CHEMISTRY LETTERS, pp. 1681-1684, 1981.

AGGREGATE FORMATION OF TRIS(1,10-PHENANTHROLINE)IRON(II) IONS WITH IONIC SURFACTANTS. KINETIC STUDIES OF RACEMIZATION AND DISSOCIATION OF THE COMPLEX

Satoshi TACHIYASHIKI* and Hideo YAMATERA†
Laboratory of Chemistry, Kagawa Nutrition College, Sakado,
Saitama 350-02
†Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464

Kinetic studies of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ in the presence of sodium alkanesulfonates ($C_nH_{2n+1}SO_3Na$, n=10, 14) showed the formation of at least two kinds of aggregates of the complex ion with alkanesulfonate ions (1:1 and 1:8 for n=10, and 1:1 and 1:3 for n=14).

Recently, micellar catalysis of chemical reactions has been paid much attention.[1)] However, less attention has been paid to the role of monomeric surfactant ions in micellar systems, in spite of the fact that there are systems where the change in rate was observed below the critical micelle concentration (cmc).[2)] In this communication, we report kinetic studies of racemization and dissociation of $[Fe(phen)_3]^{2+}$ in sodium alkanesulfonate solutions, where the interaction of the complex ion with monomeric surfactant ions, rather than with micelles, may play an important role for the change in the reaction rate of the complex.

Sodium alkanesulfonates (Tokyo Kasei Kogyo Co. Ltd.) were recrystallized three times from an ethanol-methanol (5:1) mixture. Kinetic data were obtained at 25.0°C in solutions containing the perchlorate of the complex (5×10^{-5} mol dm^{-3}) and a sodium alkanesulfonate. Racemization was followed by polarimetry, and dissociation, by spectrophotometry. For measuring the dissociation rates, 5×10^{-4} mol dm^{-3} $NiCl_2$ was added to the sample solution as the scavenger of liberated phenanthroline. The first-order rate constants for racemization and dissociation, k_r^{obsd} and k_d^{obsd}, were obtained respectively from the $\ln[\alpha_0/\alpha_t]$ vs. t and $\ln[D_0/D_t]$ vs. t plots, where α and D, with the subscripts showing the time, represents the optical rotation (546 nm) and the absorbance (510 nm) of the sample solutions, respectively. The reaction rates were almost independent of the concentration of the complex in the range of $(0.25-1.0)\times10^{-4}$ mol dm^{-3}.

Figure 1 shows the plots of the observed first-order rate constants of the racemization and dissociation of the complex against the logarithm of the sodium alkanesulfonate concentration. The cmc values of the alkanesulfonates in the sample solutions were determined[3)] in order to make clear whether micelles are concerned with the observed changes in the rates. It is clearly shown in Fig. 1

that the rate changes occurred at alkanesulfonate concentrations below cmc, which is indicated by an arrow in the figure for each alkanesulfonate. Since surfactant ions existed in the monomeric form below cmc,4) the interaction of the complex with monomeric surfactant ions, rather than with micelles, will explain the observed changes in the rates.

Figure 1 shows that the rate changes occurred at least by two steps. The first step appearing at the lower alkanesulfonate concentrations was also observed as a one-step change for the system containing an alkanesulfonate of a shorter alkyl chain (n=2 and 4).5) This step of the rate change is similar to those observed for the $[Fe(phen)_3]^{2+}$-alkyltrimethylammonium systems,6) for which the changes in the racemization and dissociation rates are accounted for by the formation of 1:1 aggregates due to hydrophobic interaction. The effect of inorganic anions on the rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$ was satisfactorily explained by the ion-pair formation of the complex cation with an anion.7) Thus, by the analogy with these, the rate changes at lower sulfonate concentrations are thought to arise from the formation of the 1:1 aggregate (or ion pair) of the complex ion and the anion caused by electrostatic and hydrophobic interaction. The second step of the rate change was not seen in the system of an alkanesulfonate of a shorter alkyl chain. A remarkable increase in the racemization rate as observed in the second step was also reported for systems containing an organic solvent.8) Thus, the rate changes at higher alkanesulfonate concentrations are considered to arise from the interaction of the complex ion with several alkanesulfonate ions by hydrophobic interaction.

The complex ion is expected to form 1:m (m=1, 2, 3, ···) aggregates as follows:

$$[Fe(phen)_3]^{2+} + m\,RSO_3^- \overset{\beta_m}{\rightleftharpoons} [Fe(phen)_3]^{2+}\cdot(RSO_3^-)_m \qquad (1)$$

where β_m is the concentration equilibrium constant of the reaction (1). Because

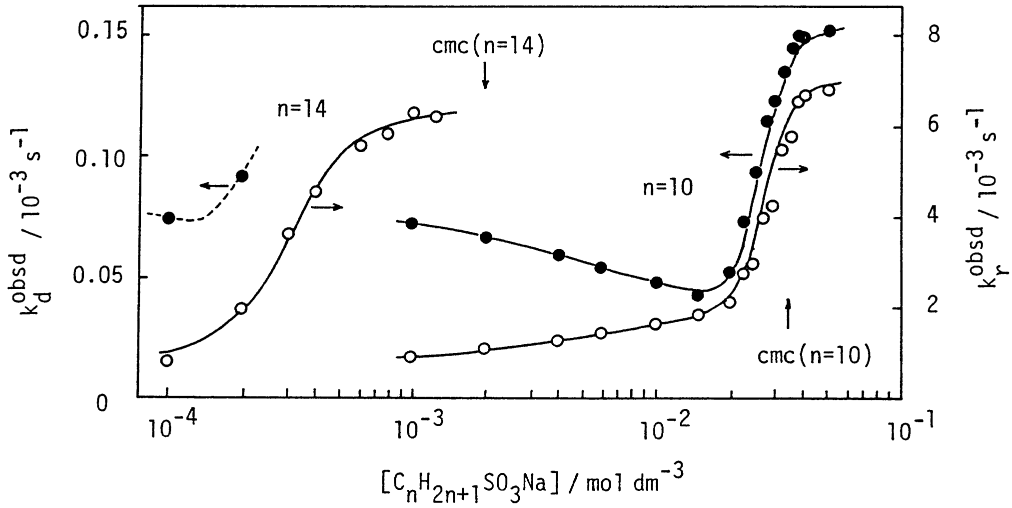

Fig. 1. Plots of the racemization (k_r^{obsd}, ○) and dissociation (k_d^{obsd}, ●) rate constants of $[Fe(phen)_3]^{2+}$ vs. the logarithm of the sodium alkanesulfonate concentration

of the difficulty in estimating the activity coefficients of higher aggregates, the concentration equilibrium constants are used in the present analysis; it can be expected, however, that the analysis in such a way will give a proper interpretation of the experimental results, at least qualitatively. Suppose the complex ions associated with zero and m alkanesulfonate ions undergo racemization (or dissociation) with the first-order rate constants of k_0 and k_m, respectively. Then, the observed first-order rate constant can be expressed by:

$$k^{obsd} = \frac{k_0 + \sum_{m=1}^{\infty} k_m \beta_m [RSO_3^-]^m}{1 + \sum_{m=1}^{\infty} \beta_m [RSO_3^-]^m} \tag{2}$$

The analysis of the kinetic results for $R=C_{10}H_{21}$ was carried out as follows. At low alkanesulfonate concentrations, the complex ions exist predominantly as the free complex cation and the 1:1 aggregate. Thus, we determined the values of k_0, k_1, and β_1 from the changes in rates at low alkanesulfonate concentrations, neglecting the formation of higher aggregates and disregarding the effect of the change in ionic strength. The correction for the change in ionic strength would give only a small effect (<10%) on the parameter values. For the analysis of the rates observed at higher concentrations, a second aggregate species (1:x) was considered in addition to the free complex ion and the 1:1 aggregate. The value of k_x, the rate constant of the 1:x aggregate, was tentatively regarded as equal to the k^{obsd} value at the plateau toward the right end of Fig. 1. The value of x was determined so as to fit the shape of the k^{obsd} vs. $[C_{10}H_{21}SO_3Na]$ curve in the region of the higher concentrations. Analyses of the racemization and dissociation rate data gave a consistent value of x=8 within the experimental errors (x=7.9±0.3 and 8.5±0.7, respectively). Considering only the terms of m=1 and 8 in the summation of Eq. 2 and using the known parameter values for k_0, k_1, k_8, and β_1, we determined the value of β_8 by fitting Eq. 2 to the experimental data. The neglect of the effect of the changes in ionic strength does not seem to seriously affect the result of the analysis, since the high charge of the 1:8 aggregate would be reduced by the ion association with the Na^+ ions. The β_m values which gives the best fit to both racemization and dissociation experiments are $\beta_1=10^{2.2}$ and $\beta_8=10^{13.1}$, the latter being the mean value of $10^{12.9}$ from the racemization experiments and $10^{13.3}$ from the dissociation experiments. The rate constants are $k_0=0.67$, $k_1=2.3$, and $k_8=7.0$ for racemization, and $k_0=0.080$, $k_1=0.019$, and $k_8=0.153$ for dissociation; slight adjustments of the k_8 values have been made to give better fitting. The racemization rates in the presence of tetradecanesulfonate (n=14) were subjected to a similar analysis, which lead to the parameter values of m=3, $\beta_3=10^{11.1}$, and $k_3=6.3$ (for racemization), with the values of $\beta_1=10^{2.8}$, $k_0=0.67$, and $k_1=2.2$ previously estimated.$^{5)}$ The calculated gross rate constants on the basis of Eq. 2 with the parameter values given above are shown by the solid curves in Fig. 1. 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. The aggregates other than those shown above may be present in each system, but only in small amounts. Thus, no further analysis has been carried out. The rate changes observed here in the presence of alkanesulfonate ions can be satisfactorily explained by the formation of at least two types of premicellar aggregates of the complex ion with alkanesulfonate ions (1:1 and 1:8 for $C_{10}H_{21}SO_3^-$, and 1:1 and 1:3 for $C_{14}H_{29}SO_3^-$).

The "micellar catalysis" of chemical reactions as observed in the present systems may originate from interaction with surfactant ions, rather than with the micelles. Details of the investigation for a series of systems containing various alkanesulfonates (n=2-14) will be reported elsewhere.

References

1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.
2) See, for example, V. C. Reinsborogh and B. H. Robinson, J. C. S. Faraday I, 75, 2395 (1979) and the references therein.
3) A remarkable decrease in the surface tension of the alkanesulfonate solution was observed in the presence of $[Fe(phen)_3]^{2+}$, as was reported by Kratohvil et. al. (J. Colloid Interface Sci., 72, 106(1979)) for the sodium dodecyl sulfate solution in the presence of $[Co(phen)_3]^{3+}$; however, the cmc values of the solution were found to remain unchanged in the presence of the complex (S. Ozeki, S. Tachiyashiki, S. Ikeda, and H. Yamatera, unpublished results).
4) The formation of small aggregates (e.g. dimers) below cmc was reported previously; however, it was proved to have negligible effect on the physico-chemical properties of surfactant solutions (F. van Voorst Vader, Trans. Faraday Soc., 57, 110 (1961)).
5) S. Tachiyashiki and H. Yamatera, unpublished results.
6) S. Tachiyashiki and H. Yamatera, Bull. Chem. Soc. Jpn., submitted.
7) S. Tachiyashiki and H. Yamatera, Bull. Chem. Soc. Jpn., submitted.
8) F. M. Van Meter and H. M. Neumann, J. Am. Chem. Soc., 98, 1388 (1976).

(Received July 1, 1981)