The Determination of the Formation Constant of Triiodide Ion in Micellar Solution of Dodecyltrimethylammonium Chloride

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Spectrophotometric measurements were undertaken at 360 nm in order to estimate the formation constant of triiodide ion in micellar solution of dodecyltrimethylammonium chloride. The absorption spectra of the solutions suggested that both iodine molecule and triiodide ion are solubilized in a hydrophilic surface region of the surfactant micelle. The apparent formation constant of triiodide ion, K_a, was found to be much larger in micellar solution than in water. It was also shown that the value of K_a decreases regularly with increasing surfactant concentration. A tentative estimation based on a lamellar micelle model led to the intrinsic formation constant of triiodide ion of 650 mol^{-1} dm^3 or less at 30 °C, which is comparable with that in water. The thermodynamic consideration revealed that the formation reaction of triiodide ion from iodine and iodide ion in micellar solution is accompanied by an anomalous entropy decrease.

In a previous paper,[1)] we have reported the spectrophotometric measurements of the effect of solvent composition on the formation constant, K_c, of triiodide ion in water–methanol and water–ethanol mixed solvents. We found that in both systems the value of K_c increases remarkably with increasing mole fraction of alcohol, *e.g.*, it varies rapidly with methanol concentration from 730 in water to 12200 mol^{-1} dm^3 in methanol at 25 °C. Similar increases in K_c were also found in 2-propanol[2)] and acetonitrile.[2,3)]

In connection with a remarkable effect of solvent properties on K_c, it is of great interest to study the formation constant of triiodide ion in a solution of surfactant, since this provides an aqueous as well as a hydrophobic environment by forming a micelle, which consists of a hydrocarbon core with polar groups at the surface. In particular, the cationic surfactant micelle may be anticipated to affect K_c significantly through a strong coulombic interaction with iodide and triiodide ions. However, such studies have not been performed so far. The estimation of K_c in micellar solution is also essential for the clear understanding of our recent studies on the rate of catalytic oxidation of formate ion by iodine in micellar solutions.[4)]

The present paper is concerned with the spectrophotometric determination of the formation constant of triiodide ion in a micellar solution of dodecyltrimethylammonium chloride.

Experimental

Materials. Dodecyltrimethylammonium chloride (DTAC), purchased from Tokyo Kasei Kogyo Co., Ltd., was recrystallized twice from methanol. Other chemicals were of guaranteed grade. Sodium iodide was dried at 120 °C and used without further purification. Iodine was purified further by sublimation.

Measurements. The apparent formation constant of I_3^- in a mixed solution of I_2, NaI, and DTAC was determined spectrophotometrically at 360 nm. The absorption spectra were recorded on a Hitachi spectrophotometer model 200-20 equipped with a thermoregulated cell compartment. The change in absorbance at 360 nm was followed as a function of NaI concentration at constant concentrations of I_2 and DTAC.

The chloride ion activity in DTAC solution was measured potentiometrically by using a National chloride ion selective ceramic electrode IE-510103. The electromotive force was measured with an Orion digital pH/mV meter model 701A with an accuracy of ±0.1 mV. In the concentration range below the critical micelle concentration (CMC) of DTAC, the semilogarithmic plots of electromotive force *versus* chloride ion activity taken from Kieland's data[5)] gave a linear relation with an ideal Nernst slope, suggesting that the electrode responds exclusively to chloride ions.

All measurements were conducted at 21, 30, and 40 °C.

Results and Discussion

The Absorption Spectra. In the presence of DTAC micelles, the absorption spectrum of the solution of I_2 and NaI is characterized by an absorption band at 360 nm. Figure 1 shows the typical change in

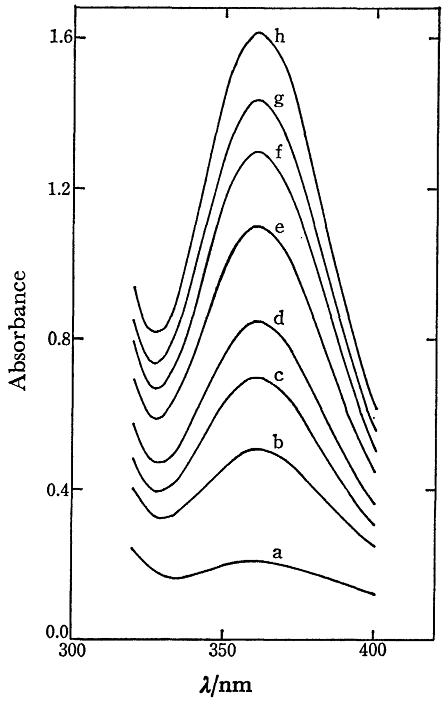

Fig. 1. The dependence of the absorbance spectrum of iodine in DTAC micellar solution on the concentration of sodium iodide at 30 °C; I_2 7.82 × 10^{-5} mol dm^{-3}, DTAC 0.13 mol dm^{-3}, NaI a: 0, b: 3.36, c: 6.71, d: 10.1, e: 16.8, f: 25.2, g: 33.6, h: 58.2 × 10^{-5} mol dm^{-3}.

absorption spectrum with NaI concentration, under the condition where concentrations of I_2 and DTAC are kept constant. Similar results were also obtained at the different DTAC concentrations studied. The important aspects of Fig. 1 are that the absorbance at 360 nm increases progressively with increasing NaI concentration, while the peak location is independent of NaI and DTAC concentrations. Unfortunately, only limited data are available in the concentration range of DTAC below CMC, since the occurrence of an appreciable amount of precipitate makes it difficult to obtain the reliable absorption spectra. However, the measurement of I_2 solution, though it was somewhat less accurate, showed that the absorption peak shifts successively from 460 to 360 nm with increasing DTAC concentration. At higher DTAC concentrations above CMC, the complex redissolved and the peak location remained at 360 nm. These observations suggest that an iodine molecule can interact strongly with a DTAC ion to give rise to a complex which is sparingly soluble in water but is easily solubilized in DTAC micelle.

The absorption spectrum of an iodine molecule is known to depend significantly on the polarity of the surrounding medium. Thus, an iodine molecule has the absorption band with a peak at 525 nm in a hydrophobic medium such as hexane,[6] but at 460 nm in water.[7] It is, therefore, reasonable to assume that the iodine molecules in micellar solution of DTAC are solubilized not in the hydrocarbon core but in a hydrophilic surface region of the DTAC micelle. The pronounced blue shift in peak location from 460 nm in water to 360 nm in micellar solution would provide additional evidence for the strong interaction between the iodine molecule and the ionic head group of DTAC.

As is shown in Fig. 1, the addition of sodium iodide results in a successive increase in absorbance but in no shift in peak location. This change can reasonably be ascribed to the formation of triiodide ion. Since, however, the peak location is red-shifted by 8 nm in micellar solution as compared with that in water,[7] triiodide ion is also considered to be solubilized in the surface region of the DTAC micelle.

The Formation Constant of Triiodide Ion. The foregoing considerations suggest that the formation reaction of triiodide ion in micellar solution will take place at the micellar surface, *i.e.*, between the iodine molecules solubilized in the surface region of DTAC micelle and the surrounding iodide ions in the close neighborhood of the micellar surface. Thus, if the inside and outside regions of micellar surface are denoted by suffix m and s respectively, the formation reaction of triiodide ion can be written as

$$I_{2,m} + I_s^- \rightleftharpoons I_{3,m}^-. \tag{1}$$

By taking into account the fact that the electrical potential at I_s^- is virtually identical with that at $I_{3,m}^-$, we can safely set the activity coefficient ratio of these ions equal to unity without introducing serious errors. Moreover, the activity coefficient of $I_{2,m}$ may probably be set equal to unity, since the total concentration of I_2 is sufficiently small as compared with that of DTAC under our experimental conditions. With this simplification, the intrinsic formation constant of triiodide ion may be written as

$$K_c = [I_3^-]_m/[I_2]_m[I^-]_s, \tag{2}$$

where the bracket represents an equilibrium concentration in moles per liter of the respective phase. Denoting the electrical potential at the micellar surface by ψ_0, the concentration of iodide ion near the micellar surface, $[I^-]_s$, can be described in terms of the apparent iodide ion concentration, $[I^-]_t$, as

$$[I^-]_s \exp(-e\psi_0/kT) = \gamma_-[I^-]_t, \tag{3}$$

where γ_- is the activity coefficient of the iodide ion. Since both iodine molecule and triiodide ion are solubilized in the same surface region of the DTAC micelle, their concentration ratio $[I_3^-]_m/[I_2]_m$ in Eq. 2 may be replaced by the ratio of the number of moles of solubilized triiodide ions per mole of iodine molecules. Therefore, if we denote an apparent concentration in moles of solubilized species per liter of solution by suffix t, we have

$$[I_3^-]_m/[I_2]_m = [I_3^-]_t/[I_2]_t. \tag{4}$$

Substitution of Eqs. 3 and 4 into Eq. 2 gives

$$K_c = K_a/\gamma_- \exp(e\psi_0/kT), \tag{5}$$

where K_a represents an apparent formation constant of triiodide ion defined by

$$K_a = [I_3^-]_t/[I_2]_t[I^-]_t. \tag{6}$$

It is worth noting here that in micellar solution the counterion concentration is a primary determinant of ψ_0 and γ_-. Accordingly, K_a can be regarded as constant at a given concentration of DTAC, because the iodide ion does not contribute appreciably to the total counterion concentration. Denoting $[I_3^-]_t$ by x, and the total concentrations of iodine and sodium iodide by a and b, we have

$$K_a = x/(a-x)(b-x). \tag{7}$$

Substituting $y=x/a$ and $z=b/a$, Eq. 7 may be rearranged to

$$y/(1-y) = K_a a(z-y). \tag{8}$$

Eq. 8 suggests that $y/(1-y)$ should be proportional to $(z-y)$. Since sodium iodide and DTAC do not show an appreciable absorption at 360 nm, the absorption coefficient of the solution, A, may be written as

$$A = \varepsilon_0(a-x) + \varepsilon_1 x = A_0 + (A_1-A_0)y \tag{9}$$

with

$$A_0 = \varepsilon_0 a, \qquad A_1 = \varepsilon_1 a, \tag{10}$$

where ε_0 refers to the molar absorption coefficient of iodine and ε_1 to that of triiodide ion, respectively. Equation 9 allows one to estimate the value of y as a function of b or z, with the knowledge of $\Delta A_\infty(=A_1-A_0)$ which corresponds to an increment in absorbance of a hypothetical solution in which iodine molecules are converted completely to triiodide ions. In order to estimate ΔA_∞, therefore, the increment in absorbance, $\Delta A(=A-A_0)$, was conveniently plotted against the reciprocal of sodium iodide concentration and was extrapolated to infinite iodide concentration. Using the value of y so determined, we can easily evaluate the apparent formation constant at a given

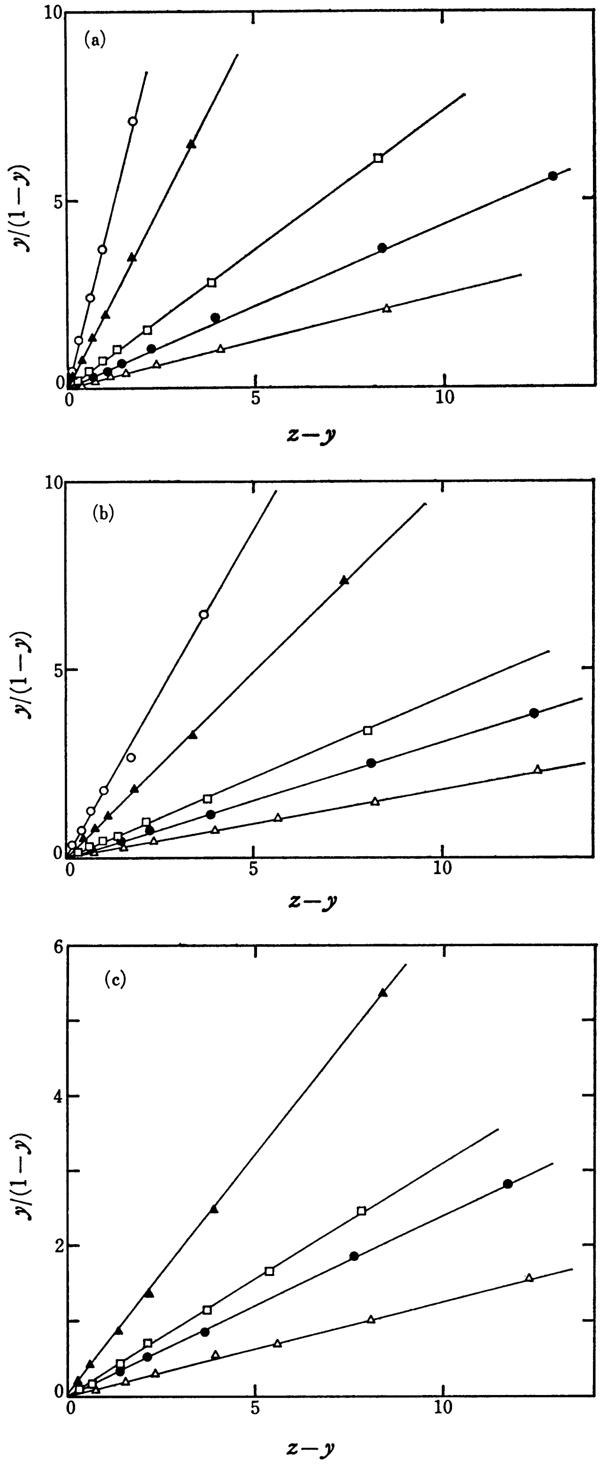

Fig. 2. The plot of $y/(1-y)$ *versus* $z-y$. (a): 21 °C, (b): 30 °C, (c): 40 °C; [DTAC] ○: 0.03, ▲: 0.04, □: 0.06, ●: 0.08, △: 0.13 mol dm^{-3}.

surfactant concentration from the slope of $y/(1-y)$ *versus* $(z-y)$ plots according to Eq. 8. Equation 5 then serves to estimate the intrinsic formation constant, K_c, provided that an appropriate expression is available for ψ_0.

Figure 2 shows $y/(1-y)$ *versus* $(z-y)$ plots at the given concentrations of iodine and surfactant. In all cases, the linearity of the plots is satisfactory over the whole concentration range of sodium iodide studied.

TABLE 1. THE APPARENT FORMATION CONSTANT OF TRIIODIDE ION IN DTAC MICELLAR SOLUTION

[DTAC] / mol dm^{-3}	$10^{-4}K_a$/mol^{-1} dm^3 (21 °C)	(30 °C)	(40 °C)
0.03	10.4	4.35	—
0.04	4.97	2.47	1.8
0.06	2.05	1.16	0.80
0.08	1.20	0.82	0.60
0.13	0.67	0.48	0.32

Standard deviation: 2% at 21 and 30 °C, 7% at 40 °C.

The values of K_a calculated from Eq. 8 are summarized in Table 1. According to Eq. 5, K_a should decrease with increasing surfactant concentration, since both ψ_0 and γ_- are decreasing functions with respect to surfactant concentration. This is the case for the present results. The value of K_a shown in Table 1 tends to decrease regularly with increasing DTAC concentration, reflecting the significant contribution of electrostatic term in Eq. 5. It should also be noted that even in the highest concentration of DTAC studied the observed values of K_a are much larger than those in water.

Information regarding the intrinsic formation constant of triiodide ion can now be obtained by introducing an appropriate expression for the electrical work, $e\psi_0$, into Eq. 5. To this end, we applied an expression based on the lamellar micelle with uniformly charged surface. It is well known that the lamellar model can account for most of the interesting features of ionic surfactant solutions, *e.g.*, the effect of added salt on CMC, and a linear dependence of log CMC on the number of carbon atoms, m, for the homologous series of surfactants described as[8]

$$\log \mathrm{CMC} = A - Bm. \tag{11}$$

In his theoretical study of ionic surfactant solutions, Shinoda[8] has derived the following expression for the effective electrical work, E_{el}, needed to introduce a unit charge e into the surface of a lamellar micelle, by taking into consideration the counterion fixation effect of a highly charged micellar surface.

$$E_{el} = K_g kT \ln(2000\pi\sigma^2/\varepsilon_r N_A kTC_g) \tag{12}$$

where, σ is the surface charge density, ε_r the relative permittivity of the solution, and C_g the total counterion concentration in equivalents per liter; other symbols than K_g have their usual meanings. For a given homologous series of surfactants, K_g is an experimental constant which can be correlated to the constant B in Eq. 11 by

$$B = \omega/2.303(1+K_g)kT, \tag{13}$$

where ω refers to the cohesive energy change involved in transferring one methylene group from a hydrocarbon environment to an aqueous medium.[8] The value of ω was estimated by Shinoda[9] to be $1.08\,kT$. By introducing the critical micelle concentrations reported for dodecyltrimethyl- and hexadecyltrimethylammonium chlorides,[10] K_g for alkyltrimethylammonium chloride may be estimated from Eqs. 11 and 13 to be 0.62 at 30 °C. It is to be noted that K_g is nearly

TABLE 2. THE FORMATION CONSTANT OF TRIIODIDE ION IN SOME SOLVENTS

Medium	K_c/mol^{-1} dm^3			ΔH/kJ mol^{-1}
DTAC	910 (21 °C)	650 (30 °C)	430 (40 °C)	−30
H_2O	1010 (9.5 °C)	730 (25 °C)	550 (38 °C)	−15.4
MeOH	13600 (20 °C)	10900 (31 °C)	9590 (39 °C)	−14.3
EtOH	28700 (17 °C)	20700 (28 °C)	15100 (39 °C)	−21.4

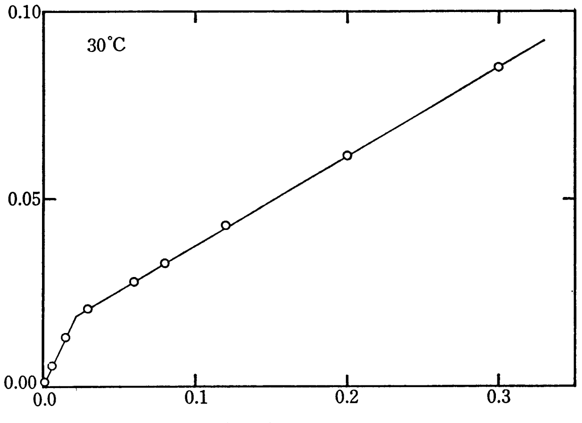

Fig. 3. The plot of chloride ion activity *versus* the total concentration of DTAC at 30 °C.

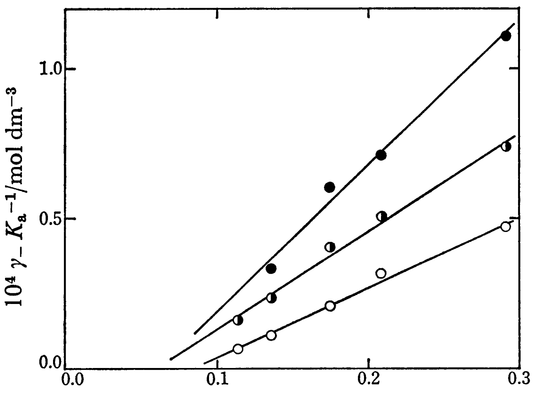

Fig. 4. The plot of γ_-/K_a *versus* $C_g{}^{0.62}$. ●: 40 °C, ◑: 30 °C, ○: 21 °C.

independent of temperature.[8)]

Substituting E_{el} for $e\psi_0$ in Eq. 5, we have

$$\frac{\gamma_-}{K_a} = \frac{1}{K_c}\left(\frac{\varepsilon_r N_A kT}{2000\pi\sigma^2}\right)^{K_g}(C_g)^{K_g}. \tag{14}$$

This equation implies that γ_-/K_a should be proportional to $(C_g)^{K_g}$ if surface charge density σ remains constant over the concentration range of DTAC studied. Though C_g in Eq. 14 can safely by replaced by the total concentration of DTAC, the use of this equation still requires a knowledge of the activity coefficient of an iodide ion in the presence of excess chloride ions, which is experimentally rather difficult to estimate. Therefore, on the assumption that the activity coefficient of iodide ion is equal to that of chloride ion, we made the potentiometric measurements of chloride ion activity in a solution of DTAC alone. Figure 3 shows the typical plot of chloride ion activity *versus* the total concentration of DTAC at 30 °C. Similar results were also obtained at different temperatures. In agreement with the results reported for counterion activities in solutions of various ionic surfactants,[11)] the observed chloride ion activity first increases almost linearly with increasing DTAC concentration up to CMC, then it continues to increase linearly but less steeply with further increases in DTAC concentration. According to the earlier assumption, this chloride ion activity divided by total DTAC concentration gives γ_- in Eq. 14. In Fig. 4, γ_-/K_a is plotted against $C_g{}^{0.62}$. As would be expected, the plots are linear, but the straight lines do not converge to the origin. At the present time, no conclusive explanation can be offered as to whether the observed deviation in the intercept comes from the underlying lamellar model which assumes an infinitely extended plane surface with uniform charge density or from the assumption of equal activity coefficients for iodide and chloride ions. In fact, the micellar aggregation number of DTAC was determined from a light scattering experiment to be 57 in 0.05 mol dm^{-3} sodium chloride solution.[12)] However, in view of the fact that the predicted linear relationship is found between γ_-/K_a and $C_g{}^{0.62}$, Eq. 14 can presumably be applied for a tentative estimation of the intrinsic formation constant of triiodide ion, K_c. On the basis of geometric considerations, Tanford[13)] has calculated the surface area per polar head group of micelle forming surfactant molecules, S, for various micelle shapes as a function of micellar aggregation number. According to his calculation for globular micelles, the micellar aggregation number of 57 corresponds to the value of S of 78 A^2. Substituting e/S for σ and assuming that S is independent of temperature, the values of K_c were tentatively estimated from the slopes of straight lines given in Fig. 4. The results are summarized in Table 2 together with those in various solvents.[1)] It should be emphasized that the value of K_c estimated above depends considerably on the selected value of S. For instance, it decreases up to 190 at 30 °C if we assume $S \approx 30$ A^2, which corresponds to the surface area per polar head group of a lamellar micelle.[13)] With these reservations in mind, the intrinsic formation constant of triiodide ion in DTAC micellar solution is expected to be comparable with or slightly less than that in water, but small enough as compared with those in alcohols. This result supports well the assumption that the formation reaction of the triiodide ion in the micellar solution will take place at a hydrophilic surface region of the micelle. Thus the remarkable increase in the apparent formation constant of triiodide ion may be ascribed to an increase in surface concentration of iodide ions due to the strong coulombic interaction between iodide ion and polyvalent micellar ion. Other factors seem to play at best a minor role.

Apart from a plausible estimation of K_c, we can easily evaluate the enthalpy change for Reaction 1 from the change in the slope of the straight line in Fig. 4 with temperature. As can be seen from Eq. 14, the enthalpy change so calculated is independent of the value of σ, so long as it remains constant over the temperature range studied.

It is worth noting that the enthalpy change in micellar solution shown in Table 2 is not only negative but about twice as large as that in water. Nevertheless, the values of K_c are nearly the same in both solvents. This implies that the formation reaction of triiodide ion in micellar solution is accompanied by an anomalous entropy decrease, contrary to the increases observed in water and alcohols.[1] The situation is somewhat complicated by the fact that in micellar solution both iodine molecule and triiodide ion are solubilized in the surface region of the micelle. It seems probable that the solubilized triiodide ions are restricted in their molecular motion through a strong coulombic interaction with highly charged micellar surface.

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