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Kinetics of the Racemization and Dissociation of Tris(1,10-phenanthroline)iron(II). The Aggregate Formation of the Complex Cation with 1-Alkanesulfonate Anions through Hydrophobic Interaction

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The kinetics of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ were investigated in the presence of a series of 1-alkanesulfonate ions (n-$C_nH_{2n+1}SO_3^-$, $n=2, 4, 6, \dots, 14$). The racemization rate increased, while the dissociation rate decreased, gradually as a function of the alkanesulfonate concentration at low concentrations of each alkanesulfonate. With alkanesulfonates of $n \geqq 8$, the second phase of rate changes, *i.e.*, steep increases in both rates, were observed at higher concentrations. The gradual initial changes in the rates were explained in terms of the formation of the 1:1 aggregate of the complex cation with the alkanesulfonate ion caused by hydrophobic interaction. The formation constant ($mol^{-1}\,dm^3$) increased almost exponentially from 4 ($n=4$) to 770 ($n=14$) with the increase in the alkyl-chain length, the energy of the hydrophobic interaction of the complex cation and the alkanesulfonate anion being 0.9 kJ mol^{-1} per methylene group of the latter. The second phase of the rate changes were explained in terms of the formation of the 1:m aggregate of the complex cation with the alkanesulfonate ions. The rate behavior of the hydrophobic aggregates is discussed in connection with the reaction mechanisms of the racemization and dissociation of $[Fe(phen)_3]^{2+}$.

A study of hydrophobic interaction is very important not only for understanding the nature of the interaction determining the tertiary and quarternary structures of proteins in biological systems,[1] but also for discerning the nature of the solute–solute interaction in an aqueous solution containing a hydrophobic metal complex.[2–4] However, few investigations have so far been done to clarify the nature of the interaction of a complex with a monomeric surfactant,[5] although much attention has been paid recently to the interaction of metal complexes with micelles.[6–11]

The $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline) ion is known to racemize by means of an intramolecular twist mechanism.[12] The nature of the twist mechanism, however, does not seem to be fully understood.[12] We previously studied the effects of inorganic anions,[13,14] inorganic cations,[15] and organic cations[15] on the rates of the racemization and dissociation of $[Fe(phen)_3]^{2+}$. The changes in the rates in the presence of inorganic anions were reasonably explained in terms of the ion-pair formation of the complex ion with the anions.[13,14] On the other hand, the effects of organic cations such as alkylammonium ions on the racemization and dissociation rates were explained by a consideration of the formation of the 1:1 aggregate of the complex and the alkylammonium cations caused by hydrophobic interaction between them.[15]

The present study is concerned with the effects of 1-alkanesulfonate ions (n-$C_nH_{2n+1}SO_3^-$, $n=2, 4, 6, \cdots, 14$) on the rates of the racemization and dissociation of $[Fe(phen)_3]^{2+}$. As the hydrophobicity of alkanesulfonate anions varies with the alkyl-chain length, different effects can be expected for alkanesulfonates with different chain lengths. A comparison of the effect of each alkanesulfonate with that of the alkylammonium cation of the same alkyl-chain length will show the roles of the charge and the hydrophobic group in the interaction between the complex and organic ions, and their effects on the racemization and dissociation rates. The results will also give a basis for understanding the nature of the interaction of a metal-complex cation with ionic surfactants.

Experimental

The sodium 1-alkanesulfonates used were guaranteed-grade reagents of the Tokyo Kasei Kogyo Co., Ltd. They were recrystallized three times from an ethanol–methanol (5:1) solution and dried at 70 °C *in vacuo* for 5 h. The concentrations of the solutions of these salts were determined by weighing well-dried reagents. The surface tension of the solutions of these surfactants showed no minimum around the cmc (critical micelle concentration).[16] Kinetic data were obtained at 25 °C in solutions containing the perchlorate of the complex ($5 \times 10^{-5}\,mol\,dm^{-3}$) and a sodium alkanesulfonate. Racemization was followed by polarimetry, and dissociation, by spectrophotometry. For measuring the dissociation rates, $NiCl_2$ ($5 \times 10^{-4}\,mol\,dm^{-3}$) was added to the sample solution as a scavenger of the liberated phenanthroline. For the systems containing dodecane- and tetradecanesulfonates, the measurements were carried out at a low $NiCl_2$ concentration of $1 \times 10^{-4}\,mol\,dm^{-3}$ to minimize the precipitation of nickel(II) sulfonate. The first-order rate constants for racemization and dissociation were obtained, respectively, from the $\ln [\alpha_0/\alpha_t]$ *vs.* t and $\ln[(D_0-D_t)/(D_0-D_\infty)]$ *vs.* t plots, where α and D, with the subscripts showing the time, represent the optical rotation (546 nm) and the absorbance (510 nm) of the sample solution respectively. A Union SM401 spectrometer was used for the observation of the absorption spectra. The other chemicals and procedures were the same as those described in our previous paper.[13]

Results

Profile of the Rate Changes with the Alkanesulfonate Concentrations. The kinetic results for the racemization and dissociation of $[Fe(phen)_3]^{2+}$ in the presence of various sodium alkanesulfonates (n-$C_nH_{2n+1}SO_3Na$, $n=2, 4, \cdots, 14$) are depicted in Figs. 1 ($n \leqq 6$), and 2 ($n \geqq 8$, with the abscissa on a logalithmic scale); a linear scale plot for a part of the latter is drawn in Fig. 3 for ease of comparison with Fig. 1. In solutions of the alkanesulfonates of $n=2$ and 4 (Fig. 1), the racemization rates increased, and the dissociation rates decreased,

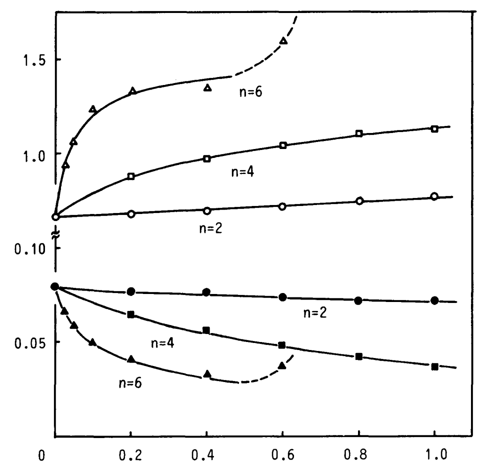

Fig. 1. The racemization (open marks) and dissociation (closed marks) rate constants of $[Fe(phen)_3]^{2+}$ in alkanesulfonate ($n \leqq 6$) solutions at 25.0 °C.
○, ●: $C_2H_5SO_3Na$; □, ■: n-$C_4H_9SO_3Na$; △, ▲: n-$C_6H_{13}SO_3Na$.
The solid lines in the figure are those calculated by substituting the parameter values (Table 1) into Eq. 5.

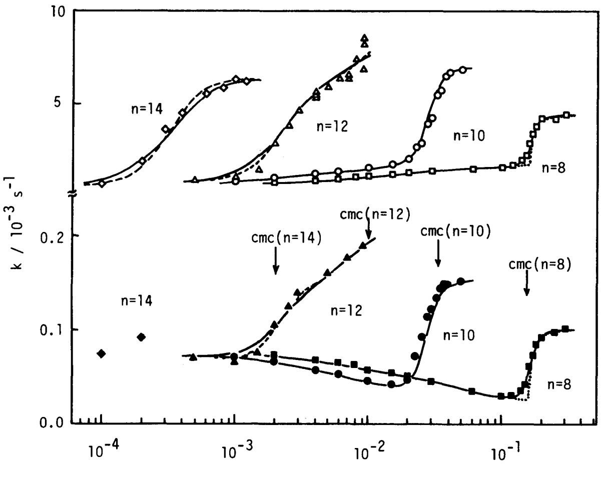

Fig. 2. The racemization (open marks) and dissociation (closed marks) rate constants of $[Fe(phen)_3]^{2+}$ in alkanesulfonate ($n \geqq 8$) solutions at 25.0 °C.
○, ●: n-$C_8H_{17}SO_3Na$; □, ■: n-$C_{10}H_{21}SO_3Na$; △, ▲: n-$C_{12}H_{25}SO_3Na$; ◇, ◆: n-$C_{14}H_{29}SO_3Na$.
The solid and dotted lines in the figure are those calculated on the basis of Eqs. 10 and 15, respectyvely. For systems containing dodecane- or tetradecanesulfonate, the solid lines are those calculated by assuming the presence of 1:3 aggregates, and the broken lines, 1:4 aggregates. The parameter values given in Table 2 were used in these calculations.

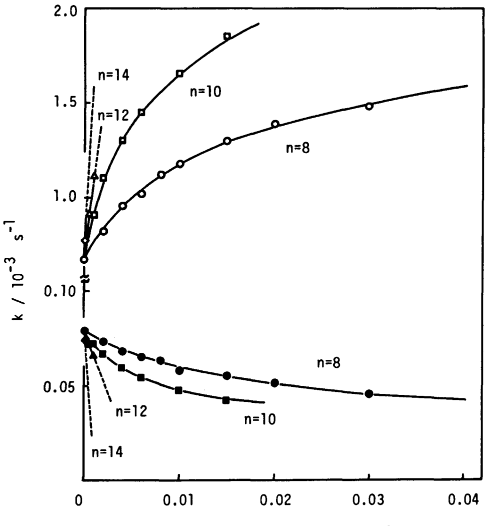

Fig. 3. The racemization (open marks) and dissociation (closed marks) rate constants of $[Fe(phen)_3]^{2+}$ in alkanesulfonate ($n \geqq 8$) solutions of low concentrations at 25.0 °C.
○, ●: n-$C_8H_{17}SO_3Na$; □, ■: n-$C_{10}H_{21}SO_3Na$; △, ▲: n-$C_{12}H_{25}SO_3Na$, ◇, ◆: n-$C_{14}H_{29}SO_3Na$.

monotonously with the increase in the alkanesulfonate concentration. Similar changes in the rates were also observed for sulfonates of $n=6$, 8, 10, 12, and 14 at concentrations lower than 0.5, 0.10, 0.015, 0.001, and 0.0001 mol dm^{-3} respectively (see Figs. 1 and 3). The changes in both the racemization and dissociation rates with the alkanesulfonate concentration were larger for the sulfonate with a longer alkyl chain. At higher concentrations of the sulfonates than those mentioned above (Fig. 2), the racemization rate increased steeply with the increase in the alkanesulfonate concentration to a rate several times as large as that in water, and then it reached a plateau. The dissociation rates also increased to a rate larger than that in pure water.

Kinetics in Alkanesulfonate Solutions of the Lower Concentrations (Figs. 1 and 3): The changes in rates with the alkanesulfonate concentrations in this region are similar to those observed for $[Fe(phen)_3]^{2+}$–alkyltrimethylammonium systems. Thus, the rate changes can be thought to arise from the formation of the 1:1 aggregate[15] (or ion pair[13]) of complex ion and an alkanesulfonate ion. The following mechanism was considered:

$$[Fe(phen)_3]^{2+} + RSO_3^- \overset{K_1}{\rightleftharpoons} [Fe(phen)_3]^{2+}\cdot RSO_3^-, \tag{1}$$

$$\Delta\text{-}[Fe(phen)_3]^{2+} \xrightarrow{k_{0r}} rac\text{-}[Fe(phen)_3]^{2+}, \tag{2r}$$

$$[Fe(phen)_3]^{2+} \xrightarrow{k_{0d}} [Fe(phen)_2]^{2+} + phen \xrightarrow{fast} Fe^{2+} + 3\,phen, \tag{2d}$$

$$\Delta\text{-}[Fe(phen)_3]^{2+}\cdot RSO_3^- \xrightarrow{k_{1r}} rac\text{-}[Fe(phen)_3]^{2+}\cdot RSO_3^-, \tag{3r}$$

$$[Fe(phen)_3]^{2+}\cdot RSO_3^- \xrightarrow{k_{1d}} [Fe(phen)_2]^{2+}\cdot RSO_3^- + phen \xrightarrow{fast} Fe^{2+} + 3\,phen + RSO_3^-, \tag{3d}$$

$$K_1 = \frac{[Fe(phen)_3^{2+}\cdot RSO_3^-]}{[Fe(phen)_3^{2+}][RSO_3^-]}\,\frac{f_1}{f_2 f_1}, \tag{4}$$

where k_0 and k_1 are the rate constants of the complex cations not associated with and associated with the alkanesulfonate ion respectively, and where f_z represents the activity coefficient of an ion with a charge of

TABLE 1. THE FORMATION CONSTANTS OF THE 1 : 1 AGGREGATES BETWEEN $[Fe(phen)_3]^{2+}$ AND ALKANESULFONATES AND THE RATE CONSTANTS OF THE COMPLEX IN THE 1 : 1 AGGREGATES

Alkanesulfonate	Racemization		Dissociation	
	$k_{1r}/10^{-3}\ s^{-1}$	K_1/mol dm^{-3}	$k_{1d}/10^{-3}\ s^{-1}$	K_1/mol dm^{-3}
None	$(0.67\pm0.03)^{a)}$	—	$(0.0795\pm0.0016)^{b)}$	—
n-$C_4H_9SO_3^-$	1.24±0.06	5.5±2.0	0.0180±0.0040	3.2±0.5
n-$C_6H_{13}SO_3^-$	1.51±0.13	33±14	0.0172±0.0050	18±3
n-$C_8H_{17}SO_3^-$	2.03±0.20	85±20	0.0160±0.0030	64±8
n-$C_{10}H_{21}SO_3^-$	2.30±0.15	208±40	0.0180±0.0040	156±27
n-$C_{12}H_{25}SO_3^-$	2.5±0.6	$(320\pm40)^{c)}$	$(0.017)^{d)}$	320±40
n-$C_{14}H_{29}SO_3^-$	2.0±0.7	$(770\pm120)^{c)}$	$(0.017)^{d)}$	770±120

a) k_{0r}. b) k_{0d}. c) The values obtained from dissociation experiments. d) The value estimated from those obtained for systems containing alkanesulfonate of shorter alkyl-chain lengths.

±z and can be calculated with the Debye-Hückel equation.[14] The rate constants for racemization and dissociation are expressed as:

$$k^{obsd} = \frac{k_0 + k_1K_1f_2[RSO_3^-]}{1 + K_1f_2[RSO_3^-]}. \tag{5}$$

Additional subscripts, r and d, may be attached to the symbols for rate constants to distinguish between racemization and dissociation. The kinetic data for $n=4$—10 (Figs. 1 and 3) were analyzed in terms of the least-squares fit to Eq. 5. The K_1 and k_1 values thus obtained are listed in Table 1.

In the cases of $n=12$ and 14 (Fig. 3), where the alkanesulfonate concentrations are very low ($[RSO_3^-] \ll 1/K_1$), Eq. 5 can be reduced to:

$$k^{obsd} = k_0 + (k_1 - k_0)K_1[RSO_3^-]. \tag{6}$$

The k_{1d} value of $0.017\times10^{-3}\ s^{-1}$ was assumed for $n=$ 12 and 14 by extrapolation from the k_{1d} values for $n\leqq$ 10, which are shown to be independent of the alkyl-chain length of the alkanesulfonate ion (Table 1). The k_{1r} values were obtained from Eq. 6 with the K_1 values obtained from dissociation experiments. The solid lines in Figs. 1 and 3 are those calculated with the parameter values listed in Table 1.

Kinetics in Solutions of Higher Alkanesulfonate Concentrations: The rate behavior of the complex ion at the sulfonate concentrations higher than 0.10, 0.015, 0.001, and 0.0001 mol dm^{-3} for n=8, 10, 12, and 14 respectively may be related to the formation of higher aggregates than 1:1 or to the interaction with micelles.

In order to ascertain whether or not the micelles are concerned with the observed changes in rates, the cmc values of the alkanesulfonates were determined in the presence of 5×10^{-5} mol dm^{-3} $[Fe(phen)_3]^{2+}$ by means of the surface-tension and light-scattering methods.[16] The surface tension of the solutions containing sodium alkanesulfonates decreased remarkably in the presence of 5×10^{-5} mol dm^{-3} $[Fe(phen)_3]^{2+}$, and the break-point of the surface tension *vs.* concentration curve appeared at a lower concentration. This appears to be consistent with a previous finding that the cmc value of sodium dodecyl sulfate (SDS) decreased remarkably in the presence of 1×10^{-4} mol dm^{-3} $[Co(phen)_3]^{3+}$.[17] However, light-scattering measurements, which can detect the micelle formation more directly, showed that the cmc values[18] remained almost unchanged in the presence of the complex ions, and that the pre-aggregation of the complex cation with the alkanesulfonate ions took place at a concentration below the cmc. The contradictory results of the surface-tension and light-scattering experiments may have arisen from the fact that the surface-tension measurements are an indirect method of determining the cmc value, or that they cannot distinguish between the formation of micelles and that of premicellar aggregates such as a 1:m aggregate.

Since a steep rise in the rate was observed before the alkanesulfonate concentration reached the cmc value for the $[Fe(phen)_3]^{2+}$-containing system, the observed rate changes cannot be attributed to the interaction of the complex ion with the alkanesulfonate micelle.

Let us now consider the formation of 1:m ($m\geqq2$) aggregates. The following equations must be added to Eqs. 1-4:

$$[Fe(phen)_3]^{2+} + m\,RSO_3^- \overset{\beta'_m}{\rightleftharpoons} [Fe(phen)_3]^{2+}\cdot m\,RSO_3^-, \tag{7}$$

$$\Delta\text{-}[Fe(phen)_3]^{2+}\cdot m\,RSO_3^- \xrightarrow{k_{mr}} rac\text{-}[Fe(phen)_3]^{2+}\cdot m\,RSO_3^-, \tag{8r}$$

$$[Fe(phen)_3]^{2+}\cdot m\,RSO_3^- \xrightarrow{k_{md}} [Fe(phen)_2]^{2+}\cdot m\,RSO_3^- + \text{phen} \xrightarrow{\text{fast}} Fe^{2+} + 3\,\text{phen} + m\,RSO_3^-, \tag{8d}$$

$$\beta'_m = \frac{[Fe(phen)_3{}^{2+}\cdot m\,RSO_3^-]}{[Fe(phen)_3{}^{2+}][RSO_3^-]^m}. \tag{9}$$

Then, the observed reaction rate constant can be expressed as:

$$k^{obsd} = \frac{k_0 + k_1\beta'_1[RSO_3^-] + \sum_{m=2}^{\infty} k_m\beta'_m[RSO_3^-]^m}{1 + \beta'_1[RSO_3^-] + \sum_{m=2}^{\infty}\beta'_m[RSO_3^-]^m}, \tag{10}$$

where k_m represents the rate constant of the complex cation associated with m alkanesulfonate anions, and where $\beta'_1(=K_1f_2)$ and β'_m are the concentration formation constants of the 1:1 and 1:m aggregates. Because of the difficulty in estimating the activity coefficients of higher aggregates, the concentration equilibrium constants were used in the analysis. Although the ionic strength of the medium was not maintained constant, it can be expected that an analysis in such a way will at least qualitatively give a proper interpretation

TABLE 2. THE m AND $\log\beta'_m$ VALUES OBTAINED FROM THE ANALYSIS OF THE KINETIC RESULTS IN SOLUTIONS OF HIGH ALKANESULFONATE CONCENTRATIONS, AND OTHER PARAMETER VALUES ASSUMED FOR THE ANALYSIS[a)]

Alkanesulfonate	m	$\log\beta_m'$	β_1'[b)]	$k_{md}/10^{-3}\ s^{-1}$	$k_{mr}/10^{-3}\ s^{-1}$
n-$C_8H_{17}SO_3^-$	14±2	11.8±1.6	34	0.100	4.4
n-$C_{10}H_{21}SO_3^-$	8±1	13.1±1.2	107	0.153	7.0
n-$C_{12}H_{25}SO_3^-$[c)]	3	8.0±0.3	260	0.180±0.010	7.0±1.5
	8	18.0±1.6		0.220±0.020	9.5±2.4
	4	10.8±0.1	260	0.160±0.010	6.3±0.5
	8	19.0±1.3		0.220±0.020	9.5±1.5
n-$C_{14}H_{29}SO_3^-$[d)]	3	10.8±0.3	710	—	6.3
	4	14.4±0.4	710	—	6.3

a) Each of the figures under m and $\log\beta'_m$ is the average of the values obtained from the racemization and dissociation experiments. b) $\beta'_1 = K_1 f_2$. c) The m values for this system are assumed by analogy with the values for the systems containing decane- and tetradecanesulfonates. d) The value of m which best fits the experimental data is 3.4. Thus, the experimental results were analyzed by assuming an integer m value of 3 or 4.

of the experimental results for two reasons. Firstly, the high charge of the higher aggregate will be reduced by ion association with sodium ions, and therefore the activity coefficient of the higher aggregate will not so greatly depend on the ionic strength of the medium. Secondly, the rate changes at the higher alkanesulfonate concentrations are observed in a narrow range of the sulfonate concentration; accordingly, the activity coefficients of the ions involved in the reaction can be regarded as almost constant in the region where the most remarkable change in rate was observed.

In addition to the free complex ion and the 1:1 aggregate, one higher aggregate species (1:m) was considered for the systems containing octane-, decane-, and tetradecanesulfonate. Under these conditions, the transformation of Eq. 10 leads to:

$$\log\left\{\frac{(k^{\text{obsd}}-k_0)+(k^{\text{obsd}}-k_1)\beta_1'[\text{RSO}_3^-]}{(k_m-k^{\text{obsd}})}\right\} = \log\beta_m' + m\log[\text{RSO}_3^-]. \qquad (11)$$

The values of m and β'_m were obtained by analyzing the kinetic data in the following way. The values of k_0, k_1, and β'_1 have been obtained above from the analysis of the rates at lower sulfonate concentrations. The rate constant of the 1:m aggregate, k_m, was regarded as equal to the rate constant at the plateau (Fig. 2, Table 2). By assuming that $[RSO_3^-]$ equals the total alkanesulfonate concentration, the plot of the left-side term of Eq. 11 *vs.* $\log[RSO_3^-]$ gave approximate values of m and $\log\beta'_m$. Then, these values of m and $\log\beta'_m$ were used to calculate the $[RSO_3^-]$ value, with which the plot as described above was repeated to give better values of m and $\log\beta'_m$. This procedure was repeated until reproducible values of m, β'_m, and $[RSO_3^-]$ were obtained. The values of m and β'_m thus obtained for the systems containing octane-, decane-, and tetradecanesulfonate are listed in Table 2, along with the value of k_m assumed for the analysis. The m and β'_m values given for the octanesulfonate system are the lower limits, since the decrease in $[RSO_3^-]$ upon micelle formation was disregarded. The solid lines in Fig. 2 show the k_r and k_d values calculated with the parameter values listed in Tables 1 and 2. In the case of tetradecanesulfonate-containing systems, the solid and broken curves correspond to the formation of the 1:3 and 1:4 aggregates respectively. The good agreement between the observed and the calculated rate constants suggests that the approximations adopted in the analysis of the experimental results are reasonably good in these cases. Aggregates other than those considered above may be present in each system, but they will not appreciably differ in the aggregation number from those considered or, if they do appreciably differ, they will not be present in appreciable concentrations. Thus, no further analysis has been carried out.

The dodecanesulfonate-containing system shows a feature different from the octanesulfonate-, decanesulfonate-, and tetradecanesulfonate-containing systems; at least two steps of changes are observed in the rate increase occurring in the region of 10^{-3}—10^{-2} mol dm^{-3} (Fig. 2). In this case, analysis was carried out by assuming the presence of the 1:3 and 1:8 aggregates or the 1:4 and 1:8 aggregates. These particular aggregates were chosen by analogy with the systems containing decane- and tetradecanesulfonate. The least-squares fit of the kinetic data to Eq. 10 with $m=3$ and 8 or $m=4$ and 8 led to the parameter values listed in Table 2. These parameter values were used to calculate the rate constants at each dodecanesulfonate concentration. The solid and broken lines in Fig. 2 were obtained by assuming the formation of the 1:3 and 1:8 aggregates and of the 1:4 and 1:8 aggregates respectively. Better fits of the calculated lines to the observed rate constants were obtained when the 1:4 aggregate was assumed to exist, although the 1:3 aggregate seems more natural from the shape of the complex.

Kinetics in Micellar Solutions: As has been described above for system containing octanesulfonate, the change in rate observed above the cmc was accounted for by considering the interaction of the complex ion with monomeric sulfonate ions. If we consider the aggregate of the complex ion with the micelle in place of the 1:m aggregate, the following reactions are substituted for Eqs. 7—10:

$$[\text{Fe(phen)}_3]^{2+} + \text{micelle} \xrightleftharpoons{K_M} [\text{Fe(phen)}_3]^{2+}\cdot\text{micelle}, \qquad (12)$$

$$\Delta\text{-}[\text{Fe(phen)}_3]^{2+}\cdot\text{micelle} \xrightarrow{k_{rM}} rac\text{-}[\text{Fe(phen)}_3]^{2+}\cdot\text{micelle}, \qquad (13r)$$

$$[\mathrm{Fe(phen)_3}]^{2+}\cdot\text{micelle} \xrightarrow{k_{\mathrm{dM}}} [\mathrm{Fe(phen)_2}]^{2+}\cdot\text{micelle} + \text{phen} \xrightarrow{\text{fast}} \mathrm{Fe}^{2+} + 3\,\text{phen} + \text{micelle}, \qquad (13d)$$

$$K_{\mathrm{M}} = \frac{[\mathrm{Fe(phen)_3}^{2+}\cdot\text{micelle}]}{[\mathrm{Fe(phen)_3}^{2+}][\text{micelle}]}. \qquad (14)$$

Then, the observed rate constant is expressed as:

$$k = \frac{k_0 + k_1\beta'_1[\mathrm{RSO_3}^-] + k_{\mathrm{M}}K_{\mathrm{M}}[\text{micelle}]}{1 + \beta'_1[\mathrm{RSO_3}^-] + K_{\mathrm{M}}[\text{micelle}]}. \qquad (15)$$

When the total concentration of the surfactant (C_S) is much larger than that of the complex, [micelle] can be expressed as:

$$[\text{micelle}] = \frac{C_{\mathrm{S}} - cmc}{N}, \qquad (16)$$

where N is the aggregation number of the micelle. An analysis of the kinetic data for the systems of octanesulfonate leads to $K_{\mathrm{M}}=(800\pm300)N\,\mathrm{mol^{-1}\,dm^3}$, $k_{\mathrm{Mr}}=(4.6\pm0.3)\times10^{-3}\,\mathrm{s^{-1}}$, and $k_{\mathrm{1d}}=(0.105\pm0.004)\times10^{-3}\,\mathrm{s^{-1}}$. Calculation with the parameter values gives the dotted curve shown in Fig. 2. The poor agreement between the calculated and observed rates strongly suggests the existence of at least one 1:m ($m\geqq2$) species.

Discussion

The formation of aggregates of $[\mathrm{Fe(phen)_3}]^{2+}$ with alkansulfonate ions and the racemization and dissociation of the complex in the aggregates will now be discussed in comparison with the case of the aggregates with alkyltrimethylammonium ions.

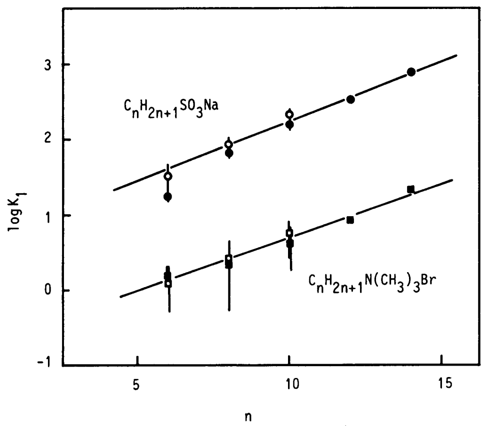

Fig. 4. Plots of logK_1 versus the alkyl chain length (n) of the alkanesulfonate and alkyltrimethylammonium ions. The open marks are the results for racemization and the closed marks are those for dissociation.
○, ●: n-$\mathrm{C_nH_{2n+1}SO_3Na}$; □, ■: n-$\mathrm{C_nH_{2n+1}N(CH_3)_3Br}$.

Formation of 1:1 Aggregate: Figure 4 shows the plot of the logarithm of the 1:1-aggregate formation constant (log K_1) against the alkyl-chain length (n) of the sulfonate ion, together with a similar plot previously obtained for the systems containing alkyltrimethylammonium salts. A linear relationship was found between log K_1 and n ($n\geqq8$), suggesting that the formation of the 1:1 aggregate is caused by hydrophobic interaction. The almost identical slopes of the two lines (Fig. 4) suggest that the interactions of the complex cation with alkanesulfonate anions and with alkyltrimethylammonium cations are of the same nature, or that hydrophobic interaction is responsible for the formation of the 1:1 aggregates. This is also supported by the result of our NMR study that the hexanesulfonate ion associates with $[\mathrm{Fe(phen)_3}]^{2+}$ in such a way that the alkyl chain of the sulfonate ion lies on the phenanthroline ligand.[19] The energy of hydrophobic interaction between the complex and alkanesulfonate ions was estimated to be (0.9±0.1) kJ mol^{-1} per methylene group from the slope of the line in Fig. 4. This is consistent with the value of (0.8±0.1) kJ mol^{-1} obtained previously for the $[\mathrm{Fe(phen)_3}]^{2+}$-alkyltrimethylammonium system.[15] The value of K_1 for each of the alkanesulfonate ions was about 40 times as large as that for the alkyltrimethylammonium ion of the same alkyl-chain length, reflecting the difference in the electrostatic energy between the cation–cation and the cation–anion interaction; this corresponds to a difference of 9.2 kJ mol^{-1} in the free-energy change in the ion-pair formation.

Formation of 1:m *Aggregates*: Aggregates higher than 1:1 were found to be formed for the $[\mathrm{Fe(phen)_3}]^{2+}$–$\mathrm{RSO_3}^-$ system, but not for the $[\mathrm{Fe(phen)_3}]^{2+}$–alkyltrimethylammonium system. This indicates that electrostatic attraction between the complex cation and sulfonate anions partly compensates for the repulsion between sulfonate anions, thus facilitating the formation of the 1:m aggregate. Since a remarkable increase in the rates of racemization and dissociation of $[\mathrm{Fe(phen)_3}]^{2+}$ occurred below the cmc, premicellar aggregates must be responsible for the changes in the rates. Thus, "micellar catalysis" may, in some cases, originate from interaction with surfactant ions rather than from that with micelles.

Racemization-rate Constants of $[Fe(phen)_3]^{2+}$ in the Aggregates: The values of k_{1r} for $[\mathrm{Fe(phen)_3}]^{2+}$ in the 1:1 aggregate were two (n=4) to three (n=10) times as large as the value of k_{0r}. This resembles our previous finding that the formation of the 1:1 aggregate with the alkyltrimethylammonium cation (n-$\mathrm{C_nH_{2n+1}N^+(CH_3)_3}$, n=6—10) increased the racemization rate of the complex ion by a factor of two to four. The similarity between these two cases shows that the difference in the charge of the organic ions has little effect on the racemization rate. This confirms the previous argument that the effect of the organic ions accelerating the racemization of $[\mathrm{Fe(phen)_3}]^{2+}$ is caused by an interaction of the complex ion with the alkyl group of the organic ions, and not by their action as electron donors.[15]

The following mechanism is proposed for this acceleration. In a transition state of the racemization through a twist process, the metal-ligand bonds of the complex ion have to stretch to a considerable extent so as to relax the steric repulsion between the phenanthroline ligands, especially between hydrogen atoms at the 2 and 9 positions of the ligands. As a result, the hydrophobic phenanthroline ligands are exposed to the solvent more extensively in the transition state of the racemization than in the initial state; therefore, the transition state is more hydrophobic than the initial state[20] and is more strongly stabilized by the hydrophobic interaction. Thus, the association of the complex ion with the alkylammonium or alkanesulfonate ion may lead to the acceleration of the racemization. An alternative explanation of the role of the alkyl group in accelerating the racemization may be that its aggregate formation with the complex cation removes the iceberg structure around the complex cation, thus facilitating the intramolecular twist racemization. Similar mechanisms can account for the larger values of k_{mr} for the complex in 1 : m aggregates than the values of k_{1r} in 1 : 1 aggregates (Tables 1 and 2); the hydrophobic stabilization of the transition state is greater for the 1 : m aggregate than for the 1 : 1 aggregate, or the iceberg structure is more efficiently removed from the complex in a 1 : m aggregate than in a 1 : 1 aggregate.

Dissociation-rate Constants of [Fe(phen)$_3$]$^{2+}$ in the Aggregates: The values of k_{1d} for [Fe(phen)$_3$]$^{2+}$ in the 1 : 1 aggregates were one-fourth of the value of k_{0d}, and were almost independent of the value of n (n=6, 8, and 10; Table 1). The lower rate constant for the 1 : 1 aggregate can be related to a smaller number of water molecules in direct contact with the complex ion if the dissociation of the complex ion proceeds through a 7-coordinate transition state with a coordinated water molecule.[13] The situation is similar to the case of the hydrophobic aggregate with the alkylammonium cation.[15] However, the complex ions in the present aggregates show small but appreciable values of k_{1d}, in contrast to the very small values for the complex ion in the aggregate with alkyltrimethylammonium cations.[15] This difference indicates that the dissociation-rate constant is affected by the charge of the aggregates. The higher charge (+3) of the aggregate of the complex cation with the alkylammonium cation causes a stronger electrostriction of water around the aggregate. Therefore, the activity of the water should be lowered and the water-molecule-assisted dissociation should be retarded.

The values of k_{md} for [Fe(phen)$_3$]$^{2+}$ in 1 : m aggregates were ten times as large as the value of k_{1d} (Tables 1 and 2). This may be because monomeric water molecules exist among the sulfonate ions in the 1 : m aggregates; such water molecules should have no necessity to break hydrogen bonding with bulk water to react with the complex ion. The large k_{md} values may also result from the greater stabilization of the transition state, which should be more hydrophobic than the initial state because of the expansion of metal-ligand bonds.[20]

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