Kinetics of Racemization and Dissociation of Tris(1,10-phenanthroline)-iron(II). Hydrophobic Interaction between the Complex Cation and Alkylammonium Cations

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*

(Received June 16, 1981)

The rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$ were determined in the presence of series of alkali-metal bromides, symmetrical tetraalkylammonium bromides, and alkyltrimethylammonium bromides. The alkali-metal bromides did not affect the racemization rate, but they decreased the dissociation rate. The retarding effect increased with increasing bromide concentrations and decreased in the order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The alkylammonium bromides increased the racemization rate up to three fold and decreased the dissociation rate down to half the rate in pure water; alkylammonium ions with longer alkylchains induced greater changes of the rates. The effect of alkylammonium ions on the reaction rates was analyzed in terms of the formation of 1:1 aggregates of the complex cation with the alkylammonium cation caused by hydrophobic interactions. The equilibrium constant for the aggregate formation was greater for the alkylammonium ions with longer alkyl chains. The reaction rate constants of the hydrophobic aggregates remain almost constant with the increase in the alkyl chain length. The rate behaviors of the hydrophobic aggregates are discussed in terms of the reaction mechanisms of racemization and dissociation of $[Fe(phen)_3]^{2+}$.

Tetraalkylammonium ions can be used as model compounds for investigating hydrophobic interactions.[1] Salting-in of a hydrophobic solute by tetraalkylammonium ions has mainly been attributed to hydrophobic interactions between the cations and nonelectrolytes.[2] Tris(1,10-phenanthroline)metal chelates are also considered to be hydrophobic because of the large hydrophobicity of the ligand. Tris(1,10-phenanthroline)nickel(II) is reported to salt-in tris(acetylacetonato)cobalt(III) to water by hydrophobic interactions.[3] A stacking interaction, caused by hydrophobic interaction and a polarization effect, was proposed for the enhancement of the rates of the mixed complex formation of mono(2,2′-bipyridine)-, mono(1,10-phenanthroline)-, and mono(2,2′: 6′,2″-terpyridine)-metal complexes with some aromatic nitrogen donors.[4] Thus, it is interesting to study the nature of the interaction between hydrophobic alkylammonium cations and hydrophobic metal complex cations. The rate of aquation of tris(5-nitro-1,10-phenanthroline)iron(II) was reported to be influenced by the addition of alkylammonium cations.[5] The effects were analyzed in terms of salt effects on both the initial and transition states. Jensen *et al.*[6] reported the effect of octadecyltrimethylammonium chloride on the dissociation rate of $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline).

We previously reported the effects of added inorganic salts on the rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$.[7] The racemization rate increased slightly with the increase in the polarizability of the anion, whereas the dissociation rate remarkably increased with the increase in the pK_a value of the conjugate acid of the anion. The racemization of $[Fe(phen)_3]^{2+}$ is known to occur much faster in organic solvents than in aqueous solution.[8] The ability of the solvent to accelerate the racemization rate was correlated with its solvating power to the ligand[9] or with its electron-donating ability.[10] However, the details of the nature of this acceleration effect of the solvents are not clear. Since organic salts can be regarded as compounds intermediate between inorganic salts and organic solvents, the study of the effects of added organic salts such as alkylammonium bromides and sodium alkanesulfonates on the kinetics of racemization and dissociation is expected to give information concerning the nature of the solvent effects. With this expectation, we decided to study the effect of alkali-metal and alkylammonium cations on the rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$. The comparison of the effects of inorganic and organic cations on the reaction rates will lead us to understand the solvent effects and the mechanisms of the dissociation and the intramolecular twist racemization. The present study will also give information about the interactions between the hydrophobic alkylammonium cations and the hydrophobic complex cation. The effect of organic anions on the reaction rates of $[Fe(phen)_3]^{2+}$ will be reported elsewhere.

Experimental

The symmetrical tetraalkylammonium bromides used were reagents of the best grade obtainable from Wako Pure Chemical Industries, Ltd. Ammonium bromide was recrystallized from water, tetramethylammonium bromide from aqueous methanol(1:1), tetraethyl- from ethanol, tetrapropyl- from methanol, tetrabutyl- and tetrapentyl- from acetone. They were dried by heating at 110 °C for 18 h. Alkyltrimethylammonium bromides were guaranteed-grade reagents of Tokyo Kasei Kogyo Co., Ltd. Hexyl-, octyl-, decyl-, dodecyl-trimethylammonium bromides were recrystallized from acetone, while tetradecyl- and hexadecyl-trimethylammonium bromides were recrystallized from 10:1 and 2:1 acetone–ethanol, respectively. They were dried by heating at 90 °C for 24 h. Tetraphenylphosphonium chloride of Dojindo Laboratories, and lithium, sodium, potassium, rubidium, and caesium bromides of Merck(Suprapur) were used without further purification. The concentrations of the solutions of tetraethylammonium bromide, hexyltrimethylammonium bromide, and lithium bromide were determined by argentometry. Those of other salts were determined by weighing well-dried reagents. The purities of tetrapentylammonium bromide, and octyl-, decyl-, dodecyl-, and tetradecyl-trimethylammonium bromides were more than 99%, as determined by argentometry. Kinetic data were obtained at 32.0 °C using the perchlorate of the complex. The bromide of the metal complex was preferred to the perchlorate for the systems containing dodecyl- and tetradecyl-trimethylammonium ions, since the addition of perchlorate would precipitate alkylammonium perchlorate. In measuring the dissociation rate for the systems containing tetrapentylammonium bromide and alkyltrimethylammonium bromides, hydrochloric acid was added to the solution up to two percent of the alkylammonium bromide concentration; otherwise iron hydroxide might be precipitated in the course of the reaction due to the presence of a trace amount of the alkylamines contained in alkylammonium bromides. Other chemicals and procedures were the same as those described in a previous paper.[7]

Results and Discussion

Alkali-metal Cations. Table 1 and Fig. 1 show the observed first order rate constants of racemization and dissociation of $[Fe(phen)_3]^{2+}$ in the presence of a series of alkali-metal bromides. The racemization rate was not appreciably influenced by the addition of the alkali-metal bromides. The dissociation rate decreased with the increase in the alkali-metal bromide concentration. The order of the cation efficiency in decreasing the rates was $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, which is consistent with the previously reported order of $Li^+ > K^+$.[11] As the order is the same as that for the effect of decreasing the activity of water,[12] the effect of cations on the dissociation rates can be at least partly explained in terms of the changes in the activity of water; this change should affect the dissociation rate if the dissociation proceeded through a 7-coordinate transition state with an H_2O ligand.[7]

TABLE 1. RACEMIZATION RATE CONSTANTS OF $[Fe(phen)_3]^{2+}$ IN 1.0 mol dm^{-3} ALKALI-METAL BROMIDE SOLUTIONS AT 32.0 °C

Added salt	$k_r/10^{-3}\ s^{-1}$
LiBr	1.78, 1.85
NaBr	1.86, 1.88
KBr	1.83, 1.85
RbBr	1.83, 1.85
CsBr	1.86, 1.90

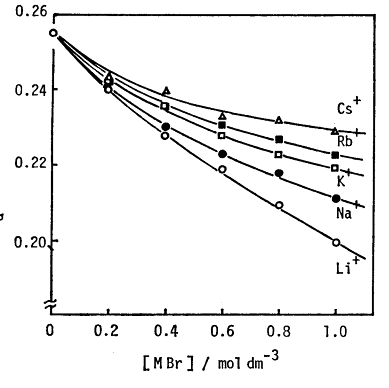

Fig. 1. Dissociation rate constants of $[Fe(phen)_3]^{2+}$ in alkali-metal bromide solutions at 32.0 °C.
○, Li^+; ●, Na^+; □, K^+; ■, Rb^+; △, Cs^+.

Alkylammonium Cations. The racemization rate increased and the dissociation rate decreased with the increase in the concentration of tetraalkyl- and alkyltrimethyl-ammonium bromides, as shown in Figs. 2—5. These also show that the extent of the rate change with the alkylammonium ion concentrations becomes greater with increasing length of the alkyl chain for both racemization and dissociation. However, both the racemization and dissociation rates are almost constant above certain concentrations of tetraphenylphosphonium cation and alkyltrimethylammonium cations, as shown in Figs. 2, 3, and 5. The critical concentrations above which the rates were almost constant shifted toward lower concentrations with the increase

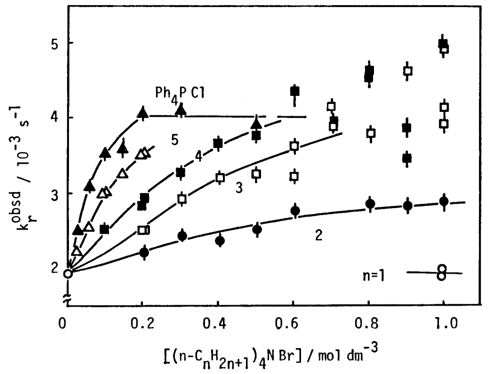

Fig. 2. Racemization rate constants of $[Fe(phen)_3]^{2+}$ in symmetrical tetraalkylammonium bromide and tetraphenylphosphonium chloride solutions at 32.0 °C.
○, $(CH_3)_4NBr$; ●, $(C_2H_5)_4NBr$; □, $(n\text{-}C_3H_7)_4NBr$; ■, $(n\text{-}C_4H_9)_4NBr$; △, $(n\text{-}C_5H_{11})_4NBr$; ▲, $(C_6H_5)_4PCl$.

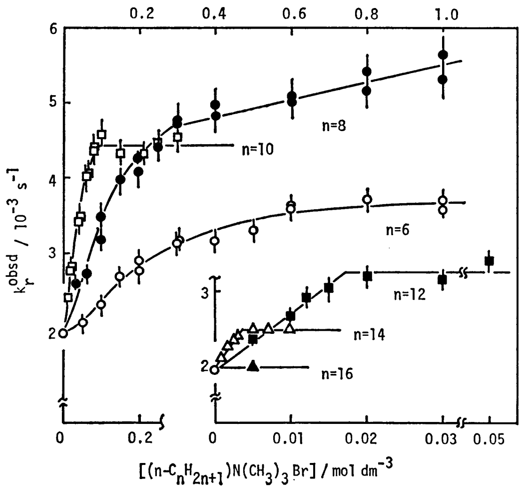

Fig. 3. Racemization rate constants of $[Fe(phen)_3]^{2+}$ in alkyltrimethylammonium bromide solutions at 32.0 °C.
○, $(n\text{-}C_6H_{13})N(CH_3)_3Br$; ●, $(n\text{-}C_8H_{17})N(CH_3)_3Br$; □, $(n\text{-}C_{10}H_{21})N(CH_3)_3Br$; ■, $(n\text{-}C_{12}H_{25})N(CH_3)_3Br$; △, $(n\text{-}C_{14}H_{29})N(CH_3)_3Br$; ▲, $(n\text{-}C_{16}H_{33})N(CH_3)_3Br$.

in the length of the alkyl chain. As is shown in Table 2, the critical concentration is close to the critical micelle concentration (cmc) for each electrolyte. Thus, these phenomena can reasonably be correlated with the micelle formation of the cations above cmc. As the concentration of the monomeric cations remains unchanged above cmc, the kinetic results suggest that the interaction of the complex ion with the monomeric cations is responsible for the observed features of the rate changes. A previously reported phenomenon,[6] that the added octadecyltrimethylammonium chloride had no effect on the rate of dissociation of $[Fe(phen)_3]^{2+}$, can be reasonably accounted for by the very low concentration of the monomeric alkylammonium ion, as indicated by the extremely low cmc value. The slight increase of the rates observed for octyl- and decyl-trimethylammonium ions above cmc would be caused by some interactions of the complex with micelles.

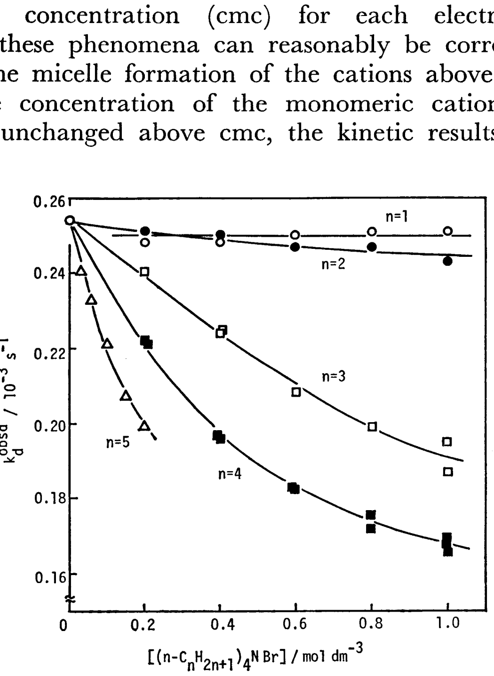

Fig. 4. Dissociation rate constants of $[Fe(phen)_3]^{2+}$ in symmetrical tetraalkylammonium bromide solutions at 32.0 °C.
○, $(CH_3)_4NBr$; ●, $(C_2H_5)_4NBr$; □, $(n\text{-}C_3H_7)_4NBr$; ■, $(n\text{-}C_4H_9)_4NBr$; △, $(n\text{-}C_5H_{11})_4NBr$.

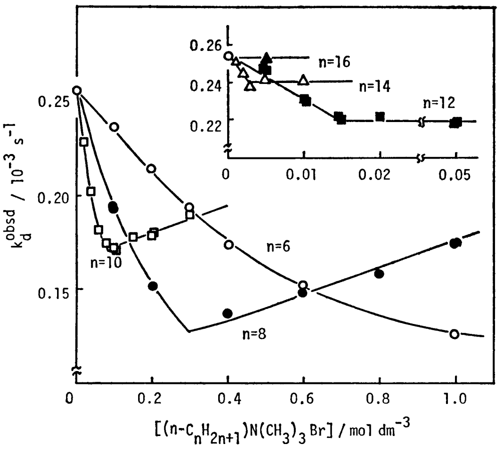

Fig. 5. Dissociation rate constants of $[Fe(phen)_3]^{2+}$ in alkyltrimethylammonium bromide solutions at 32.0 °C.
○, $(n\text{-}C_6H_{13})N(CH_3)_3Br$; ●, $(n\text{-}C_8H_{17})N(CH_3)_3Br$; □, $(n\text{-}C_{10}H_{21})N(CH_3)_3Br$; ■, $(n\text{-}C_{12}H_{25})N(CH_3)_3Br$; △, $(n\text{-}C_{14}H_{29})N(CH_3)_3Br$; ▲, $(n\text{-}C_{16}H_{33})N(CH_3)_3Br$.

As the alkali-metal cations have no effects on the racemization rate, the acceleration of the racemization rate by the monomeric alkylammonium ions can be attributed to the hydrophobic interactions between the complex and the alkylammonium ions. The kinetic results can reasonably be accounted for by assuming the formation of 1:1 hydrophobic aggregates between the alkylammonium ions and complex cations. The following mechanism was considered:

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

$$[Fe(phen)_3]^{2+} + R_4N^+ \xrightleftharpoons{K_2} [Fe(phen)_3]^{2+}\cdot R_4N^+, \tag{2}$$

$$[Fe(phen)_3]^{2+}\cdot Br^- + R_4N^+ \xrightleftharpoons{K_3} [Fe(phen)_3]^{2+}\cdot Br^-\cdot R_4N^+, \tag{3}$$

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

$$K_2 = \frac{[Fe(phen)_3{}^{2+}\cdot R_4N^+]}{[Fe(phen)_3{}^{2+}][R_4N^+]}\cdot\frac{f_3}{f_2 f_1}, \tag{5}$$

$$K_3 = \frac{[Fe(phen)_3{}^{2+}\cdot Br^-\cdot R_4N^+]}{[Fe(phen)_3{}^{2+}\cdot Br^-][R_4N^+]}\cdot\frac{f_2}{f_1 f_1}, \tag{6}$$

$$[Fe(phen)_3]^{2+} \xrightarrow{k_0}, \tag{7}$$

$$[Fe(phen)_3]^{2+}\cdot Br^- \xrightarrow{k_1}, \tag{8}$$

$$[Fe(phen)_3]^{2+}\cdot R_4N^+ \xrightarrow{k_2}, \tag{9}$$

$$[Fe(phen)_3]^{2+}\cdot Br^-\cdot R_4N^+ \xrightarrow{k_3}, \tag{10}$$

where f_z means the activity coefficient of an ion with a charge of $\pm z$, and can be expressed by the Debye-Hückel equation, as discussed previously.[7] The closest distance of approach, a, was assumed to be 8, 9, and 9—11×10^{-8} cm for $z=\pm1$, ±2, and ±3, respectively. The rate constants k_0, k_1, k_2, and k_3 mean the first order rate constants (Eqs. 7—10) for either racemization (r) or dissociation (d) of each chemical species. Additional subscripts, r and d, may be used to specify the type of reaction. The observed

TABLE 2. THE CRITICAL CONCENTRATIONS (C/mol dm^{-3}) ABOVE WHICH THE RATES SHOW CONSTANT VALUES

Salt	Racemization	Dissociation	cmc values[a]
$(C_6H_5)_4PCl$	0.20 ±0.02	—	—
$n\text{-}C_8H_{17}N(CH_3)Br$	0.32 ±0.02	0.29 ±0.01	(≈0.3)
$n\text{-}C_{10}H_{21}N(CH_3)Br$	0.065 ±0.003	0.068 ±0.003	0.068
$n\text{-}C_{12}H_{25}N(CH_3)Br$	0.0173±0.0010	0.0155±0.0005	0.0153
$n\text{-}C_{14}H_{29}N(CH_3)Br$	0.0036±0.0003	0.0030±0.0002	0.00302

a) J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).

rate constant is expressed as:

$$k^{\mathrm{obsd}} = \frac{k_0 + k_1K_1[\mathrm{Br}^-]f_2 + k_2K_2[\mathrm{R_4N^+}]f_1f_2/f_3 + k_3K_1K_3[\mathrm{Br}^-][\mathrm{R_4N^+}]f_1^2}{1 + K_1[\mathrm{Br}^-]f_2 + K_2[\mathrm{R_4N^+}]f_1f_2/f_3 + K_1K_3[\mathrm{Br}^-][\mathrm{R_4N^+}]f_1^2}, \tag{11}$$

where $[\mathrm{Br}^-]$ and $[\mathrm{R_4N^+}]$ can be taken to be equal to the total alkylammonium ion concentration (C_t) at a very low concentration of the complex. At very low alkylammonium ion concentrations, Eq. 11 is transformed to:

$$\begin{aligned} k^{\mathrm{obsd}} &= k_0 + (k_1-k_0)K_1[\mathrm{Br}^-]f_2 + (k_2-k_0)K_2[\mathrm{R_4N^+}]f_1f_2/f_3 \\ &= k_0 + \{(k_1-k_0)K_1 + (k_2-k_0)K_2\}C_t. \end{aligned}$$

The gradient (m) of k^{obsd} *vs.* C_t is then;

$$m = (k_1-k_0)K_1 + (k_2-k_0)K_2. \tag{12}$$

For systems containing symmetrical tetraalkylammonium ions, tetraphenylphosphonium ion, hexyl-, octyl-, and decyl-trimethylammonium ions, the kinetic data were analyzed on the basis of Eq. 11. Among the parameter values in Eq. 11, $k_{0r}=k_{1r}=(1.94\pm0.09)\times10^{-3}\ \mathrm{s^{-1}}$, $k_{0d}=(2.54\pm0.03)\times10^{-4}\ \mathrm{s^{-1}}$, $k_{1d}=(2.1\pm0.2)\times10^{-4}\ \mathrm{s^{-1}}$, and $K_1=3\ \mathrm{mol^{-1}\ dm^3}$ were previously obtained.[7] Since the simultaneous determination of the values of k_2, K_2, k_3, and K_3 was impossible because of experimental errors in the kinetic data, they were determined in the following way. The formation constant of $[\mathrm{Fe(phen)_3}]^{2+}\cdot\mathrm{R_4N^+}$ would be small compared with that of $[\mathrm{Fe(phen)_3}]^{2+}\cdot\mathrm{Br^-}\cdot\mathrm{R_4N^+}$. Therefore, we analyzed the kinetic data, considering only the formation of $[\mathrm{Fe(phen)_3}]^{2+}\cdot\mathrm{Br^-}$ and $[\mathrm{Fe(phen)_3}]^{2+}\cdot\mathrm{Br^-}\cdot\mathrm{R_4N^+}$, to obtain approximate k_3 and K_3 values. Using the approximate k_3 and K_3 values and taking the formation of $[\mathrm{Fe(phen)_3}]^{2+}\cdot\mathrm{R_4N^+}$ into account, the kinetic data were reanalyzed to obtain approximate k_2 and K_2 values. Then using the values of k_2, K_2, k_3, and K_3 thus obtained as the initial values, the least-squares fitting[13] of the kinetic data to Eq. 11 were carried out to give more reliable values for k_2, K_2, k_3, and K_3. The results of the analysis are listed in Table 3.

For the systems containing dodecyl- and tetradecyl-trimethylammonium ions, their small cmc values restricted the measurement of the rates within a narrow range of the ammonium ion concentrations; therefore, Eq. 11 was not applicable in the analysis of the kinetic data. Thus, Eq. 12 was used to analyze the kinetic data for these systems, as well as for the systems containing octyl- and decyl-trimethylammonium ions. As the values of k_0, k_1, and K_1 have been previously obtained, Eq. 12, together with the experimental determination of the value of m, gives us the relation between k_2 and K_2. Then, K_2 can be obtained on the assumption that k_{2d} values for the complex in the hydrophobic aggregates with octyl-, decyl-, dodecyl-, and tetradecyl-trimethylammonium cations are negligibly small, an assumption which seems reasonable if we compare the k_{2d} values for the homologs (see Table 3). Then, the K_2 value thus obtained and the m_r value experimentally determined will be substituted in Eq. 12 to give the value of k_{2r}. The K_2 and k_{2r} values obtained in this manner are listed in Table 3 within parentheses.

The K_2 and K_3 values increased with the increase in the number of carbon atoms of the alkyl chains, as shown in Table 3 and Fig. 6. This implies that the formation of the aggregates is caused by the hydrophobic interaction between the complex and alkylammonium cations, which is presumed to be larger for a longer alkyl chain. The aggregate formation constant (K_2) for the complex and tetraphenylphosphonium ions falls on the line of the K_2 values for tetraalkylammonium ions as shown in Fig. 6; this shows the similarity of the interaction of the complex ion with phenyl groups to that with alkyl groups. Figure 6 also shows that the dependence of the log K_2 value on the total carbon number of the ammonium ion is twice as large for alkyltrimethylammonium ions as for tetraalkylammonium ions. That is, the energies of hydrophobic interaction with complex cations were 0.8 kJ/mol and 0.4 kJ/mol per methylene group for alkyltrimethylammonium cations and tetraalkylammonium cations, respectively.

TABLE 3. THE FORMATION CONSTANTS OF THE HYDROPHOBIC AGGREGATES AND THE RATE CONSTANTS OF RACEMIZATION AND DISSOCIATION OF $[\mathrm{Fe(phen)_3}]^{2+}$ IN THE AGGREGATES[a)]

Cation	$k_2/10^{-3}\ \mathrm{s^{-1}}$		$K_2/\mathrm{mol^{-1}\ dm^3}$		$k_3/10^{-3}\ \mathrm{s^{-1}}$		$K_3/\mathrm{mol^{-1}\ dm^3}$	
	Racem.	Diss.	Racem.	Diss.	Racem.	Diss.	Racem.	Diss.
$(C_2H_5)_4N$	7±4	—	0.2±0.2	—	3.6±0.5	—	2.2±1.6	—
$(n\text{-}C_3H_7)_4N$	7±5	0.03 ±0.04	0.2±0.2	0.6±0.2	5.0±0.3	—	2.9±0.8	—
$(n\text{-}C_4H_9)_4N$	5±2	0.04 ±0.02	1.1±0.5	1.4±0.3	4.8±0.2	—	5.7±2.1	—
$(n\text{-}C_5H_{11})_4N$	4±3	0.15 ±0.15	1.9±1.5	1.6±0.7	3.9±0.2	0.187±0.015	45± 20	29± 7
$(C_6H_5)_4P$	5±2	—	4.0±4.0	—	4.2±0.2	—	66± 46	—
$n\text{-}C_6H_{13}N(CH_3)_3$	3±2	0.002±0.015	1.2±0.7	1.5±0.3	4.0±0.1	—	12± 2	—
$n\text{-}C_8H_{17}N(CH_3)_3$	5±2 (8±1)	0.000±0.002	2.5±2.0	2.1±0.3 (2.3±0.2)	5.4±0.2	0.110±0.010	28± 5	15± 3
$n\text{-}C_{10}H_{21}N(CH_3)_3$	8±3 (10±1)	0.003±0.004	5.4±2.9	3.9±2.1 (5.0±0.3)	4.7±0.2	0.162±0.013	171±112	175±120
$n\text{-}C_{12}H_{25}N(CH_3)_3$	(11±2)	—	—	(8.4±1.2)	—	—	—	—
$n\text{-}C_{14}H_{29}N(CH_3)_3$	(9±1)	—	—	(20.9±1.6)	—	—	—	—

a) The values were obtained from the analysis based on Eq. 11, except for a few cases where the results from the analysis based on Eq. 12 are given in parentheses.

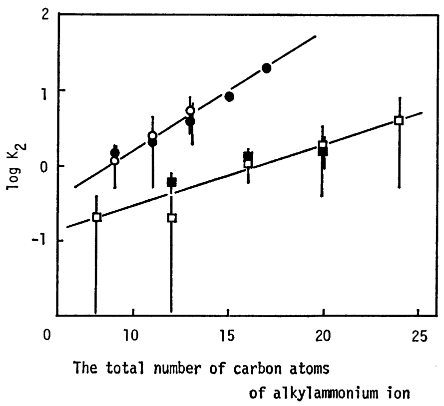

Fig. 6. Plot of log K_2 against the total number of carbon atoms of the alkylammonium ion.
The open marks are the results of the analysis based on Eq. 11 and the closed marks are those based on Eq. 12. ○,●: Alkyltrimethylammonium ion. □,■: Symmetrical tetraalkylammonium ion.

The k_2 and k_3 values both for racemization and for dissociation did not significantly depend on the alkyl chain length, as shown in Table 3. The k_2 values for the racemization rate of the complex were about three times as large as k_0, and for the dissociation rate, the k_2 values were much smaller than k_0 (Table 3). As the alkylammonium ions have no electron-donating ability, the increase in the racemization rates due to the formation of the hydrophobic aggregates may come from a kind of solvating effect of the alkyl groups of the ammonium ions and/or from the modification of the iceberg structure[14] surrounding the complex ion. The exceptionally slow racemization in water, compared with the rates in other solvents, may result from the cage effect of the iceberg structure. The slow dissociation rate of the complex in the aggregate would result from the decrease in the water concentration around the complex cation by the formation of the aggregates and/or from the decrease in the activity of water due to modification of the iceberg structure.

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