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## Electron Transfer in Micellar Systems.<sup>1</sup> Separation of Electrostatic and Environmental Effects for Some Electron-Transfer Reactions in Micellar Solutions of Sodium Dodecyl Sulfate

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The effects of sodium dodecyl sulfate micelles on some outer-sphere electron-transfer reactions involving  $\text{IrCl}_6^{2-}$ ,  $\text{Os}(\text{bpy})_3^{3+}$ , and  $\text{Os}(\text{dmbpy})_3^{3+/2+}$  with  $\text{Fe}^{3+/2+}$  have been investigated. A method for the computation of the local ion concentrations in the vicinity of the charged surface has been applied. This method distinguishes between the electrostatic and nonelectrostatic contributions to the micellar effect on the equilibrium constant as well as on the reaction rates. The importance of the type of ligand involved for the nonelectrostatic contribution will be investigated in a subsequent paper.

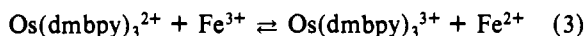
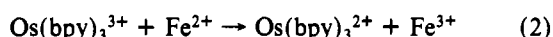
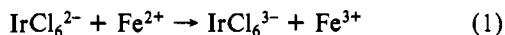
The effect of micellar systems on photochemical<sup>2</sup> and thermal electron-transfer reactions<sup>1,3</sup> has received increasing attention in the last years.

The interest arises from the possible applications in several areas, including energy conversion problems<sup>4</sup> and biochemical aspects,<sup>5</sup> e.g., electron-transfer reactions involving metallo-proteins or reactions at membrane surfaces.

Preceding studies<sup>1,3</sup> have been discussed in terms of theories proposed mainly for organic reactions.<sup>6,7</sup>

In the present paper, a previously developed method<sup>8</sup> is applied to electron-transfer reactions involving metal ion complexes. The method is used to compute diffuse double-layer properties, in particular local ion distributions as a function of distance from the micellar surface, by means of the cell model of polyelectrolyte solutions and a numerical solution of the nonlinearized Poisson-Boltzmann equation with experimental surface potentials.

Electron-transfer reactions 1-3 were investigated, where bpy and dmbpy refer to 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine, respectively.



### Experimental Section

**Reagents.** Sodium hexachloroiridate(IV) was supplied by Alfa. Tris(2,2'-bipyridine)osmium(II) perchlorate,  $\text{Os}(\text{bpy})_3^{2+}$ , and tris(4,4'-dimethyl-2,2'-bipyridine)osmium(II) perchlorate,  $\text{Os}(\text{dmbpy})_3^{2+}$ , were prepared by following the literature procedure starting from  $(\text{NH}_4)_2\text{OsBr}_6$  and the corresponding ligand.<sup>9</sup> The compounds were purified, and the collected absorption spectra were in agreement with the literature data.<sup>10</sup> The corresponding oxidized complexes were obtained by electrooxidation. Iron(II) perchlorate was obtained by dissolving pure iron wire in perchloric acid and standardized by oxidimetric titration. Perchloric acid and sodium perchlorate (Merck) were applied to achieve the desired acidity and ionic strength. Sodium dodecyl sulfate (SDS) (Merck) was purified by recrystallization.

**Apparatus.** Absorption spectra were recorded on a Cary 219 spectrophotometer.

A Dognon-Abribat tensiometer with platinum blade was used for surface tension measurements.

The kinetic runs were carried out with Durrum-Gibson stopped-flow spectrophotometer.

The calculations were performed with use of the facilities of the Gesellschaft für Wissenschaftliche Datenverarbeitung, Göttingen, West Germany.

**Kinetics.** Reaction 1 was followed at 488 nm:  $[\text{IrCl}_6^{2-}] = 10^{-5}$  M,  $[\text{Fe}^{2+}] = (2-10) \times 10^{-5}$  M,  $[\text{HClO}_4] = 0.01$  M, ionic strength  $\mu = 0.01-0.10$  M ( $\text{NaClO}_4$ ), and  $[\text{SDS}] = 10^{-4}-5 \times 10^{-2}$  M.

Table I. Critical Micelle Concentrations for SDS in the Presence of Different Reaction Mixtures

system 2	concn/M	$\mu$ /M	cmc/ $10^4$ M
$\text{Os}(\text{bpy})_3^{3+}$	$10^{-5}$ <sup>a</sup>	0.02	8.2
		0.10	7.7
$\text{Mg}^{2+}$	$10^{-4}$ <sup>a</sup>	0.20	7.2
$\text{Os}(\text{bpy})_3^{2+}$	$10^{-5}$ <sup>b</sup>	0.02	11
$\text{Fe}^{3+}$	$10^{-5}$ <sup>b</sup>	0.10	10
$\text{Fe}^{2+}$	$9 \times 10^{-5}$ <sup>b</sup>	0.20	8.5

<sup>a</sup>  $\text{Mg}^{2+}$  replaces  $\text{Fe}^{2+}$  in the determination of cmc before reaction. <sup>b</sup> Composition of the reactant mixture after reaction.

Reaction 2 was followed at 480 nm:  $[\text{Os}(\text{bpy})_3^{3+}] = 10^{-5}$  M,  $[\text{Fe}^{2+}] = 3 \times 10^{-5}-1.8 \times 10^{-4}$  M,  $[\text{HClO}_4] = 0.01$  M,  $\mu = 0.02, 0.10, 0.20$  M ( $\text{NaClO}_4$ ), and  $[\text{SDS}] = 10^{-4}-0.10$  M.

Reaction (3) was followed at 488 nm:  $[\text{Os}(\text{dmbpy})_3^{2+}] = 10^{-5}$  M,  $[\text{Fe}^{3+}] = 3 \times 10^{-5}-2 \times 10^{-4}$  M,  $[\text{Fe}^{2+}] = 0, 3 \times 10^{-3}-5 \times 10^{-4}$  M,  $[\text{HClO}_4] = 0.01$  M, and  $\mu = 0.02, 0.10$  M ( $\text{NaClO}_4$ ).

The temperature was kept constant at  $25.0 \pm 0.1$  °C. The kinetic data was treated with a weighted least-squares method. Second-order conditions were adopted for reaction 1 and, in some runs, for reactions 2 and 3. Otherwise, pseudo-first-order conditions were chosen, and in some cases the data were analyzed with the Corbett method.<sup>11</sup> Each presented result is the average of several kinetic runs. The accuracy of the results varies; generally it is within 4-6%.

### Results and Discussion

**Surface Tension.** Plots of the surface tension of the solutions containing the reactant mixtures as a function of the logarithm

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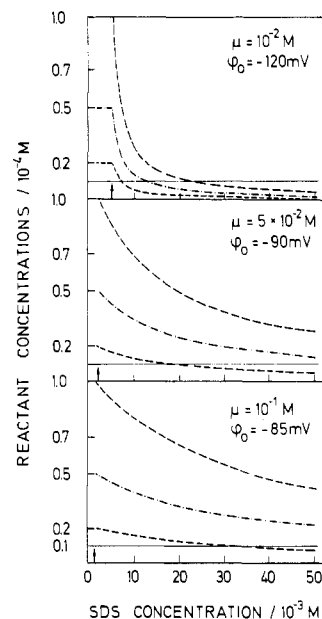
of SDS concentration showed the usual trend. The bulk phase concentrations at the point of the interaction of the two linear portions were taken as the critical micellar concentration. It is well-known that addition of electrolytes to surfactant solutions causes a decrease in the cmc. This effect is more pronounced by increasing the charge and the hydrophobicity of the ligands;<sup>12</sup> the cmc of SDS in the absence of added electrolyte is  $8 \times 10^{-3}$  M.<sup>13</sup>

For system 1, the presence of small concentrations of  $\text{Fe}^{2+}$  does not change significantly the cmc values reported for corresponding ionic strengths.<sup>13</sup>

The effect of  $\text{Os}(\text{bpy})_3^{3+/2+}$  and  $\text{Os}(\text{dmbpy})_3^{3+/2+}$  on the cmc of SDS is considerably larger than simple cations with the same charge. For example, the addition of  $2 \times 10^{-5}$  M of  $\text{Os}(\text{bpy})_3^{3+}$  depresses the cmc to  $5 \times 10^{-4}$  M; this behavior was previously reported for the analogous  $\text{Co}(\text{bpy})_3(\text{ClO}_4)_3$ : in the presence of  $[\text{Co}(\text{bpy})_3^{3+}] = 2 \times 10^{-5}$  M, the cmc is reduced to ca.  $4 \times 10^{-4}$ .<sup>12</sup> The cmc data obtained for system 2 are collected in Table I for the same experimental conditions as for the kinetic runs. The two sets of data show the change of the cmc in going from the beginning to the end of the reaction. A more complex situation occurs for system 3 since the concentrations of the species are controlled by the equilibrium constant. The cmc values examined are slightly lower than those observed for  $\text{Os}(\text{bpy})_3^{3+/2+}$  ( $\text{Co}(\text{phen})_3^{3+}$  showed a somewhat more pronounced effect on the cmc in comparison with  $\text{Co}(\text{bpy})_3^{3+}$ ).<sup>12</sup>

In all cases it was possible to evaluate a range of cmc values that could be used in the calculations (the cmc ranges are indicated in the figures concerning the kinetic data).

**Models and Calculations.** The presently adopted model of a micellar solution replaces the complex size distribution by monomers and monodisperse micelles.<sup>14</sup> Thermodynamics of this system can only consider average quantities of the fluctuating micellar structure. Therefore, micelles are assumed to be spheres with homogeneous surface charges. Micellar surface potentials have been measured by means of a method proposed by Fernandez and Fromherz.<sup>15</sup> Two fluorescent pH indicators, which are substituted with long alkyl chains, are incorporated into micelles. NMR measurements confirmed that the center of the chromophore is located near the second  $\text{CH}_2$  group of the surfactant, whereas the titrated group is in the plane of the micellar headgroups.<sup>16</sup> Therefore, the mean radius,  $r_{\text{mic}}$ , needed for the electrostatic calculations has to refer to this plane. In the analyzed concentration range, the value of  $r_{\text{mic}}$  is taken to be independent of surfactant concentration and temperature. In the presence of additional salt,  $r_{\text{mic}}$  is correlated to the mean aggregation number by a third root dependence. In a preceding paper,<sup>18</sup> the measured surface potentials were shown to yield surface charges which can be attributed to the number of dissociated monomer head groups of the real micelle. Thus the average dissociation constant for these systems was found to be 0.4. Since the assumed micelle cannot account for different surface site or states, this model distinguishes between bound states within the surface and free states in the diffuse double layer outside the mean micellar

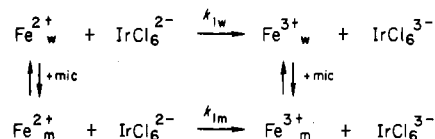


**Figure 1.** Calculated bulk concentrations for the system  $\text{IrCl}_6^{2-}$ - $\text{Fe}^{2+}$ -SDS as a function of surfactant concentration for various  $\text{Fe}^{2+}$  concentrations and ionic strengths: —,  $[\text{Fe}^{2+}] = 10^{-4}$  M; - - -,  $[\text{Fe}^{2+}] = 5 \times 10^{-5}$  M; - · - ·,  $[\text{Fe}^{2+}] = 2 \times 10^{-5}$  M; — — —,  $[\text{Fe}^{2+}] = 10^{-5}$  M. The vertical arrows indicate the cmc's.

radius  $r_{\text{mic}}$ . Thus no Stern layer<sup>19</sup> is considered.

The numerical procedure is based on a modified nonlinearized Poisson-Boltzmann equation which allows for the effects of finite ion sizes and the dependence of the dielectric constant on the local electric field strength.<sup>8</sup> The radii of the hydrated ions (counterions as well as coions) are taken to be 2.5 Å. The influence of these modifications for applications to micellar systems has been shown to become important for high surface potentials and/or in the presence of additional electrolyte concentrations.<sup>8</sup> For the kinetic analysis of a metal complex formation catalyzed at the surface of sodium decyl sulfate micelles,<sup>20</sup> deviations of ca. 10% were found for the electrostatic parameters needed to fit the rate data by using the nonlinearized Poisson-Boltzmann equation with and without the modifications. "Surface concentrations" of counterions attracted to the vicinity of the micellar surface have been computed by integrating the appropriate ion distributions within a shell of a sphere with thickness 5 (or 8) Å corresponding to the analyzed system. The influence of the shell thickness will be discussed below.

**The System  $\text{IrCl}_6^{2-}$ - $\text{Fe}^{2+}$ .** The reaction has been carefully investigated in the absence of surfactant by varying the ionic strength from 0.01 to 0.15 M. The rate constant gradually changes from  $2.8 \times 10^7$  to  $7.2 \times 10^6$   $\text{M}^{-1} \text{s}^{-1}$  (see Table II, supplementary material). In the literature a value of  $3.2 \times 10^6$   $\text{M}^{-1} \text{s}^{-1}$  in 0.5 M  $\text{HClO}_4$  is quoted.<sup>21</sup> The addition of SDS causes a decrease of the reaction rate, which is due to the strong attraction of  $\text{Fe}^{2+}$  to the anionic micelles. The following reaction scheme can be suggested where the subscripts w and m refer to water and the micellar pseudophase, respectively:



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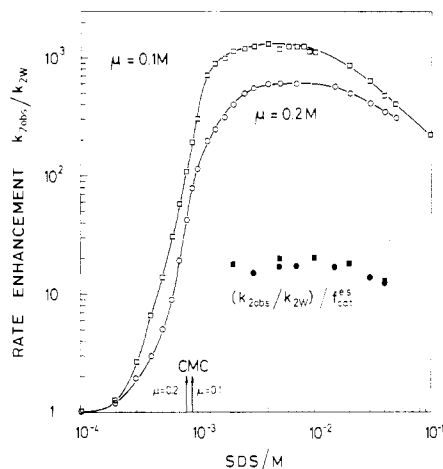
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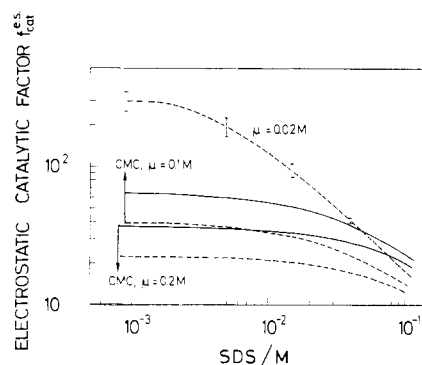
**Figure 2.** Experimental rate enhancement  $k_{2\text{obs}}/k_{2w}$  for the system  $\text{Os}(\text{bpy})_3^{3+}\text{-Fe}^{2+}\text{-SDS}$  as a function of surfactant concentration for two ionic strengths ( $\square$  and  $\blacksquare$ ,  $\mu = 0.1$  M;  $\circ$  and  $\bullet$ ,  $\mu = 0.2$  M) (the lines are drawn for a better visual impression). The nonelectrostatic contribution  $(k_{2\text{obs}}/k_{2w})/f_{\text{Cat}}^{\text{es}}$  has been calculated with the theoretically determined electrostatic enrichment factors displayed in Figure 3 (shell of 5 Å thickness).

The bulk concentrations of  $\text{Fe}^{2+}$  and  $\text{IrCl}_6^{2-}$  have been calculated with the method previously described; the results concerning some  $\text{Fe}^{2+}$  concentrations at different ionic strengths are reported in Figure 1.<sup>13,22</sup> The bulk concentration of  $\text{Fe}^{2+}$  is remarkably decreased, while that of  $\text{IrCl}_6^{2-}$  is only slightly increased as compared to the corresponding values in the absence of SDS. If the "true" second-order rate constants are evaluated with these bulk concentrations in the presence of SDS, then their values are approximately independent of SDS concentration (data not presented) and equal to the rate constants determined in the absence of SDS (see Table II). This confirms that the reaction proceeds in the bulk of the solution (following reaction path  $k_{1w}$ ). It can be quantitatively described by pure electrostatics.

Also for the previously investigated reactions of  $\text{Ru}(\text{bpy})_3^{3+}$  with  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$ , respectively,<sup>23</sup> the reaction partners are separated by the anionic micelles: the positively charged  $\text{Ru}(\text{bpy})_3^{3+}$  is attracted by the micelles, whereas the negatively charged molecules stay in the bulk solution. Again the separation of the reaction partners leads to a decrease of the observed reaction rate. In contrast to the  $\text{IrCl}_6^{2-}\text{-Fe}^{2+}\text{-SDS}$  system, however, the reaction path at the micellar surface  $k_{1m}$  has been found to predominate<sup>23</sup> due to the very strong interaction of  $\text{Ru}(\text{bpy})_3^{3+}$  with the micelles: in the  $\text{IrCl}_6^{2-}\text{-Fe}^{2+}\text{-SDS}$  system,  $\text{Fe}^{2+}$  (eq) is distributed within the entire diffuse double layer with an enrichment close to the micellar surface, while in the former case the availability of  $\text{Ru}(\text{bpy})_3^{3+}$  for a bulk reaction seems to be totally prevented by additional hydrophobic interactions of the bpy ligands with the micelles. The influence of the ligand (e.g., water or bipyridine) on the details of electron-transfer reactions is further emphasized by the results obtained for the following systems.

**The System  $\text{Os}(\text{bpy})_3^{3+}\text{-Fe}^{2+}$ .** The specific rate constant in the absence of surfactant ( $k_{2w}$ ) is not greatly affected by the ionic strength ( $1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at  $\mu = 0.02$  M,  $1.65 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at  $\mu = 0.10$  and  $0.20$  M) and quite similar to the literature value ( $1.43 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at  $0.5 \text{ M HClO}_4$ ).<sup>21</sup>

The presence of SDS causes a pronounced increase in the reaction rate which reaches a maximum and then again decreases. In general, this behavior is expected when both the reactants are attracted to micelles.<sup>6</sup>



**Figure 3.** Calculated electrostatic surface enrichment factors  $f_{\text{Cat}}^{\text{es}}$  for  $\text{Fe}^{2+}$  ions in the presence of SDS micelles as a function of surfactant concentration. Presented are the values for three ionic strengths and two different values for the thickness of the reaction shell at the surface: 5 Å (full lines) and 8 Å (dashed lines). The error bars correspond to the uncertainty in the surface potential ( $\pm 5$  mV) drawn only for  $\mu = 0.02$  M.

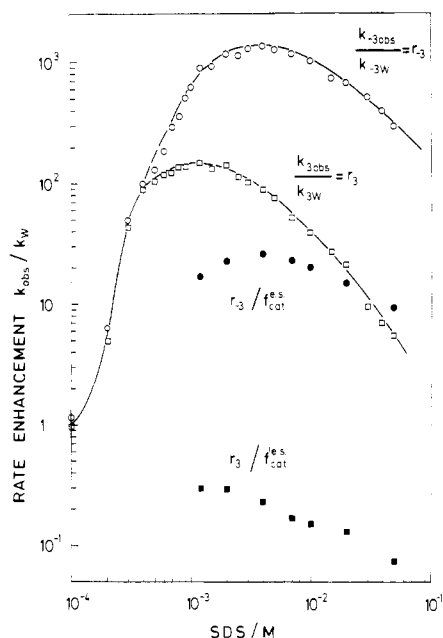
The reaction rate constants ( $k_{2\text{obs}}$ ) are collected in Table III (supplementary material), and the ratio  $r_2 = k_{2\text{obs}}/k_{2w}$  is plotted in Figure 2.<sup>24</sup> The kinetic results show a comparatively large transition range around the cmc (going from  $k_{2w}$  to the maximum value), which can be understood theoretically.<sup>20</sup> This effect is more pronounced for the system with the higher ionic strength. Due to the high charge and the hydrophobic character of the ligands,  $\text{Os}(\text{bpy})_3^{3+}$  can be assumed to be located entirely at the micellar surface. For the other reactant,  $\text{Fe}^{2+}$ , the concentration at the surface was calculated by means of the diffuse double-layer theory reported above, taking into account the presence of  $\text{Os}(\text{bpy})_3^{3+}$ .

Figure 3 displays the electrostatic surface catalytic factor,  $f_{\text{Cat}}^{\text{es}}$  (this factor represents the increase in the rate due to electrostatic interactions, and is calculated as a ratio between the estimated concentration at the micellar surface and the concentration of the species with the assumption that it has been dissolved in the actual volume of the aqueous phase), for different ionic strengths including the uncertainty in the surface potential ( $\pm 5$  mV) and the variation obtained with the assumption of different shells for the surface reaction environment (5-Å thickness corresponds to the diameter of a hydrated ion and should be a minimum value, whereas 8 Å has shown to provide reasonable results for a metal ion complex formation<sup>20</sup>). The calculated values for  $f_{\text{Cat}}^{\text{es}}$  have been used for a comparison with the total rate enhancement  $r_2$ . The full points in Figure 2 correspond to the ratio  $r_2/f_{\text{Cat}}^{\text{es}}$ . These numbers,  $17 \pm 5$  for a 5-Å thickness of the reaction volume at the micellar surface, differ significantly from 1 and are almost independent of the ionic strength and SDS concentration. This remaining factor is considered to represent a nonelectrostatic contribution to  $r_2$ . It should be noted, that this qualitative behavior cannot be explained by adjusting the well-known micelle parameters (i.e., cmc, surface potential, thickness of the shell). In fact, by varying the shell thickness from 5 to 8 Å  $r_2/f_{\text{Cat}}^{\text{es}}$  the remaining factor  $r_2/f_{\text{Cat}}^{\text{es}}$  becomes even larger ( $30 \pm 5$ ). The main part of this nonelectrostatic contribution may be ascribed to the ligand-micelle interaction, which indeed should not be very much affected by the ionic strength and surfactant concentration. In a previous report,<sup>1</sup> it was concluded that the increase of the reaction rate for a similar system,  $\text{Fe}(\text{tmphen})_3^{3+}\text{-Fe}^{2+}\text{-SDS}$ , was almost entirely due to the electrostatic enrichment of the reaction partners at the charged micellar surface. However, if the present treatment

(24) At  $\mu = 0.02$  M, the reaction rates in the range of  $(1.2\text{--}8) \times 10^{-3} \text{ M SDS}$  were rather scattered around ca.  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . For  $[\text{SDS}] = (2\text{--}7) \times 10^{-4} \text{ M}$ , precipitations occur. Therefore, the data for this ionic strength are not shown in Figure 2.

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**Figure 4.** Experimental rate enhancement  $k_{3obs}/k_{3w}$  for the forward and backward reaction in the system  $\text{Os}(\text{dmbpy})_3^{2+/3+}\text{-Fe}^{3+/2+}\text{-SDS}$  as a function of surfactant concentration ( $\mu = 0.1$  M) (the lines are drawn for a better visual impression). The full points represent the nonelectrostatic catalytic factors ( $f'_{\text{Cat}}^{\text{nes}}$  and  $f_{\text{Cat}}^{\text{nes}}$  for the forward and backward reaction, respectively). They have been calculated from the total rate enhancement with theoretical values for the electrostatic enrichment factors.

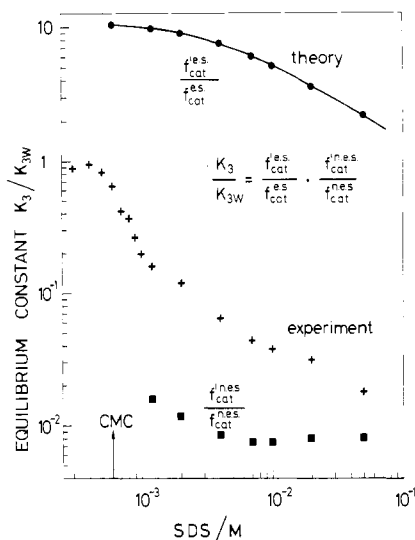
is applied to the  $\text{Fe}(\text{tmphen})_3^{3+}\text{-Fe}^{2+}$  system as well, a nonelectrostatic factor of about  $5 \pm 1$  can be observed. In general it can be concluded that electrostatics seem to provide a significant contribution to rate enhancements of typical 3–4 orders of magnitude, although other important effects have to be considered for a complete interpretation of electron-transfer reaction rates in micellar systems. A more detailed discussion of the nonelectrostatic part is given in the next paragraph.

**The System  $\text{Os}(\text{dmbpy})_3^{3+/2+}\text{-Fe}^{3+/2+}$ .** This system offers the possibility of investigating the influence of SDS micelles upon the equilibrium constant of a redox reaction together with the effect on the forward and backward rate constants.

The equilibrium constants evaluated spectrophotometrically were found in good agreement with those determined from the kinetic data.<sup>25,26</sup>

In the absence of SDS, the equilibrium constant,  $K_{3w}$ , has a value  $3.7 \pm 0.3$ . The specific rate constants  $k_{3obs}$  and  $k_{-3obs}$  at different SDS concentrations are collected in Table IV (supplementary material) together with the equilibrium constants.

From Figure 4, where  $r_3 = k_{3obs}/k_{3w}$  and  $r_{-3} = k_{-3obs}/k_{-3w}$  are reported as functions of SDS ( $\mu = 0.1$  M), it is evident that the increase in the reaction rate is greater for the backward than for the forward reaction. This finding is opposite of what could be expected on pure electrostatic basis because the forward rate might be increased by a factor  $f'_{\text{Cat}}^{\text{es}}$ , representing the attraction of  $\text{Fe}^{3+}$  ions to the micellar surface, which is higher than the corresponding factor  $f_{\text{Cat}}^{\text{es}}$  for the  $\text{Fe}^{2+}$



**Figure 5.** Experimental equilibrium constants  $K_3/K_{3w}$  for the system  $\text{Os}(\text{dmbpy})_3^{2+/3+}\text{-Fe}^{3+/2+}\text{-SDS}$  as a function of surfactant concentration ( $\mu = 0.1$  M). Electrostatic and nonelectrostatic contributions have been separated as in Figures 2 and 4.

ions in the back-reaction (provided that the  $\text{Os}(\text{dmbpy})_3^{2+/3+}$  complexes can be assumed to be totally bound to the micelles in either case). If the same analytical treatment is adopted as above, it can be seen from Figure 4 that the nonelectrostatic contribution for the back-reaction,  $f_{\text{Cat}}^{\text{nes}} = r_{-3}/f_{\text{Cat}}^{\text{es}}$ , is significantly different from 1 with values in the same order of magnitude as found for system 2:  $20 \pm 5$ . Again the calculations are performed for a 5-Å shell. On the contrary, the ratio  $r_3/f'_{\text{Cat}}^{\text{es}} = f'_{\text{Cat}}^{\text{nes}}$  for the forward reaction is less than 1 (e.g., 0.15 at  $10^{-2}$  M SDS), indicating that in this case an inhibition factor is operating. A possible although speculative interpretation of this fact involves a charge-dependent specific interaction of the bulky dmbpy ligands with the micelles in the  $\text{Os}^{2+}$  – and  $\text{Os}^{3+}$  complexes.

As can be seen from Figure 4, the nonelectrostatic factors  $f'_{\text{Cat}}^{\text{nes}}$  and  $f_{\text{Cat}}^{\text{nes}}$  for the forward and backward reaction, respectively, are slightly dependent on the SDS concentration (possibly due to a change of micellar parameters) but virtually independent of the ionic strength (not shown). The variation of the observed equilibrium constant (for  $\mu = 0.1$  M) as a function of SDS concentration is illustrated in Figure 5. For a discussion of the various influences, the apparent equilibrium constant  $K_3$  in the presence of SDS can be written as

$$K_{3obs} = \frac{k_{3obs}}{k_{-3obs}} = \frac{k_{3w}}{k_{-3w}} \frac{f'_{\text{Cat}}^{\text{es}}}{f_{\text{Cat}}^{\text{es}}} \frac{f'_{\text{Cat}}^{\text{nes}}}{f_{\text{Cat}}^{\text{nes}}}$$

In Figure 5 it is shown that the ratio of the nonelectrostatic contributions becomes approximately constant for SDS concentrations greater than  $2 \times 10^{-3}$  M. The value of  $f'_{\text{Cat}}^{\text{nes}}/f_{\text{Cat}}^{\text{nes}} = 8 \times 10^{-3}$  has been calculated from the experimental ratio  $K_3/K_{3w}$  within the theoretically determined electrostatic surface catalytic factors  $f_{\text{Cat}}^{\text{es}}$  and  $f'_{\text{Cat}}^{\text{es}}$ . The higher values for concentrations below  $10^{-3}$  M SDS probably have to be ascribed to the cmc transition range. Thus the decrease of the equilibrium constant  $K_3$  in the presence of SDS appears to be the result of two effects: (1) a decrease of the ratio  $f'_{\text{Cat}}^{\text{nes}}/f_{\text{Cat}}^{\text{nes}}$  in the cmc transition range due to the appearance of micelles and (2) a decrease of the ratio  $f'_{\text{Cat}}^{\text{es}}/f_{\text{Cat}}^{\text{es}}$  for higher SDS concentrations. Both effects, however, can be rationalized in terms of the number of appropriate ions present at the micellar surface. The nonelectrostatic contribution is determined by the  $\text{Os}(\text{dmbpy})_3^{2+/3+}$  complexes. For surfactant concentrations close to the cmc, the number of micelles is low, so that more than one Os complex is located at the micellar surface. This

(25) The equilibrium constants from kinetic data were obtained by operating with a large excess of  $[\text{Fe}^{3+}]$  and  $[\text{Fe}^{2+}]$ . For these conditions,  $k_{obs} = k_3[\text{Fe}^{3+}] + k_{-3}[\text{Fe}^{2+}]$ ; by plotting  $k_{obs}/[\text{Fe}^{2+}]$  as a function of  $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ ,  $k_3$  and  $k_{-3}$  are determined.

(26) At  $\mu = 0.02$  M, the equilibrium constants at  $[\text{SDS}] < 1.5 \times 10^{-3}$  M are scattered.  $k_3$  has been estimated by performing the runs without initial  $[\text{Fe}^{2+}]$  in order to minimize the influence of the reverse reaction and by deriving the rate constant from the early part of the reaction progress (initial slope).

may result in a disturbed structure with a corresponding influence on nonelectrostatic interactions. Since only few micelles are occupied with an Os complex at higher surfactant concentrations, the effect is expected to diminish. For higher SDS concentrations, the properties of the undisturbed micelles are reestablished on average due to the dilution of the Os complexes in the micellar pseudophase.

However, it cannot be excluded that the disturbed structure of the occupied micelles changes significantly the electrostatic properties of the micelles. Thus the (electrostatic) enrichment in the transition range might be affected differently from that which has been accounted for in the calculations. The "direct" electrostatic effect, on the other hand, is caused by the  $\text{Fe}^{3+/2+}$  distributions. Since for the experimental conditions of system 3 the enrichment factors for 3+ ions are more strongly decreased for increasing surfactant concentrations than those of 2+ ions, the behavior shown in Figure 5 is obtained for the ratio of both factors. (Of course, the same argument holds for the enrichment of 2+ ions compared to monovalent ions. The plateau region close to the cmc has already been assessed for the single electrostatic enrichment factors.<sup>8,20</sup>)

A change in the redox potential on association with micelles was previously reported for equilibria involving partially solubilized quinones<sup>27</sup> while the shift in the reversible half-wave potentials for some Os complexes with bipyridine-like ligands has been recently found.<sup>28</sup> It is noteworthy that the shift for  $\text{Os}(\text{dmbpy})_3^{3+/2+}$  in SDS is quoted to be 0.14 V for different experimental conditions. This value should be related to the presently determined nonelectrostatic effect. The dielectric constant at the surface of the micelles is decreased in respect to water solutions,<sup>15</sup> and decreasing solvent polarity is known to increase the reduction potential of cationic metal complexes.<sup>29</sup> In general, the environmental changes (specific

interactions, medium properties) of reactants embedded in micelles are expected to modify the thermodynamic properties of the system. Since the rate constants of electron-transfer reactions depend strongly on the free energy involved, this aspect is supposed to have a relevant effect on reaction kinetics.<sup>30</sup>

### Conclusions

For micellar solutions of SDS, local ion concentrations have been calculated by means of experimental surface potentials and a numerical method based on the nonlinearized Poisson-Boltzmann equation. Thus electrostatic enrichment factors could be obtained which have been applied to kinetic investigations of different electron-transfer reactions in appropriate systems.

The approach was proven to be successful for a system in which only one reactant is attracted to the micellar surfaces. In a system where both reactants associate with the micelles, it was possible to estimate both the electrostatic and nonelectrostatic contributions to the reaction rates as well as to the equilibrium constant for varied surfactant concentrations. To our knowledge the present method for the first time provides a reliable separation of electrostatic and environmental effects on micellar catalysis.

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**Registry No.** SDS, 2386-53-0;  $\text{IrCl}_6^{2-}$ , 16918-91-5;  $\text{Os}(\text{bpy})_3^{3+}$ , 30032-51-0;  $\text{Os}(\text{dmbpy})_3^{3+}$ , 47838-06-2;  $\text{Os}(\text{dmbpy})_3^{2+}$ , 33247-24-4; Fe, 7439-89-6.

**Supplementary Material Available:** Tables of rate constants for the  $\text{IrCl}_6^{2+}$ - $\text{Fe}^{2+}$  system (Table II), rate constants for the  $\text{Os}(\text{bpy})_3^{2+}$ - $\text{Fe}^{2+}$  system (Table III), and rate and equilibrium constants for the  $\text{Os}(\text{dmbpy})_3^{2+/3+}$ - $\text{Fe}^{3+/2+}$  system (Table IV) (4 pages). Ordering information is given on any current masthead page.

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