[\mathrm{CD}]} \tag{15}$$

Thus, a decrease in the rate observed in cyclodextrin solutions arises from the fact that the ruthenium complexes has a greater affinity for the cyclodextrin cavity than the transition state.

Before leaving this section, it is worth pointing out that, according to eqs 4 and 15, it follows that[26]

$$k_{\mathrm{m}} K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}} = k_{\mathrm{w}} K_{\neq} \tag{16}$$

or, alternatively,[27]

$$\kappa_{[\mathrm{Ru(NH_3)_5pz}]^{2+}} \kappa_{\mathrm{S_2O_8}^{2-}} k^{\mathrm{m}} = \kappa_{\neq} k_{\mathrm{w}} \tag{17}$$

(b) Dendrimer Solutions. As can be seen in Table 3, the behavior observed in the solutions of dendrimer is qualitatively similar to the one observed in the case of cyclodextrin solutions; that is, a decrease in the rate of the reaction when the concentration of dendrimer is increased. However, eq 4 cannot fit the complete set of data in the present case. Before continuing we will rewrite this equation as

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{w}}'}{1 + K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}}[\mathrm{D}]} + k_{\mathrm{m}} \tag{18}$$

[D] being the concentration of dendrimer and $k_w' = k_w - k_m$.

It is interesting to note that eqs 18 or 4 can fit the data if we limit ourselves to small ranges of [D]. This implies that some, or all, of the parameters appearing in these equations depend on [D]. Since k_w is fixed, and k_m is small (in such a way that its variations, although relatively big, would not cause the impossibility of the fit), failure of the equations must lie in the dependence of K on the dendrimer concentration. At first, this dependence is unknown, but we first tried a linear dependence of K on [D]; that is

$$K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}} = a + b[\mathrm{D}] \tag{19}$$

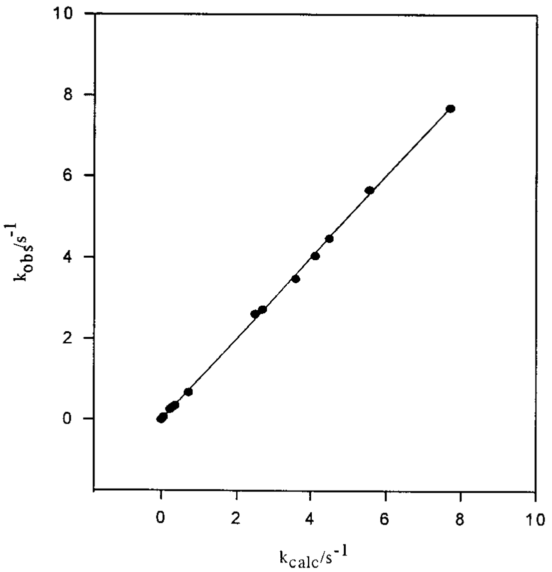

Figure 2. Plot of k_{obs}/s^{-1} (experimental) vs k_{calc}/s^{-1} (calculated from eq 20) for the process $[\mathrm{Ru(NH_3)_5pz}]^{2+} + \mathrm{S_2O_8}^{2-}$ in dendrimer solutions.

Thus, eq 18 becomes

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{w}}'}{1 + a[\mathrm{D}] + b[\mathrm{D}]^2} + k_{\mathrm{m}} \tag{20}$$

Equation 20 fits well the values of k_{obs} (see Figure 2) with the following values of the parameters: $k'_w = 7.7$ s^{-1}, $a = 2.0 \times 10^6$ mol^{-1} dm^3, $b = 3.8 \times 10^{10}$ mol^{-2} dm,^{6} and $k_m = 1.8 \times 10^{-3}$ s^{-1}. Notice that a and b are positive. This implies that $K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}}$ increases as the concentration of dendrimers does. In other words, the binding of the ruthenium complex to dendrimers (in this case the negative charge of dendrimers permits the safe exclusion of $S_2O_8^{2-}$ as the reactant being retained at the surface of the dendrimers) is anticooperative in character.[28]

Before closing this section, the following comment seems pertinent: The linear dependence of $K_{[\mathrm{Ru(NH_3)_5pz}]^{2+}}$ with the concentration of dendrimer is probably due to the small range of [D]. Or, in other words, it must be the consequence of the linearization of a more complex variation of K with [D], valid only in a limited range of concentrations. This question will be reconsidered in the following section.

(c) DNA Solutions. The pseudophase model in its simplest version (eqs 4 and 18) cannot explain the results corresponding to DNA solutions. Neither can eq 20, which, as mentioned above, is derived from previous equations by allowing a linear dependence of K with DNA concentration. In this regard, we will take another look at the question concerning the linear variation of K on the concentration (of DNA or dendrimers). The linear variation, as indicated, can be valid only in a limited range of concentration because this dependence predicts an unlimited growth of K, which is meaningles. In other words, K must reach a constant value after a given value of concentration.

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(25) Brönsted, J. N. *Z. Phys. Chem.* **1922**, *102*, 169.
(26) Muriel-Delgado, F.; Jiménez, R.; Gómez-Herrera, C.; Sánchez, F. *Langmuir* **1999**, *15*, 4344.
(27) López-Cornejo, P.; Sánchez, F. *J. Phys. Chem. B* **2001**, *105*, 10523.
(28) McGhee, J. D.; Von Hippel, P. H. *J. Mol. Biol.* **1974**, *86*, 489.

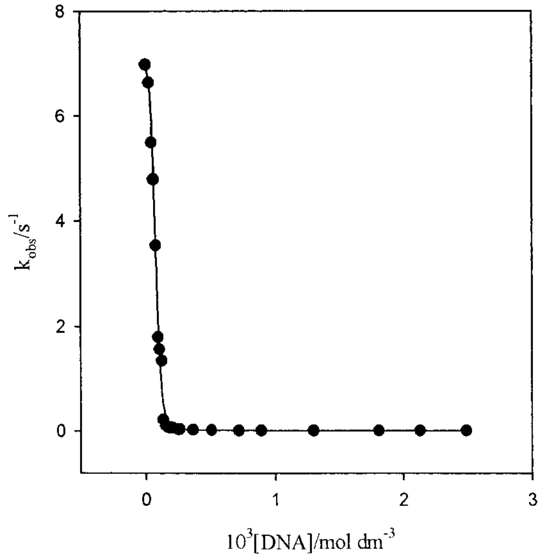

Figure 3. Plot of k_{obs}/s^{-1} of the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8{}^{2-}$ vs DNA concentration. The points are experimental data, and the line is the best fit obtained by using a combination of eqs 4, 21a, and 21b.

There is a huge dependence of K on this variable that can accomplish this requirement. However, for anti-cooperative binding, a sigmoidal dependence is frequently found.[12] Thus, we have used for K the equation

$$K = \frac{K_{max}e^t}{1 + e^t} \tag{21a}$$

where

$$t = \frac{[DNA] - h}{j} \tag{21b}$$

K_{max} being the maximum (limiting) value of K, h the value of [DNA] for which $K = (1/2)K_{max}$, and j an adjustable parameter.

In fact, the data corresponding to DNA are well-fitted by eq 4, after substitution in this equation of K by its values given in eqs 21a and 21b. In this case, $K_{max} = 2.6 \times 10^6$ mol^{-1} dm^3, $h = 2.3 \times 10^{-4}$ mol dm^{-3}, $j = 3.0 \times 10^5$ mol dm^{-3}, $k_w = 7.0$ s^{-1}, and $k_m = 6.0 \times 10^{-3}$ s^{-1}. The quality of the fit is shown in Figure 3. In this figure, the continuous curve corresponds to the calculated values of k_{obs}, by using the parameters given above and the points corresponding to the experimental data. For comparative purpose, in Figure 4, a representation of k_{obs} vs k_{calc} is given.

These results seems to prove that the ruthenium complex binds to DNA with an anti-cooperative character of the binding. The maximum strength of this binding can be quantified from the value of K_{max}. To compare this strength with the value obtained in other closely related systems, as micellar solutions of the negatively charged SDS surfactant,[10] it is important to realize that, in the latter case, K is established from the concentration of surfactant micellized monomers. Thus, the value of K_{max} should be expressed in terms of the concentration of DNA base pairs. Given that there are ca. 3000 base pairs by DNA molecule,[29] the resulting value of $K^{DNA/bp}{}_{max}$ would be about 800 mol^{-1} dm^3. This gives a value for the bonding free energy of about 16 kJ mol^{-1}, which compares quite well with the value of 17 kJ mol^{-1} for the binding of the $[Ru(NH_3)_5pz]^{2+}$ complex (for monomer of surfactant) at micelles of sodium dodecyl sulfate (SDS).[10] Indeed, the magnitude of this bonding free energy is similar to the one corresponding to DNA−cation interactions obtained by simulation methods[30] or through experimental determinations.[31]

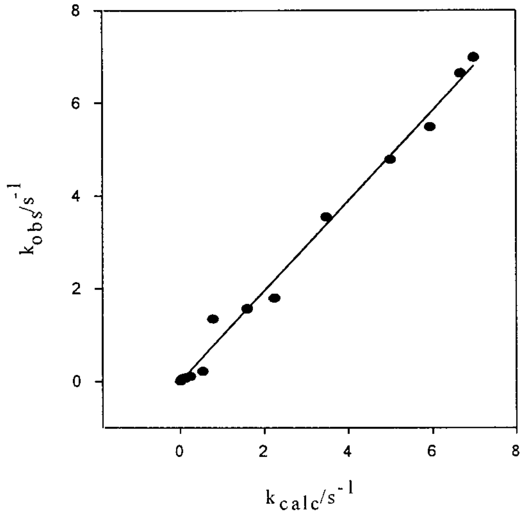

Figure 4. Plot of k_{obs}/s^{-1} (experimental) vs k_{calc}/s^{-1} (calculated from eqs 4, 21a, and 21b) for the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8{}^{2-}$ in DNA solutions.

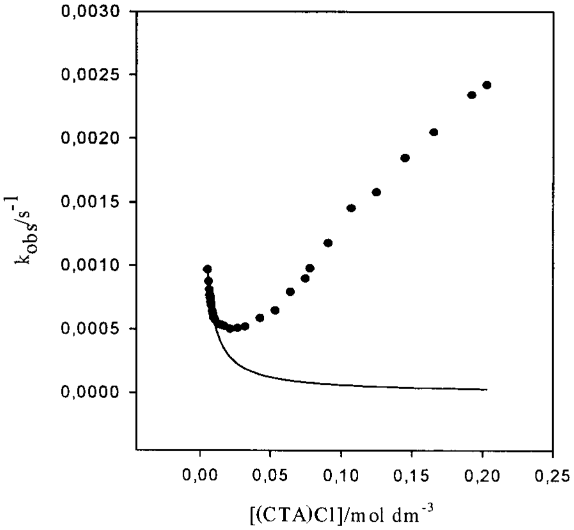

Figure 5. Plot of k_{obs}/s^{-1} of the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8{}^{2-}$ versus (CTA)Cl concentration. The points are experimental data, and the line is the best fit obtained by using eq 4.

(d) Micellar Solutions of (CTA)Cl. As shown in Table 5, the situation in the case of solutions containing (CTA)Cl is somewhat different from the behavior considered in previous cases. Now, k_{obs} first decreases on increasing (CTA)Cl concentration, reaching a minimum (see Figure 5). After this minimum, k_{obs} increases as the (CTA)Clconcentration increases. This behavior cannot be considered a consequence of a cooperative

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(29) *Bio Directory _97*; Catalog Information, Pharmacia Biotech: Amersham, U.K., 1997; p 383.
(30) Lyubartsev, A. P.; Laaksonen, A. *J. Chem. Phys.* **1999**, *111*, 11207.
(31) Hiort, C.; Norden, B.; Rodger, A. *J. Am Chem. Soc.* **1999**, *121*, 1971.

binding of the peroxodisulfate ions with the micelles because cooperative effects should be more marked at the lower concentrations and, in this case, the *abnormal* behavior corresponds to the higher concentrations of the surfactant. However, it is clear that the increase in rate must be due to a change in K. In fact, the first part of the curve in Figure 5 (up to [(CTA)Cl] $= 9.6 \times 10^{-3}$ mol dm^{-3}) can be fitted by eq 4 with a constant value of $K = 546$ mol^{-1} dm^3, $k_w = 3.5 \times 10^{-3}$ s^{-1}, and $k_m \approx 0$ (see Figure 5). The value of k_m is indicative of the absence of a surface reaction (in fact, $k_m \ll k_w$ also in the case of dendrimer and DNA solutions). On the other hand, *k_w is different from the value in water*, ~14.0 s^{-1}. This fact can be rationalized by taking into account that k_w in eq 4 represents the rate constant of the reaction which takes place in the aqueous pseudophase *in the presence of a concentration of monomers of the surfactant equal to the cmc value*. Consequently, we ascribe the difference in k_w observed for the micellar solutions (as compared to the value of this parameter in water) to an effect of the monomers of the surfactant on the kinetics. The important effect of monomers (or premicellar aggregates) on the kinetics of the reactions in micellar solutions has been well-documented for a long time.[32] The important point of this discussion is that K remains a true constant in the range of concentrations mentioned previously, that is, at the lower concentrations of the surfactant. At these lower concentrations, the association degree of the counterions of the surfactant with the micelles, and thus, the surface potentials of the micelles, remains a constant.[1b,c] For higher concentrations of surfactant, there is a condensation of counterions on the surface of the micelles producing a decrease of the surface potential (see Table 7) and, consequently, a decrease of K. Thus, we adscribe the raising part of the curve in Figure 5 to this decrease of K. This decrease in K corresponds obviously to a change of the free energy of the process in Scheme 1. This free energy can be written as the sum of two contributions: (i) a potential independent contribution, ΔG_{nel} (nonelectrostatic or intrinsic) and (ii) a potential dependent (or electrostatic) contribution, ΔG_{el} (notice that the determination of surface potentials is, in fact, based on this assumption):

$$\Delta G = \Delta G_{nel} + \Delta G_{el} \tag{22}$$

The latter contribution can be expressed as

$$\Delta G_{el} = z\alpha F\Psi \tag{23}$$

where z is the charge of the ion whose binding to the surface is described by K ($z = -2$ in the present case) and α is a parameter which takes into account the location of the ion at the interface (this location, as mentioned previously, is not necessarily the same as the location of the probe used in the determination of Ψ); that is, α gives the fraction of surface potential (determined with a given probe) that determines ΔG_{el} (for another probe). F is the constant of Faraday.

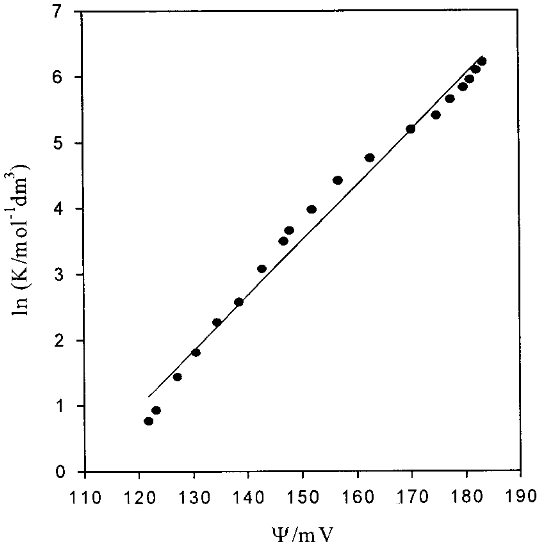

Figure 6. Plot of ln(K/(mol^{-1} dm^3)) vs the surface potential of the (CTA)Cl micellar solutions for the process [Ru(NH$_3$)$_5$pz]$^{2+}$ + S$_2$O$_8$$^{2-}$.

If K_o (nonelectrostatic binding constant) is defined as

$$K_o = e^{-\Delta G_{nel}/RT} \tag{24}$$

it follows from previous equations that

$$K = K_o e^{-\Delta G_{el}/RT} = K_o e^{-z\alpha F\Psi/RT} \tag{25}$$

or

$$\ln K = \ln K_o - \frac{z\alpha F\Psi}{RT} \tag{26}$$

To check that the raising part of the curve in Figure 5 is due to the variations of Ψ at the corresponding concentrations of (CTA)Cl, we have obtained K from k_{obs} (in this range of concentrations) by using eq 4 (with $k_m = 0$, as obtained in the fit of the first part of the curve, and the value of k_w also obtained in this fit, $k_w = 3.5 \times 10^{-3}$ s^{-1}). These K values, according to our hypothesis, must conform to eq 26, and they do, as can be seen in Figure 6.

Thus, one can conclude that the behavior of k_{obs} in (CTA)Cl solutions can be described using the pseudophase model, if one takes into account adequately the variations of K, caused by the changes in the surface potential. This latter, as previously mentioned, changes as a consequence of the decrease of the degree of dissociation of the counterions of the surfactant.

(e) Microemulsions. Figure 7 gives the plot of k_{obs} vs $1/W$ corresponding to microemulsions. The points in the figure, *including the point on the Y* axis, are the experimental data (see Table 6). The line corresponds to an interpolation because it was imposible to maintain the stability of the microemulsions (containing the reactants) for $W > 45$.

The similarity of Figure 7 and Figure 5 is striking. Thus, it seems possible to advance that the situation in both media must be similar.

Obviously, classical equations of pseudophase model (eqs 4 and 18) cannot be used directly in the present case: The concentration (of cyclodextrin, dendrimer, DNA, and (CTA)Cl micelles) variable cannot be employed in the case of microemulsions. Consequently, these equations (but not their founda-

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(32) See for example: (a) Biresaw, G.; Bunton, C. A. *J. Phys. Chem.* **1986**, *90*, 5854. (b) Shiffman, R.; Rav-acha, C.; Chevion, M.; Katzhendler, S.; Sarel, S. *J. Org. Chem.* **1977**, *20*, 3279.

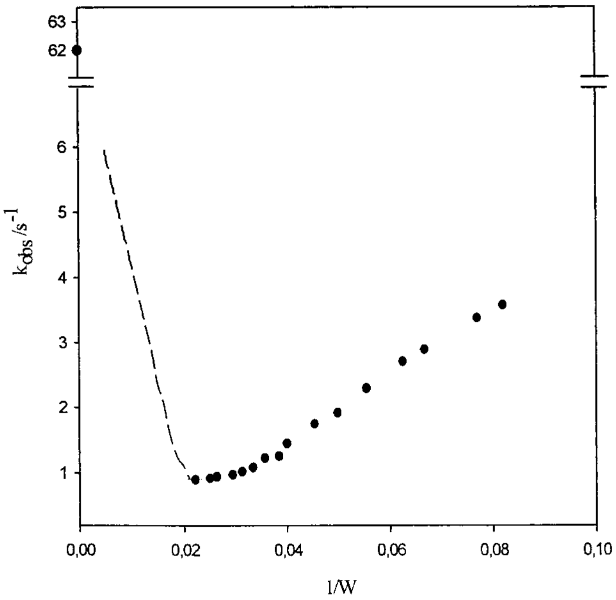

Figure 7. Plot of k_{obs}/s^{-1} of the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8^{2-}$ vs $1/W$. The points are experimental data, and the dashed line is an extrapolation of the experimental results for values of $W > 45$. The point on the Y axis is the value of k_{obs}/s^{-1} of the process studied in aqueous solution.

tions) need some modifications. To perform this, consider a microemulsion in which the molar ratio $[H_2O]/[AOT]$ has a given value, W. Assuming, as is habitual, that all the surfactant and water molecules are incorporated into the droplets, if V is the volume of the water pool, it is possible to write

$$\text{moles of water in a droplet} = \frac{V\rho_w}{M_w} \qquad (27)$$

M_w and ρ_w being the molar mass and the density of water. From the value of the molar ratio, it follows

$$\text{moles of surfactant in a droplet} = \frac{V\rho_w}{M_w W} \qquad (28)$$

This number is equal (or proportional) to the number of binding sites in a droplet. Thus,

$$\text{moles of binding sites in a droplet} \equiv N = \beta\frac{V\rho_w}{M_w W} \qquad (29)$$

where β is a proportionality constant. This constant is introduced with the purpose of generality in order to take into account the possibility of a substrate binding to more than one polar head of surfactant.

Now, consider the (micro)heterogeneous equilibrium

$$S_w + \text{Site} \overset{K}{\rightleftharpoons} \text{S/Site} \qquad (30)$$

The equilibrium constant, K, for this equilibrium, assuming it is of the Langmuir type, is given by[33]

$$K = \theta/[S_w](1 - \theta) \qquad (31)$$

θ being the fraction of occupied sites.

On the other hand

$$\text{moles of } S_w = [S_w]V \qquad (32a)$$

$$\text{moles of (S/Sites)} = N\theta = \beta\frac{V\rho_w}{M_w W}\theta \qquad (32b)$$

and, evidently,

$$V[S_T] = [S_w]V + \beta\frac{V\theta\rho_w}{M_w W} \qquad (33)$$

From eq 31, and taking into account that *in the present case* $\theta \ll 1$ (even if all the ruthenium complex was bonded), we have

$$K = \theta/[S_w] \qquad (34)$$

and thus

$$V\,[S_T] = \frac{\theta}{K}V + \beta\frac{V\theta\rho_w}{M_w W} \qquad (35)$$

From this equation, it is clear that

$$\theta = \frac{[S_T]}{\dfrac{1}{K} + \dfrac{\beta\rho_w}{M_w}\dfrac{1}{W}} = \frac{K[S_T]}{1 + K\beta'\left(\dfrac{1}{W}\right)} \qquad (36)$$

where $\beta' = \beta\rho_w/M_w$, and from eq 34

$$[S_w] = \frac{\theta}{K} = \frac{[S_T]}{1 + K\beta'\left(\dfrac{1}{W}\right)} \qquad (37)$$

From eqs 36 and 37 it follows that

$$k_{obs} = \frac{k_w + k_s K}{1 + K\beta'\left(\dfrac{1}{W}\right)} \qquad (38)$$

k_s being the rate constant for the surface reaction.

And taking into account eq 25,

$$k_{obs} = \frac{a + b e^{-z\alpha F\Psi/RT}}{1 + c e^{-z\alpha F\Psi/RT}\left(\dfrac{1}{W}\right)} \qquad (39)$$

with $a = k_w$, $b = k_s K_o$, and $c = K_o\beta'$.

Equation 39 fits reasonably well the data corresponding to microemulsions with the following values of the parameters $a = 3.6\ s^{-1}$, $b \approx 0\ s^{-1}$, $c = 0.31$, and $\alpha = 1$. However, it is clear from Figure 8 that the fit is not as good as in the previous cases. A much better fit is obtained by allowing a linear dependence of k_w on $1/W$, that is, using the equation

$$k_{obs} = \frac{k_w^\circ\left(1 + m\dfrac{1}{W}\right)}{1 + c e^{-z\alpha F\Psi/RT}\left(\dfrac{1}{W}\right)} \qquad (40)$$

This linear dependence is supported by the following argument: The probe reaction is a process between two ions. Thus, it must be sensitive to changes in the ionic strength in the reaction medium. Consequently, since a change in W would

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(33) Barrow, G. M. *Physical Chemistry*; McGraw-Hill: New York, 1961; pp 626−629.

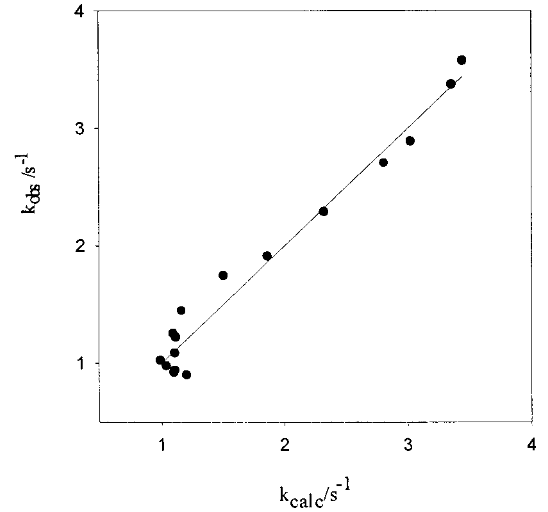

Figure 8. Plot of k_{obs}/s^{-1} (experimental) vs k_{calc}/s^{-1} (calculated from eq 39) for the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8^{2-}$ in microemulsions.

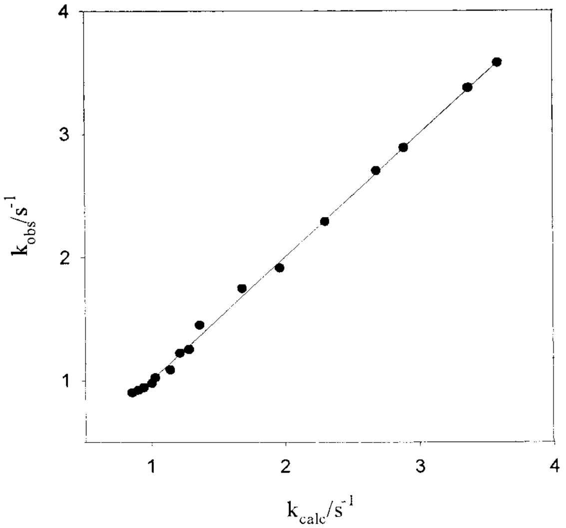

Figure 9. Plot of k_{obs}/s^{-1} (experimental) vs k_{calc}/s^{-1} (calculated from eq 40) for the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8^{2-}$ in microemulsions.

produce a change in the ionic concentration at the water pool, a variation in k_w when W (or $1/W$) changes is to be expected.

In fact, eq 40 fits well the results corresponding to our data in microemulsions with the following values of the parameters: $k_w^\circ = 0.30$ s^{-1}, $m = 134$, $c = 0.059$, and $\alpha = 1$. The results of the fit are given in Figure 9.

There is one point that deserves special comment. This point has to do with the *positive* sign of parameter m. Notice that this positive sign implies a *positive* ionic strength effect. This effect could be considered *abnormal*, taking into account that the probe reaction is a reaction between two oppositely charged ions. In this regard, it is important to realize that the prediction of the Brönsted–Debye equation:[34]

$$\log k = \log k_o + \frac{2Az_Az_B\sqrt{I}}{1 + B\sqrt{I}} \tag{41}$$

of a negative ionic strength effect on reactions between ions of opposite charge sign is valid only in a *dilute* solution of salts because only under this circumstance does the Debye–Hückel equation hold. In concentrated solutions, the activity coefficients (and thus eq 41) are given by an equation containing a linear term in the ionic strength:[35]

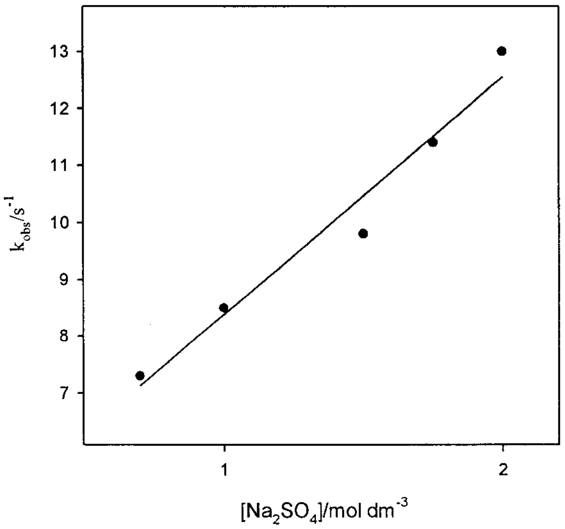

Figure 10. Plot of k_{obs}/s^{-1} vs the salt concentration for the process $[Ru(NH_3)_5pz]^{2+} + S_2O_8^{2-}$ studied in the presence of Na_2SO_4 as background electrolyte. The circles are data taken from ref 13, and the triangles are data obtained in the present work.

$$\log k = \log k_o + \frac{2Az_Az_B\sqrt{I}}{1 + B\sqrt{I}} + CI \tag{42}$$

Thus, the effect of ionic strength in concentrated salt solutions depends on the sign of parameter C in the extended Brönsted–Debye equation (eq 42). In fact, there are precedents of *positive* salt effects on reactions between ions of opposite sign. For example, a positive salt effect is found in the oxidation of Fe^{2+} by $[Co(C_2O_4)_3]^{3-}$ in acid media,[36] in the OH^- catalyzed isomerization of $[Co(NH_3)_5NO_2]^{2+}$,[36] and in the oxidation of Br^- by BrO_3^- in acid media.[37] Moreover, to check that in the reaction studied here the linear term in I (eq 42) causes a positive salt effect, we have studied this reaction in concentrated salt solutions of Na_2SO_4. As can be seen in Figure 10, a linear and positive salt effect is found.

A final argument supporting eq 40 is the following: This equation, for a neutral substrate ($z = 0$), becomes

$$k_{obs} = \frac{k_w^\circ\left(1 + m\frac{1}{W}\right)}{1 + c\frac{1}{W}} \tag{43}$$

This equation, in fact, fits the data corresponding to the oxidation of $[Fe(CN)_2(bpy)_2]$ by $S_2O_8^{2-}$ in microemulsions well.[38] Thus,

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(34) Laidler, K. J. *Chemical Kinetics*; McGraw-Hill: London, 1965; p 220.

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

(36) Burgess, J.; Sánchez, F.; Morillo, E.; Gil, A.; Tejera, J. I.; Galán, A.; García, J. M. *Trans. Met. Chem.* **1986**, *11*, 166.

(37) In this reaction, the rate determining step implies the reaction between BrO_2^+ and Br^- ions. See: Burgos, F. S.; Graciani, M. M.; Muñoz, E.; Moyá, M. L.; Capitán, M. J.; Galán, M.; Hubbard, C. D. *J. Solution. Chem.* **1988**, *17*, 653, and references therein.

the use of eq 40 in the present case seems to us to be well-supported.

A final comment seems pertinent in relation to the influence of the potential. Some authors have taken into account these variations, in an indirect way, using the pseudophase ion-exchange model.[39] This model takes into account the competition between the reactants and the counterions by the sites at the surfaces of micelles (or microemulsions). In fact, this competition implies that some sites are occupied by the counterions. But this occupation, which implies formally a neutralization of the micellar charge, is taken into account through a parameter that describes the dissociation degree of the counterions. In fact, this approach is similar to the one we have used because the charge at the surface of the micelles determines the electric field close to the micelles through[40]

$$E = \frac{\sigma}{\epsilon} \tag{44}$$

σ being the surface charge density and ϵ the permittivity of the medium. Thus, the use of the pseudophase ion-exchange model is equivalent to our approach, assuming a linear dependence of Ψ on the distance at the surface, that is, assuming a Helmholtz–Perrin type of interface.[41]

However, the determination of the surface potential is more straigthforward than the determination of the degree of dissociation of the micelles. Thus, the approach based on the consideration of the surface potential seems somewhat better.

Concluding Remarks

In this paper it is shown that the pseudophase model is a *broad spectra* model, in the sense that it can be applied to a variety of situations, all of them corresponding to processes carried out under restricted geometry conditions. In fact, the basic equation of the model is not very different from the equations corresponding to enzimatic reactions[42] and heterogeneous catalysis,[43] which, in some sense, are also considered as reactions under restricted geometry conditions. However, the use of the pseudophase model requires taking into account the possible variations in the parameters (rate constants and equilibrium constants) of the model. These variations, as have been shown here, can have several causes, such as cooperative effects in binding (dendrimers and DNA), influence of surface potential (micelles and microemulsions), and effects of substances in the aqueous pseudophase (monomers or ions in micellar and microemulsions systems, respectively).

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(38) Sánchez, F.; Moyá, M. L.; Rodríguez, A.; Jiménez, R.; Gómez-Herrera, C.; Yanes, C.; López-Cornejo, P. *Langmuir* **1997**, *13*, 3084. It is worth pointing out that in this paper some of the present authors made a mistake in the sense that they considered that the term $k_w^\circ m(1/W)$ in the numerator of eq 43 represents the product $k_m K_o(1/W)$; that is, this term was considered to be a consequence of the surface reaction instead of coming from the dependence of k_w upon the ionic strength of the medium.

(39) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.

(40) Kip, A. F. *Fundamentals of Electricity and Magnetism*; McGraw-Hill: New York, 1962; p 37.

(41) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum Press: New York, 1970; Vol. II, p 718.

(42) Reference 34, pp 434 and following.

(43) Reference 34, pp 256 and following.