

be expected for the direct and indirect "bypass" mechanisms of IET, inasmuch as assistance in maintaining the specific configuration for maximal orbital overlap may be obtained from H-bonding interactions between the nitro group and the coordinated ammine ligands. However, the diminished rates in acid solution for the complexes exhibiting these modes of IET (ONBZ, ONPA, PNPB, PNDG) are not significantly different from those of the other complexes in the series, suggesting that a requirement for H-bonding in these "bypass" mechanisms may be of minor importance.

When compared with values of k_1 obtained at pH 7 at an ionic strength of 1 M, the values of k_1 in acidic solution are uniformly ~50 times slower for the ortho, meta, and para isomers of the phenylacetato complexes, although different mechanisms of IET operate in neutral solution for each complex in this series. For the PNBZ, PNGB, and PNDG complexes, which also exhibit different pathways of IET, nitro protonation uniformly decreases the values of k_1 by ~15 times. However, no such uniform re-

duction in rate occurs for the cinnamato series. The general uniformity in the decreases in the values of k_1 suggests that protonation of the nitro radical affects only the driving force for the IET, while leaving the mechanism unaffected in most cases.

Acknowledgment. The use of the pulse radiolysis facilities at the U.S. Army Natick Research and Development Center and CFKR is gratefully acknowledged. CFKR is supported jointly by the Biomedical Research Technology Program of the Division of Research Resources of NIH (Grant RR 00886) and by The University of Texas.

Registry No. ONBZ, 62714-55-0; MNBZ, 62714-56-1; PNBZ, 36445-08-6; ONPA, 103241-52-7; MNPA, 103241-53-8; PNPA, 40544-48-7; DNPA, 103241-54-9; ONCM, 103241-55-0; MNCM, 103241-56-1; PNCM, 103241-57-2; PNPB, 103241-58-3; PNGB, 103241-59-4; PNDG, 103241-60-7; PNNC, 68033-17-0; PNNS, 78891-44-8; PNOS, 76024-72-1; PNPO, 80679-83-0; NCYC, 103258-82-8; NaHCO₃, 141-53-7; *CO₂⁻, 14485-07-5; *C(CH₃)₂OH, 5131-95-3; 2-propanol, 67-63-0.

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Micellar Effects on the Kinetics of the Aquation and the Base Hydrolysis of Tris(1,10-phenanthroline)iron(II) and Chloropentaamminecobalt(III) Ions

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Received October 16, 1985

Kinetics of the aquation and the base hydrolysis of Fe(phen)₃²⁺ and CoCl(NH₃)₅²⁺ were studied in aqueous SDS solutions at 35.0 °C. The rate constant of the aquation of Fe(phen)₃²⁺ increased from 4.4×10^{-4} to 6.6×10^{-4} s⁻¹ with an increase in the SDS concentration below the critical micelle concentration (cmc), while that of the base hydrolysis decreased from 0.085 to 0.010 mol⁻¹ dm³ s⁻¹. The rate constants showed no remarkable changes above the cmc. The rate constants of the aquation and the base hydrolysis of CoCl(NH₃)₅²⁺ changed only above the cmc (from 6.1×10^{-6} to 8.1×10^{-6} s⁻¹ and from 3.4 to 0.039 mol⁻¹ dm³ s⁻¹, respectively). The changes in the rate constants of the Fe(phen)₃²⁺ reactions below the cmc were related to the formation of pre-micellar aggregates of the complex ion and the monomeric dodecyl sulfate ions through hydrophobic interaction, while the changes in the rate constants of the CoCl(NH₃)₅²⁺ reactions above the cmc were explained by a partition of the complex ions to a micellar phase through electrostatic interaction. Effects of added NaCl on the rate behavior of the complexes in the micellar solutions were discussed by using an ion-exchange model. The role of the hydrophobic effect on the pre-micellar and micellar catalyses of the reaction is also discussed.

Introduction

The effects of micellar systems on chemical reactions have been studied extensively especially for organic reactions.^{2,3} On the other hand, relatively few works have been carried out for inorganic reactions. So far, studies were made on electron-transfer reactions involving metal complexes,⁴⁻¹⁰ and complex formation of Ni²⁺ or Mn²⁺ with organic ligands.¹¹⁻¹⁴ These studies are important not only from the viewpoint of inorganic reaction mechanisms but also

from biochemical aspects, i.e., as models of electron-transfer and ligand-exchange reactions on the surface of a biomembrane or at the interface of a globular protein. Among ligand-exchange reactions, the aquation and the base hydrolysis of metal complex ions have rarely been studied in surfactant solutions¹⁵ in spite of their extensive studies in aqueous solutions.^{16,17} These reactions are appropriate as models for investigating the effects of electrostatic and hydrophobic interactions on ligand-exchange reactions at interfaces.

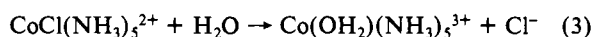
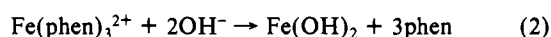
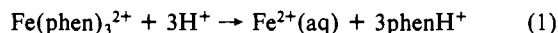
In the course of studies of the effects of micelles on chemical reactions, catalytic effects were also observed in dilute surfactant solutions below the critical micelle concentration (cmc).^{4,5,7,9,12-14,18,19} The changes in the reaction rates were attributed either to the interaction of reactants with pre-micellar aggregates of surfactants,^{5,20} to the interaction of reactants with monomeric species of surfactants to form aggregates below the

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cmc,^{13,19,21-25} or to solute-induced micellization.¹⁹ The idea of the formation of aggregates between reactants and surfactant molecules in solutions below the cmc has been extended by Piszkiwicz²⁶ to micellar solutions of surfactants to explain the catalytic effects of surfactants both below and above the cmc. The interaction of reactants with nonmicellar surfactant species takes part in the "micellar catalysis" of reactions as well. Thus, studies of the effects of nonmicellized surfactants on chemical reactions, as well as the effects of micellized surfactants, are of importance for the understanding of the nature of catalytic effects of surfactants on the reactions.

In this paper we report on the kinetics of the aquation and the base hydrolysis (eq 1-4) of a hydrophobic and a hydrophilic metal



complex, Fe(phen)_3^{2+} (phen = 1,10-phenanthroline) and $\text{CoCl(NH}_3)_5^{2+}$, in aqueous sodium dodecyl sulfate solutions containing various concentrations of sodium chloride. The study will disclose how electrostatic interaction is concerned with micellar catalysis and how hydrophobic interaction is concerned with pre-micellar and micellar catalysis in the reactions.

Experimental Section

Sodium dodecyl sulfate (SDS) from Merck (for the tensile test) was recrystallized five times from ethanol and dried under vacuum at 70 °C. The purity of the SDS was checked by measuring the surface tension of the SDS solutions.²⁷ Sodium chloride and sodium perchlorate (Merck, suprapur) were used without further purification. The $[\text{Fe(phen)}_3^{2+}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ and $[\text{CoCl(NH}_3)_5^{2+}\text{Cl}_2]$ were synthesized by conventional methods. Reactions 1-4 at 35.0 ± 0.1 °C were monitored spectrophotometrically at 245 nm for the cobalt(III) complex and at 510 nm for the iron(II) complex. The concentration of the complex ion was 5×10^{-5} mol dm⁻³ except for the solutions of low SDS concentrations ($(1-4) \times 10^{-3}$ mol dm⁻³) which contained as low as 1×10^{-5} mol dm⁻³ $\text{CoCl(NH}_3)_5^{2+}$ in order to avoid the precipitation of dodecyl sulfate with the complex. The base hydrolysis of Fe(phen)_3^{2+} was measured in 0.020 mol dm⁻³ sodium hydroxide solutions²⁸ with 0.4 mol dm⁻³ NaCl and without NaCl. The solutions contained 5×10^{-4} mol dm⁻³ NiCl_2 to scavenge liberated phenanthroline ligands and 5×10^{-4} mol dm⁻³ sodium citrate to prevent the precipitation of iron and nickel hydroxides. The rates did not depend on the concentrations of NiCl_2 or sodium citrate in the range 5×10^{-4} to 1×10^{-2} mol dm⁻³. The base hydrolysis of $\text{CoCl(NH}_3)_5^{2+}$ was measured in 0.020 mol dm⁻³ sodium hydroxide solutions²⁸ containing 0, 0.1, 0.2, and 0.4 mol dm⁻³ sodium chloride. The aquation of $\text{CoCl(NH}_3)_5^{2+}$ was observed in 0.005 mol dm⁻³ HClO_4 solutions containing 0.015 mol dm⁻³ NaClO_4 , and that of Fe(phen)_3^{2+} , in 5×10^{-4} mol dm⁻³ $\text{Ni(ClO}_4)_2$ solutions containing 0.02 mol dm⁻³ NaCl.²⁹ The aquation and the base hydrolysis followed the first-order rate law at least for 4 half-lives. The rate constants, k^{obsd} , were obtained from the usual analysis of first-order reactions. They were reproducible within $\pm 2\%$. The ob-

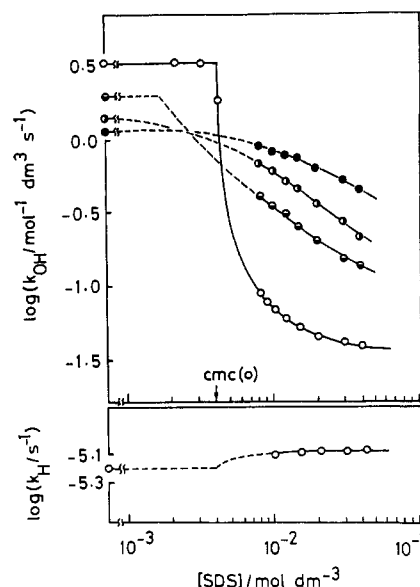


Figure 1. Rate constants for the aquation and the base hydrolysis of $\text{CoCl(NH}_3)_5^{2+}$ in SDS solutions. $[\text{HClO}_4] = 0.005$ mol dm⁻³ and $[\text{NaClO}_4] = 0.015$ mol dm⁻³ for the aquation (the lower part of the figure), and $[\text{NaOH}] = 0.02$ mol dm⁻³ and $[\text{NaCl}] = 0$ (○), 0.1 (◐), 0.2 (●), and 0.4 (●) mol dm⁻³ for the base hydrolysis (the upper part). The arrow indicates the cmc value of the SDS solution without NaCl.

served rate constants in acidic or neutral solutions give the first-order rate constants, k_{H} , for the aquation of the complexes. The second-order rate constants, k_{OH} , for the base hydrolysis of the complexes were obtained from the relation, $k^{\text{obsd}} = k_{\text{H}} + k_{\text{OH}}[\text{OH}^-]$. The chemicals and procedures other than those described above were the same as those described in our previous paper.³⁰

Results and Discussion

A. The $\text{CoCl(NH}_3)_5^{2+}$ -SDS System. The rate constants of the aquation and the base hydrolysis of $\text{CoCl(NH}_3)_5^{2+}$ measured in SDS solutions with and without NaCl are shown in Figure 1 as a function of the SDS concentration ($(8-40) \times 10^{-3}$ mol dm⁻³). In SDS solutions below 8×10^{-3} mol dm⁻³, the rate of base hydrolysis was observed without NaCl. The cmc value of pure SDS in the solution containing neither NaCl nor the complex salt³¹ is indicated by an arrow in Figure 1. When the SDS concentration (in the solution without NaCl) was increased, the second-order rate constant (k_{OH}) for the base hydrolysis remained unchanged below the cmc and sharply decreased down to a limiting value after the cmc was reached. The decrease in the rate constants with increasing SDS concentration was less remarkable for solutions of higher NaCl concentrations. The first-order rate constant (k_{H}) for the aquation of the complex was slightly larger in SDS solutions than in the solution without SDS.

a. Aquation of $\text{CoCl(NH}_3)_5^{2+}$. If we regard the micellar solution as a two-phase system, the observed rate constants (Figure 1) show that the rate constant in the micellar phase (k_{H}^{M}) is not appreciably different from that in the aqueous phase (k_{H}^{W}). This suggests that the complex ions in the micellar phase are located on the surface of the micelle.

b. Base Hydrolysis of $\text{CoCl(NH}_3)_5^{2+}$. The small effect of SDS on the rate constants below the cmc (Figure 1) shows the absence of any appreciable interaction of the complex ion with dodecyl sulfate ions. On the other hand, the decrease in the rate constants above the cmc (Figure 1) indicates that the complex ion interacts with a micelle. Quina's framework for ion exchange in micellar solutions³² is applied with modifications in the following analysis

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(27) The surface tension showed no minimum around the cmc, indicating that the SDS was practically pure.

(28) The rates were also measured in solutions containing 0.007 and 0.014 mol dm⁻³ NaOH. The total sodium ion concentration of the solutions was adjusted to 0.02 mol dm⁻³ by adding NaCl in order to keep the cmc value of the solutions unchanged. When the rates of base hydrolysis were too fast to be measured precisely in these NaOH solutions, the rates were measured in 0.001, 0.002, and 0.003 mol dm⁻³ NaOH solutions. The rate constant of the base hydrolysis linearly dependent on the hydroxide concentration in the concentration range studied.

(29) The sodium salts were added to the solutions in order to adjust the total cationic concentration to 0.02 mol dm⁻³ for the base hydrolysis; the cationic concentration affects the cmc, the micellar aggregation number, and the surface potential of the SDS micelle.

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(31) These cmc values can be regarded as a measure of the true cmc value in a solution which also contains the complex salts in addition, since the cmc value of SDS was changed only slightly by the presence of 5×10^{-5} mol dm⁻³ $[\text{Fe(phen)}_3^{2+}(\text{ClO}_4)_2]$: Ozeki, S.; Tachiyashiki, S.; Ikeda, S.; Yamatera, H. *J. Colloid Interface Sci.* **1983**, *91*, 430-8.

of the kinetic results. If $\text{CoCl}(\text{NH}_3)_5^{2+}$ and OH^- are partitioned between the aqueous and micellar phases, the observed pseudo first-order rate constant can be written as

$$\begin{aligned} k^{\text{obsd}} &= k_{\text{H}} + k_{\text{OH}}[\text{OH}]_{\text{T}} \\ &\approx k_{\text{OH}}[\text{OH}]_{\text{T}} \quad (k_{\text{H}} \ll k_{\text{OH}}[\text{OH}]_{\text{T}} \text{ at } [\text{OH}]_{\text{T}} = 0.020 \text{ mol dm}^{-3}) \\ &= k_{\text{OH}}^{\text{W}}[\text{OH}]_{\text{f}} \frac{[\text{M}]_{\text{f}}}{[\text{M}]_{\text{T}}} + k_{\text{OH}}^{\text{M}}[\overline{\text{OH}}]_{\text{b}} \frac{[\text{M}]_{\text{b}}}{[\text{M}]_{\text{T}}} \end{aligned} \quad (5)$$

Here k_{H} and k_{OH} represent the experimental first-order rate constant of the aquation and the experimental second-order rate constant of the base hydrolysis; k_{OH}^{W} and k_{OH}^{M} are the second-order rate constants of base hydrolysis in the aqueous and the micellar phase, respectively; $[\text{OH}]_{\text{T}}$, $[\text{OH}]_{\text{f}}$, $[\text{M}]_{\text{f}}$, and $[\text{M}]_{\text{b}}$ are the analytical concentrations of the total hydroxide ions, free hydroxide ions, and free and bound complex ions, respectively; $[\overline{\text{OH}}]_{\text{b}}$ is the local (bar is used to specify "local" value) concentration of bound hydroxide ions in the micellar phase; and $[\text{M}]_{\text{T}}$ is the total analytical concentration of added complex ions, i.e. $[\text{M}]_{\text{T}} = [\text{M}]_{\text{f}} + [\text{M}]_{\text{b}}$.

The local concentration of reactive ions in the micellar phase can be estimated by various models.³³ Thus, the local concentration of bound hydroxide ions, $[\overline{\text{OH}}]_{\text{b}}$, in the micellar phase and the analytical concentration of the bound complex ions, $[\text{M}]_{\text{b}}$, were estimated with Quina's ion-exchange model.^{33e} The exchange equilibrium constant for an ion exchange between H^+ and Na^+ at the surface of the SDS micelle can be written as³²

$$K_{\text{H/Na}} = \frac{[\overline{\text{H}}]_{\text{b}}[\text{Na}]_{\text{f}}}{[\text{H}]_{\text{f}}[\overline{\text{Na}}]_{\text{b}}} \quad (6)$$

where $[\text{H}]_{\text{f}}$ and $[\text{Na}]_{\text{f}}$ represent the analytical concentrations of the free counterions and $[\overline{\text{H}}]_{\text{b}}$ and $[\overline{\text{Na}}]_{\text{b}}$ represent the local concentrations of the bound ions in the micellar phase. Utilizing the ionic products of water in the aqueous and micellar phases ($K_{\text{W}} = [\text{H}]_{\text{f}}[\text{OH}]_{\text{f}}$ and $\overline{K}_{\text{W}} = [\overline{\text{H}}]_{\text{b}}[\overline{\text{OH}}]_{\text{b}}$), we obtain the following relation between the free and the bound hydroxide concentration:³²

$$K_{\text{NaOH}} = \frac{[\overline{\text{Na}}]_{\text{b}}[\overline{\text{OH}}]_{\text{b}}}{[\text{Na}]_{\text{f}}[\text{OH}]_{\text{f}}} = \frac{\overline{K}_{\text{W}}}{K_{\text{W}}K_{\text{H/Na}}} \quad (7)$$

The equilibrium constant for an ion exchange between the doubly charged complex ion (M^{2+}) and the Na^+ ion at the surface of the micelle is defined by

$$K_{\text{M/Na}} = \frac{[\overline{\text{M}}]_{\text{b}}[\text{Na}]_{\text{f}}^2}{[\text{M}]_{\text{f}}[\overline{\text{Na}}]_{\text{b}}^2} \quad (8)$$

The local concentration of the bound ion, $[\overline{\text{M}}]_{\text{b}}$, is related to the analytical concentration, $[\text{M}]_{\text{b}}$, by

$$[\overline{\text{M}}]_{\text{b}} = [\text{M}]_{\text{b}}/C\overline{V} \quad (9)$$

where C is the concentration of micellized SDS and \overline{V} is the effective volume, per mole of micellized surfactant, of the region surrounding the micelle within which the ion may be said to be "bound".^{33e} This volume may be regarded as the volume of the Stern layer per mole of the micellized surfactant. Using eq 7–9, we transformed eq 5 into

$$\begin{aligned} k^{\text{obsd}} &= \{k_{\text{OH}}^{\text{W}}[\text{OH}]_{\text{f}} + (k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}[\text{OH}]_{\text{f}}[\text{Na}]_{\text{f}}/[\overline{\text{Na}}]_{\text{b}}) \times \\ &\quad (K_{\text{M/Na}}C\overline{V}[\overline{\text{Na}}]_{\text{b}}^2/[\text{Na}]_{\text{f}}^2)\} / (1 + K_{\text{M/Na}}C\overline{V}[\overline{\text{Na}}]_{\text{b}}^2/[\text{Na}]_{\text{f}}^2) \end{aligned} \quad (10)$$

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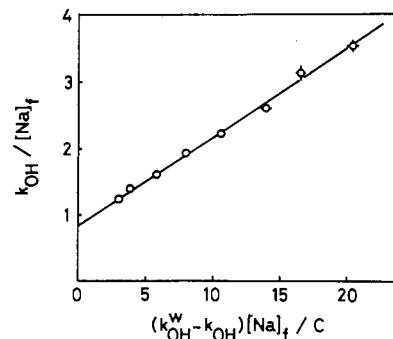


Figure 2. Plot of $k_{\text{OH}}/[\text{Na}]_{\text{f}}$ against $(k_{\text{OH}}^{\text{W}} - k_{\text{OH}})[\text{Na}]_{\text{f}}/C$ for a system without NaCl.

Table I. Experimental Values of k_{OH}^{W} , $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$, and $K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V}$ for the Base Hydrolysis of $\text{CoCl}(\text{NH}_3)_5^{2+}$ in NaCl Solutions^a

$[\text{NaCl}]/\text{mol cm}^{-3}$	$k_{\text{OH}}^{\text{W}}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$(k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}})/\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$	$K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V}/\text{mol dm}^{-3}$
0	3.40	0.83 ± 0.05	7.6 ± 0.4
0.1	1.94	0.48 ± 0.08	10.4 ± 0.6
0.2	1.50	0.17 ± 0.11	8.8 ± 0.8
0.4	1.14	0.08 ± 0.08	7.0 ± 0.6

^a The solutions contained 0.02 mol dm^{-3} NaOH in addition to NaCl.

Since only a small fraction of hydroxide ions are bound to the micelles, we reasonably assume that $[\text{OH}]_{\text{T}} = [\text{OH}]_{\text{f}} + [\overline{\text{OH}}]_{\text{b}} \approx [\text{OH}]_{\text{f}}$. Thus, the observed second-order rate constant, $k_{\text{OH}} = k^{\text{obsd}}/[\text{OH}]_{\text{T}}$, for the base hydrolysis is expressed as

$$\begin{aligned} k_{\text{OH}} \approx k^{\text{obsd}}/[\text{OH}]_{\text{f}} &= \{k_{\text{OH}}^{\text{W}} + \\ &\quad k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}([\text{Na}]_{\text{f}}/[\overline{\text{Na}}]_{\text{b}})K_{\text{M/Na}}([\overline{\text{Na}}]_{\text{b}}^2\overline{V}C/[\text{Na}]_{\text{f}}^2)\} / \\ &\quad (1 + K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V}C/[\text{Na}]_{\text{f}}^2) \end{aligned} \quad (11)$$

Transformation of eq 11 leads to the relation

$$\frac{k_{\text{OH}}}{[\text{Na}]_{\text{f}}} = k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}} + \frac{1}{K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V}} \frac{k_{\text{OH}}^{\text{W}} - k_{\text{OH}}}{C/[\text{Na}]_{\text{f}}} \quad (12)$$

In order to estimate the $[\text{Na}]_{\text{f}}$ value in eq 12, we assume the degree of ionization of the SDS micelle, α , to be effectively constant. Then, we have the relation

$$\begin{aligned} [\text{Na}]_{\text{f}} &= \text{cmc} + [\text{Na}]_{\text{add}} + \alpha C + [\text{H}]_{\text{b}} + 2[\text{M}]_{\text{b}} \\ &\approx \text{cmc} + [\text{Na}]_{\text{add}} + \alpha C \end{aligned} \quad (13)$$

where $[\text{Na}]_{\text{add}}$ is the concentration of added electrolyte (NaOH and NaCl). The $[\text{H}]_{\text{b}}$ and $2[\text{M}]_{\text{b}}$ terms can be ignored since both $[\text{H}]_{\text{T}}$ and $[\text{M}]_{\text{T}}$ are very low under the experimental conditions. With eq 13, $\alpha = 0.22$,³⁴ and a cmc value of $0.004 \text{ mol dm}^{-3}$ ³⁵ for the system $[\text{NaCl}] = 0$ used to estimate the $[\text{Na}]_{\text{f}}$ values for various SDS concentrations, $k_{\text{OH}}/[\text{Na}]_{\text{f}}$ was plotted against $(k_{\text{OH}}^{\text{W}} - k_{\text{OH}})/(C/[\text{Na}]_{\text{f}})$. The linear relationship is shown in Figure 2. The intercept and the slope of the line give the values of $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ and $1/(K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V})$, respectively. These values are listed in Table I with those obtained for other systems of $[\text{NaCl}] = 0.1, 0.2, \text{ and } 0.4 \text{ mol dm}^{-3}$ by using cmc values of $0.0015, 0.0009, \text{ and } 0.0006 \text{ mol dm}^{-3}$, respectively.³⁵

The change in $K_{\text{M/Na}}[\overline{\text{Na}}]_{\text{b}}^2\overline{V}$ with the change in the NaCl concentration is small with no systematic trend, and therefore $[\overline{\text{Na}}]_{\text{b}}$ may be regarded unchanged, as can be expected from the

(34) Romsted, L. S. Ph.D. Thesis, Indiana University, Bloomington, IN, 1975. The change in the value of α by ± 0.1 does not change the values in Table I except those of the first row, which change by $\pm 10\%$.

(35) Estimated from the data in: Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; National Bureau of Standards: Washington, DC, 1971.

Table II. Distribution Ratio (D) and Second-Order Rate Constants for the Base Hydrolysis of $\text{CoCl}(\text{NH}_3)_5^{2+}$ in 0.008 and 0.040 mol dm^{-3} SDS Solutions Containing Various Concentrations of NaCl^a

$[\text{NaCl}]/\text{mol dm}^{-3}$	0.008 mol dm^{-3} SDS		0.040 mol dm^{-3} SDS	
	D	$k_{\text{OH}}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	D	$k_{\text{OH}}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
0	49	0.088	270	0.039
0.1	4.1	0.417	23	0.136
0.2	1.2	0.691	6.5	0.225
0.4	0.29	0.917	1.5	0.468

^a The solutions contained 0.02 mol dm^{-3} NaOH in addition to NaCl .

ion-exchange model, assuming a constant degree of ionization of the micelle. The average value of the exchange equilibrium constant, $K_{\text{M}/\text{Na}}$, was calculated to be 1.9, on the assumption that $[\text{Na}]_{\text{b}} = (1 - \alpha)/\bar{V}$ and $\bar{V} = 0.14 \text{ mol}^{-1} \text{ dm}^3$.³⁶ This $K_{\text{M}/\text{Na}}$ value can be compared with the values of 2 and 6 for the ion-exchange equilibrium constants $K = \bar{M}_{\text{b}}[\text{Na}]_{\text{f}}^2/([\text{M}]_{\text{f}}[\text{Na}]_{\text{b}}^2)$ with $\text{M} = \text{Mg}^{2+}$ and Ca^{2+} , respectively, on a polystyrenesulfonate ion-exchange resin.³⁷ This suggests that the ion-exchange model is reasonable as an approximation for estimating the binding of the complex ion to the micelle. The value of $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\text{Na}]_{\text{b}}$ decreased remarkably with the increase in the NaCl concentration of the solution (Table I). A similar tendency to that observed here was also observed previously in the alkaline hydrolysis of *p*-nitrophenyl octanoate.³²

Figure 1 shows that the decrease in the rate with increasing SDS concentration is less remarkable for a solution of higher NaCl concentration. Such an effect of added electrolyte on the micellar catalysis or inhibition has been observed for many bimolecular reactions.³⁸ As is generally accepted,³⁸ the reduction of the micellar inhibition arises from displacement of the cationic $\text{CoCl}(\text{NH}_3)_5^{2+}$ from the Stern layer of the anionic micelle by the added electrolyte.

In order to investigate the effect of the added salt quantitatively, we considered the distribution ratio (D) of $\text{CoCl}(\text{NH}_3)_5^{2+}$ between the aqueous and micellar phases, using eq 8 and 9 to give

$$D = [\text{M}]_{\text{b}}/[\text{M}]_{\text{f}} = \bar{M}_{\text{b}}C\bar{V}/[\text{M}]_{\text{f}} = K_{\text{M}/\text{Na}}C\bar{V}[\text{Na}]_{\text{b}}^2/[\text{Na}]_{\text{f}}^2 \quad (14)$$

The D values for 0.008 and 0.040 mol dm^{-3} SDS solutions containing different concentrations of NaCl were calculated by substituting $K_{\text{M}/\text{Na}} = 1.9$, $\bar{V} = 0.14 \text{ mol}^{-1} \text{ dm}^3$, $[\text{Na}]_{\text{b}} = 5.6 \text{ mol dm}^{-3}$, and appropriate values of C and $[\text{Na}]_{\text{f}}$ (eq 13) into eq 14. The resulting distribution ratios, D (Table II), clearly indicate that the decrease in the micellar inhibition with increasing concentration of added NaCl (Figure 1) is caused by the remarkable decrease in the distribution ratio of the complex ion or by the remarkable decrease in the number of the complex ions associated with the micelles in the solutions. Thus, the effect of added NaCl on the micellar inhibition can be explained by the ion exchange between the complex ion and the sodium ion at the interface of the SDS micelle.

B. The $\text{Fe}(\text{phen})_3^{2+}$ -SDS System. The rate constants of the aquation and base hydrolysis of the complex in SDS solutions are shown in Figure 3 as a function of the SDS concentration. The cmc values of the SDS solutions are indicated by arrows in the figure.³¹ The rate constant of the aquation slightly increased and that of the base hydrolysis remarkably decreased with the increase in SDS concentration below the cmc. This is in marked contrast to the kinetic behavior of $\text{CoCl}(\text{NH}_3)_5^{2+}$ for which the rate constants changed above the cmc (Figure 1). The difference in the rate behavior between the two complex species most probably

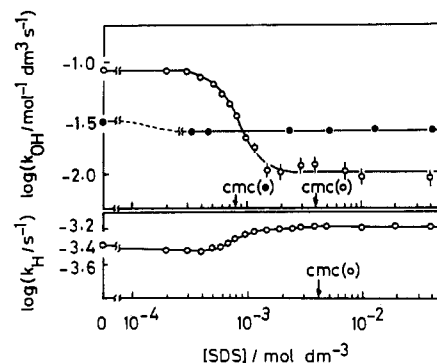


Figure 3. Rate constants for the aquation and the base hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ in SDS solutions. $[\text{NaCl}] = 0.02 \text{ mol dm}^{-3}$ for the aquation (the lower part of the figure), and $[\text{NaOH}] = 0.02 \text{ mol dm}^{-3}$ and $[\text{NaCl}] = 0$ (○) and 0.4 (●) mol dm^{-3} for the base hydrolysis (the upper part). The arrows indicate the cmc values of the SDS solutions.

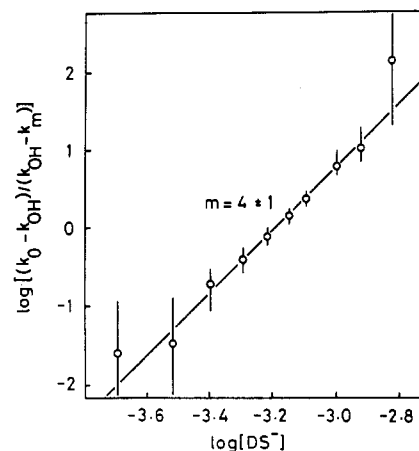
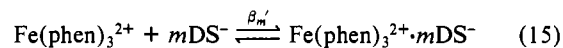


Figure 4. Plot of $\log [(k_0 - k_{\text{OH}})/(k_{\text{OH}} - k_m)]$ vs. $\log [\text{DS}^-]$ for the base hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ ($[\text{NaOH}] = 0.02 \text{ mol dm}^{-3}$). The slope and the intercept of the solid line are 4 ± 1 and 12.8 ± 3.2 , respectively.

resulted from the difference in hydrophobic interaction with dodecyl sulfate ions.

a. Base Hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ below the cmc. The decrease in the rate constant with increasing SDS concentration below the cmc (Figure 3) shows the presence of an interaction between the complex ion and monomeric dodecyl sulfate ions (DS^-), such as the formation of a pre-micellar hydrophobic aggregate^{22,23,25} as follows:



where β_m' is the concentration equilibrium constant of reaction 15. Suppose that the complex ions associated with zero and m dodecylsulfate ions undergo base hydrolysis with the second-order rate constants of k_0 and k_m , respectively. Then the observed second-order rate constant, k_{OH} , can be expressed by

$$k_{\text{OH}} = \frac{k_0 + k_m \beta_m' [\text{DS}^-]^m}{1 + \beta_m' [\text{DS}^-]^m} \quad (16)$$

Transformation of this equation leads to³⁹

$$\log \left(\frac{k_0 - k_{\text{OH}}}{k_{\text{OH}} - k_m} \right) = \log \beta_m' + m \log [\text{DS}^-] \quad (17)$$

The left-hand side of this equation was calculated by substituting the observed rate constants; k_m was assumed to be equal to 0.01

(36) Bunton, C. A.; Cerichelli, G.; Ihara, Y.; Sepulveda, L. *J. Am. Chem. Soc.* **1979**, *101*, 2429-35.

(37) The values were calculated from the selectivity coefficients reported: Kakihana, H. *J. Chem. Soc. Jpn.* **1951**, *72*, 255-8. Honda, M. *Ibid.* **1951**, *72*, 361-4.

(38) Bunton, C. A. In *Reaction Kinetics in Micelles*; Cordes, E. H., Ed.; Plenum: New York, 1973; pp 73-98.

(39) Piszkiwicz analyzed a large number of micelle-catalyzed reactions in terms of a model which is mathematically similar to that proposed here.²⁶ However, he treated rate data without differentiating whether the surfactant concentration is below or above the cmc.

$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$, the rate constant at the high SDS concentrations. Plots of the left-hand side of the equation against $\log [\text{DS}^-]$ gave a straight line with a slope of $m = 4 \pm 1$ and an intercept of $\log \beta_m' = 12.8 \pm 3.2$ (Figure 4). These values are consistent with the previous results of $m = 3-4$ and $\beta_m' = 9.6-12.8$ obtained from the racemization experiments of $\text{Fe}(\text{phen})_3^{2+}$ in SDS solutions.⁴⁰ The m and $\log \beta_m'$ values were substituted into eq 16 to obtain the solid curve in Figure 3. The good fit of the calculated curve to the observed rate constants suggests that the proposed mechanism is at least qualitatively correct, although the formation of the aggregate (eq 15) occurs stepwise. There may exist aggregates other than that considered here, but they will not appreciably differ in the aggregation number from that considered here or, if they do appreciably differ, they will not be present in appreciable concentrations. The small value of k_m as compared with the k_0 value may be related to the electrostatic and hydrophobic masking effects of dodecyl sulfate anions against hydroxide anions.

Analysis was carried out only for the system containing no NaCl. The decrease in the rate constant caused by the addition of NaCl to the solution (Figure 3) can be related to the primary salt effect⁴¹ and to ion-pair formation of the complex ion with chloride ion.³⁰

b. Aquation of $\text{Fe}(\text{phen})_3^{2+}$ below the Cmc. The rate constant changed with increasing SDS concentration in three steps in SDS solutions below the cmc (Figure 3): the decrease at low SDS concentrations, the steep increase at intermediate concentrations, and the less steep linear increase at high SDS concentrations. These changes in the rate constant below the cmc suggest the formation of at least three kinds of hydrophobic aggregates of the complex ion with dodecyl sulfate ions not forming micelles. A comparison of the changes in the aquation rate constant with those in the rate of the base hydrolysis of the same complex shows that the changes in the rate constant at intermediate concentrations of SDS were brought about by the formation of a 1:4 aggregate of the complex ion and dodecyl sulfate ions. The changes in the rate constant at lower and higher SDS concentrations, respectively, can be related to the formation of a 1:1 aggregate and aggregates containing more than four dodecyl sulfate ions per complex ion, by analogy with the systems of the same complex ion and alkane-sulfonate ions.²³

c. Aquation of $\text{Fe}(\text{phen})_3^{2+}$ above the Cmc. The rate constant showed no appreciable changes above the cmc, indicating that all the complex ion was in the micellar phase.⁴⁰ Since the complex ions interact with dodecyl sulfate ions even below the cmc, the complex ions adsorbed at the micelle-water interface or existing in the Stern layer may modify the structure of the interface so that the complex ion can make contact with the hydrophobic moiety of the dodecyl sulfate ion in the micelle, or the complex ions in the Stern layer may further enter the micellar phase. On the basis of the micellar model proposed by Menger,⁴² the complex ions were considered to be at the "Stern region" of the micelle. The experimental results plotted in Figure 3 shows that the rate constant for the aquation of the complex is only slightly larger than that in pure water. This is consistent with the fact that the aquation of the complex in aqueous solution is only slightly accelerated by the addition of methanol or ethanol,^{43,44} which may be similar in hydrophobicity to the Stern region of the micelle.

d. Base Hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ above the Cmc. The ion-exchange model applied for $\text{CoCl}(\text{NH}_3)_5^{2+}$ -SDS system should

Table III. Experimental Values of k_{OH}^{W} and $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ for the Base Hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ and the Ratios of the Second-Order Rate Constants, $k_{\text{OH}}^{\text{W}}(\text{Fe})/k_{\text{OH}}^{\text{W}}(\text{Co})$ and $k_{\text{OH}}^{\text{M}}(\text{Fe})/k_{\text{OH}}^{\text{M}}(\text{Co})$, in the Aqueous and Micellar Phases

[NaCl]/ mol dm ⁻³	k_{OH}^{W} / mol ⁻¹ dm ³ s ⁻¹	$k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ / mol ⁻² dm ⁶ s ⁻¹	$k_{\text{OH}}^{\text{W}}(\text{Fe})/$ $k_{\text{OH}}^{\text{W}}(\text{Co})$	$k_{\text{OH}}^{\text{M}}(\text{Fe})/$ $k_{\text{OH}}^{\text{M}}(\text{Co})$
0	0.083	0.31-0.40 ^a	0.024	0.37-0.48
0.4	0.031	0.052-0.053 ^a	0.027	0.65-0.66

^a The values were obtained by dividing the rate constants at high SDS concentrations (0.0100 and 0.0224 mol⁻¹ dm³ s⁻¹ for solutions without NaCl and with 0.4 mol dm⁻³ NaCl) by $[\text{Na}]_{\text{f}}$ values in 0.008-0.040 mol dm⁻³ SDS solutions.

also hold for the iron(II) complex, since ions in the Stern region are considered to be in ion-exchange equilibrium with those in bulk water.

If effectively all the complex ions are bound to the micelle, eq 5 and 7 lead to

$$k_{\text{OH}} \approx k_{\text{OH}}^{\text{M}}[\overline{\text{OH}}]_{\text{b}}/[\text{OH}]_{\text{T}} \approx k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}[\text{Na}]_{\text{f}}/[\overline{\text{Na}}]_{\text{b}} \quad (18)$$

This equation predicts that, under the specified conditions, the observed second-order rate constant, k_{OH} , will depend on $[\text{Na}]_{\text{f}}/[\overline{\text{Na}}]_{\text{b}}$. The observed rate constant remains almost unchanged with the increase in SDS concentration above the cmc (Figure 3). This resulted from slight changes in $[\text{Na}]_{\text{f}}$: from 0.42 ([SDS] = 0.001) to 0.43 ([SDS] = 0.040) in the micellar solutions with $[\text{NaCl}] = 0.4$ and $[\text{NaOH}] = 0.02$ and from 0.024 ([SDS] = 0.004) to 0.032 ([SDS] = 0.040) when $[\text{NaCl}] = 0$ and $[\text{NaOH}] = 0.02$ (concentrations in mol dm⁻³).

Assuming that the rate constant above the cmc (0.0100 and 0.0224 mol⁻¹ dm³ s⁻¹ for SDS solutions with 0 and 0.4 mol dm⁻³ NaCl, respectively) is equal to $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}[\text{Na}]_{\text{f}}/[\overline{\text{Na}}]_{\text{b}}$ (eq 18) and that the $[\text{Na}]_{\text{f}}$ value is given by eq 13, the $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ value was obtained for each SDS solution (Table III). The added NaCl decreased the $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ value; this is the same trend as that observed for the Co(II) system (Table I). Assuming that the value of $K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ in the Fe(II) system is the same as that in the Co(III) system, we have the ratio of the rate constant for the iron complex to that for the cobalt complex, $k_{\text{OH}}^{\text{M}}(\text{Fe})/k_{\text{OH}}^{\text{M}}(\text{Co})$, by dividing the value of $k_{\text{OH}}^{\text{M}}K_{\text{NaOH}}/[\overline{\text{Na}}]_{\text{b}}$ for $\text{Fe}(\text{phen})_3^{2+}$ by the corresponding value for $\text{CoCl}(\text{NH}_3)_5^{2+}$. The ratios obtained are listed in Table III along with similar ratios of the rate constants in the aqueous phase. The value of $k_{\text{OH}}^{\text{M}}(\text{Fe})/k_{\text{OH}}^{\text{M}}(\text{Co})$ is much larger than that of $k_{\text{OH}}^{\text{W}}(\text{Fe})/k_{\text{OH}}^{\text{W}}(\text{Co})$. This suggests that $k_{\text{OH}}^{\text{M}}(\text{Fe})$ is much larger than $k_{\text{OH}}^{\text{W}}(\text{Fe})$, since the value of $k_{\text{OH}}^{\text{M}}(\text{Co})$ is considered to be similar to that of $k_{\text{OH}}^{\text{W}}(\text{Co})$ because the cobalt complex in the micellar phase is located at the micellar surface. A second-order rate constant for a substrate at the micellar surface is well known to be similar to that in the aqueous phase.⁴⁵ The greater value of $k_{\text{OH}}^{\text{M}}(\text{Fe})$ than that of $k_{\text{OH}}^{\text{W}}(\text{Fe})$ indicates that the complex ion is located inside the micelle-water interface, or in the Stern region.

Acknowledgment. Thanks are due to the Ministry of Education, Science and Culture of Japan for financial support (Grant No. 5774032) to S.T. We are also indebted to M. Oomata for her assistance in a part of the experimental work.

Registry No. SDS, 151-21-3; $\text{Fe}(\text{phen})_3^{2+}$, 14708-99-7; $\text{CoCl}(\text{NH}_3)_5^{2+}$, 14482-76-9; NaCl, 7647-14-5.

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