Kinetic Study of the Oxidation of Formate by Iodine in Micellar Solutions of Alkyltrimethylammonium Chlorides

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The spectrophotometric study was made of the oxidation of formate by iodine in micellar solutions of decyl- and dodecyltrimethylammonium chlorides. In the presence of the cationic surfactant micelles, the reaction was found to take place only at the micellar surface according to the same mechanism as in water. The experimental second-order rate constant rose steeply to a maximum at the critical micelle concentration and then decreased monotonously with increasing surfactant concentration. A tentative estimation based on a charged-phase separation model led to the true second-order rate constant in micellar phase of 0.03—0.07 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ at 30 °C, which is comparable with that in water. Thus the observed rate enhancement in cationic surfactant solutions can be interpreted in terms of an increase in surface concentration of the formate ion arising from an electrostatic interaction with the micellar ion. The micellar effects on the formation constant of triiodide ion are also discussed.

In a previous study of the iodine-formate reaction, $I_3^- + HCO_2^- \rightarrow 3I^- + H^+ + CO_2$, in alcohol–water mixed solvents, we confirmed that the reaction proceeds according to the following mechanism.[1)]

$$I_2 + I^- \overset{K}{\rightleftharpoons} I_3^-, \tag{1}$$

$$I_2 + HCO_2^- \xrightarrow{k_2} \text{Products}. \tag{2}$$

The second-order rate constant, k_2, was found to depend strongly on the dielectric property of the solvent,[1,2)] *e.g.*, it is larger by a factor of about 100 in ethanol than in water at 30 °C.[1)] Similar behavior was also observed for the formation constant, K, of triiodide ion.[3)]

It is well known that a number of organic reactions involving ionic species such as H^+ or OH^- are catalyzed by oppositely charged micellar ions.[4)] One might, therefore, expect that the presence of the cationic surfactant micelle would affect significantly the rate of the iodine-formate reaction through an electrostatic concentration of anionic species to the micellar surface and a possible medium effect of the micellar phase. In this connection, we have determined recently the apparent formation constant, K, of triiodide ion in micellar solution of dodecyltrimethylammonium chloride.[5)] It was found that the cationic surfactant micelle solubilizes not only iodine molecule but triiodide ion in its hydrophilic surface region consisting of ionic head groups and results in a remarkable increase in K.

The purpose of the present paper is to study the kinetic aspects of the iodine-formate reaction in micellar solutions of dodecyl- and decyltrimethylammonium chlorides, and to estimate the true rate constant in micellar phase.

Experimental

Materials. Dodecyltrimethylammonium chloride (DTAC) and decyltrimethylammonium chloride (DeTAC), both from Tokyo Kasei Kogyo Co. Ltd., were recrystallized twice from methanol. Other chemicals were of guaranteed grade. Sodium iodide was dried overnight at 100 °C prior to use. Iodine was purified further by sublimation. Sodium formate was purified by recrystallization from water.

Measurements. 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.[5)] This is also the case for DeTAC solution. Since in the presence of excess NaI the absorbance at 360 nm is proportional to I_2 concentration, the reaction rate was followed spectrophotometrically as a function of time by measuring the decrease in absorbance at 360 nm. The absorbance was measured with a Hitachi Spectrophotometer model 101 connected to a Valhalla Scientific Digital Multimeter model 4440. The pH and ionic strength of the solution were uncontrolled, because the rate of this reaction in water had been found to be independent of these factors.[1)]

The chloride ion activity and the apparent formation constant of triiodide ion in micellar solution of DeTAC were determined by the method described elsewhere.[5)]

The measurements were conducted at 21, 30, and 40 °C for DTAC solution and at 21, 30, and 37 °C for DeTAC solution, respectively.

Results and Discussion

Kinetics. In the present system, the micellar effect on the reaction rate is anticipated to arise primarily from an electrostatic interaction between the anionic species and the micellar ion. Therefore, all kinetic measurements were carried out under the conditions of $[\text{Surfactant}] \gg [I^-]$, $[HCO_2^-] \gg [I_2]$, in order to minimize the change in total counterion concentration which is a primary determinant of the electrical potential at the micellar surface. Under these experimental conditions, the reaction rate defined by Eq. 3 was found to be a first-order with respect to triiodide ion.

$$\text{Rate} = -d[I_3^-]_a/dt = k_a[I_3^-]_a \tag{3}$$

Here, the bracket with suffix a refers to the apparent concentration in moles per liter of solution and k_a to the apparent first-order rate constant, respectively. In Fig. 1 is shown the typical change in k_a with surfactant concentration at varying NaI concentrations. Similar results were also obtained at higher temperatures than 21 °C. Unfortunately, we were forced to make the kinetic measurements in the concentration range above the critical micelle concentration (CMC), since at lower surfactant concentrations below CMC the measurements were subject to interference from the precipitate composed presumably of iodine-surfactant complex.[5)] However, it is likely that the apparent

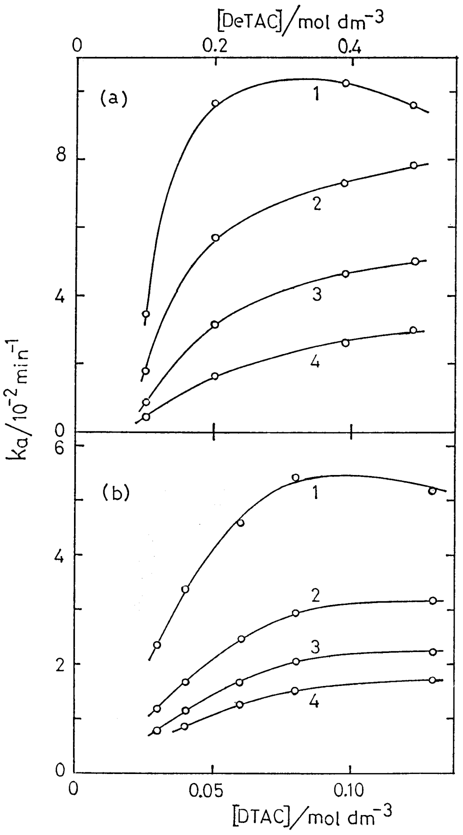

Fig. 1. Plots of the apparent first-order rate constant *vs.* total surfactant concentration at 21 °C.
(a) DeTAC solution containing 0.01 mol dm^{-3} NaHCO$_2$. [NaI]/10^{-3} mol dm^{-3}: 1; 0.188, 2; 0.375, 3; 0.751, 4; 1.50. (b) DTAC solution containing 0.006 mol dm^{-3} NaHCO$_2$. [NaI]/10^{-3} mol dm^{-3}: 1; 0.38, 2; 0.76, 3; 1.14, 4; 1.52.

first-order rate constant increases abruptly at surfactant concentration around CMC (2.1×10^{-2} mol dm^{-3} for DTAC and 8.7×10^{-2} mol dm^{-3} for DeTAC at 21 °C), though the magnitude of the increase depends regularly on NaI concentration. The k_a *versus* surfactant concentration profile resembles the results observed for micellar catalyzed organic reactions such as alkaline hydrolysis of esters in cationic surfactant solutions[4] in displaying a broad maximum or the leveling-off phenomenon above CMC.

Figure 2 shows the change in k_a with formate concentration at the given concentrations of surfactant and NaI. It can immediately be seen that k_a is directly proportional to the formate concentration, *i.e.*, $k_a = k'[\mathrm{HCO_2^-}]_a$. It should be noted here that the value of k' thus determined is still dependent on NaI concentration. In Fig. 3 is plotted the reciprocal of k' against iodide concentration at varying surfactant concentrations. An important feature of Fig. 3 is that the plot of $1/k'$ *vs.* iodide concentration gives a straight line with a small but definite intercept. Based upon these experimental results, the rate equation of the iodine-formate reaction in cationic surfactant solutions can reasonably be written as follows,

$$\mathrm{Rate} = -\frac{\mathrm{d}[\mathrm{I_3^-}]_a}{\mathrm{d}t} = \frac{k''[\mathrm{I_3^-}]_a[\mathrm{HCO_2^-}]_a}{1+K'[\mathrm{I^-}]_a}, \tag{4}$$

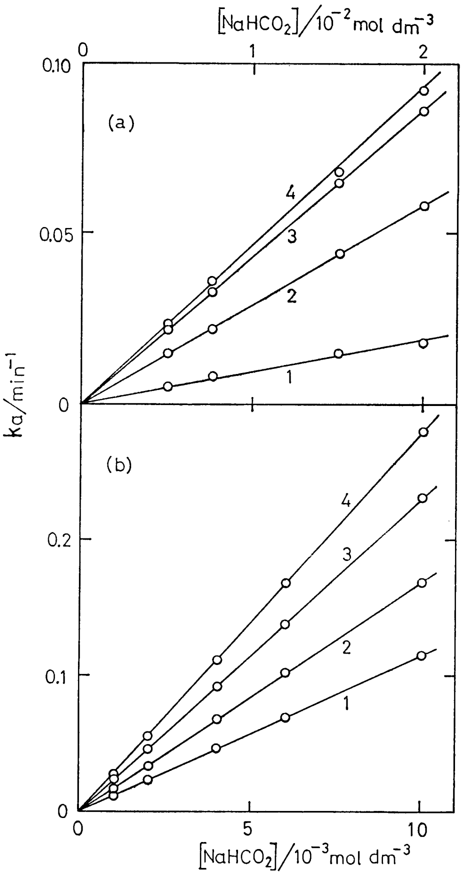

Fig. 2. Plots of the apparent first-order rate constant *vs.* sodium formate concentration at constant concentrations of surfactant and sodium iodide.
(a) DeTAC solution at 21 °C. [DeTAC]/mol dm^{-3} and [NaI]/10^{-3} mol dm^{-3}: 1; 0.10 and 0.75, 2; 0.20 and 0.83, 3; 0.39 and 0.83, 4; 0.49 and 0.85. (b) DTAC solution at 40 °C. [DTAC]/mol dm^{-3} and [NaI]/10^{-3} mol dm^{-3}: 1; 0.03 and 1.29, 2; 0.04 and 1.06, 3; 0.06 and 1.01, 4; 0.13 and 0.93.

$$k_a = \frac{k''[\mathrm{HCO_2^-}]_a}{1+K'[\mathrm{I^-}]_a}, \tag{5}$$

where k'' denotes the reciprocal of the intercept of the straight line in Fig. 3 and K' the ratio of slope to intercept of the same straight line, respectively. In the determination of these kinetic parameters, however, some inherent errors are unavoidable since the intercepts of the straight lines in Fig. 3 are considerably small. With this reservation in mind, we can estimate the change in k'' and K' with surfactant concentration. The results are summarized in Table 1.

The iodine-formate reaction in methanol–water and ethanol–water mixed solvents proceeds according to Eqs. 1 and 2 as described above.[1] We derived the following rate equation under the assumption that the reaction (1) is in pseudo-equilibrium.

$$\mathrm{Rate} = -\frac{\mathrm{d}[\mathrm{I_3^-}]_a}{\mathrm{d}t} = \frac{k_2[\mathrm{I_3^-}]_a[\mathrm{HCO_2^-}]_a}{1+K[\mathrm{I^-}]_a}. \tag{6}$$

Here, K refers to the formation constant of triiodide ion and k_2 to the rate constant for reaction (2) which is the rate determining step of the overall reaction, respectively. A comparison of Eq. 4 with Eq. 6 leads

TABLE 1. KINETIC PARAMETERS IN EQ. 4, AND THE APPARENT FORMATION CONSTANT OF TRIIODIDE ION IN MICELLAR SOLUTIONS OF DTAC AND DeTAC

Temp °C	[Surfactant] mol dm^{-3}	K' 10^4 mol^{-1} dm^3	k'' mol^{-1} dm^3 s^{-1}	K 10^4 mol^{-1} dm^3	k_2 mol^{-1} dm^3 s^{-1}
(a) DTAC solution					
21	0.03	10	2.5	10.4	2.64
	0.04	5.7	2.1	4.97	1.80
	0.06	2.1	1.1	2.05	1.11
	0.08	1.2	0.82	1.20	0.82
	0.13	0.86	0.65	0.67	0.51
30	0.03	4.3	3.8	4.35	3.89
	0.04	2.4	2.8	2.47	2.96
	0.06	1.2	1.8	1.16	1.84
	0.08	0.75	1.4	0.82	1.47
	0.13	0.47	0.90	0.48	0.90
40	0.03	2.4	6.5	—	—
	0.04	1.8	5.7	1.8	5.59
	0.06	0.87	3.7	0.80	3.42
	0.08	0.56	2.9	0.60	3.02
	0.13	0.30	1.7	0.32	1.85
(b) DeTAC solution					
21	0.10	4.7	0.56	6.09	0.726
	0.20	1.0	0.47	1.01	0.457
	0.39	0.38	0.30	0.37	0.287
	0.49	0.26	0.25	0.26	0.250
30	0.10	2.5	1.2	2.56	1.24
	0.20	0.61	0.93	0.74	1.14
	0.39	0.26	0.70	0.28	0.73
	0.49	0.20	0.61	0.22	0.68
37	0.10	1.4	1.4	1.97	1.97
	0.20	0.76	2.0	0.61	1.62
	0.39	0.25	1.2	0.26	1.19
	0.49	0.20	1.1	0.20	1.05

The values of K in DTAC solution are from Ref. 5.

immediately to the prediction that the iodine-formate reaction in surfactant solution will also proceed according to the same mechanism as in water. This, in turn, implies that k'' and K' in Eq. 4 have the same meaning as given hereinabove, *i.e.*, $k''=k_2$ and $K'=K$. It is in fact clearly shown in Table 1 that the values of K' estimated kinetically from Fig. 3 are virtually identical with the apparent formation constants, $K(=[I_3^-]_a/[I^-]_a[I_2]_a)$, of triiodide ion determined independently in solution of surfactant without formate ion. This fact enables us to evaluate more reliable values of k_2 from the relation, $k_2=K/$(the slope of the straight line in Fig. 3). The values of k_2 so determined are summarized in the last column of Table 1 and are plotted in Fig. 4 as a function of surfactant concentration. As would be expected, the agreement between k'' and k_2 is satisfactory. In view of the fact that the second-order rate constant, k_2, is much smaller in water than in surfactant solutions, the value of k_2 is considered to rise steeply to a maximum at CMC. At higher concentrations above CMC, k_2 tends to decrease monotonously with increasing surfactant concentration. It should be noted, however, that even in the highest surfactant concentrations studied, the values of k_2 are still large enough as compared with those in water (*cf.*, $k_2=0.068$ mol^{-1} dm^3 s^{-1} at 30 °C).[1] The qualitative feature of k_2 *versus* surfactant concentration plots in Fig. 4 is in accord with that predicted theoretically by Romsted[6] for second-order reactions between organic molecules and hydrophilic ions in micellar solutions.

Rate Constant in Micellar Phase. In the spectrophotometric determination of the formation constant of the triiodide ion in DTAC solution, we pointed out that both iodine molecule and triiodide ion are solubilized almost completely in the hydrophilic surface region of surfactant micelle and are in equilibrium with the surrounding iodide ions immediately adjacent to the micellar surface.[5] It is therefore highly probable that the iodine-formate reaction in cationic surfactant solutions takes place only at the micellar surface. Thus, if we denote the inside and outside regions of the micellar surface by suffix m and s, the reaction mechanism may be described as

$$I_{2,m} + I_s^- \overset{K_m}{\rightleftharpoons} I_{3,m}^- , \tag{7}$$

$$I_{2,m} + HCO_{2,s}^- \xrightarrow{k_m} 2I_s^- + CO_2 + H^+ , \tag{8}$$

where, K_m is the true formation constant of triiodide ion and k_m the true rate constant for reaction (8), both in micellar phase, respectively. The corresponding rate equation can immediately be derived from the analogy to Eq. 6.

$$-\frac{d[I_3^-]_m}{dt} = \frac{k_m[I_3^-]_m[HCO_2^-]_s}{1+K_m[I^-]_s} . \tag{9}$$

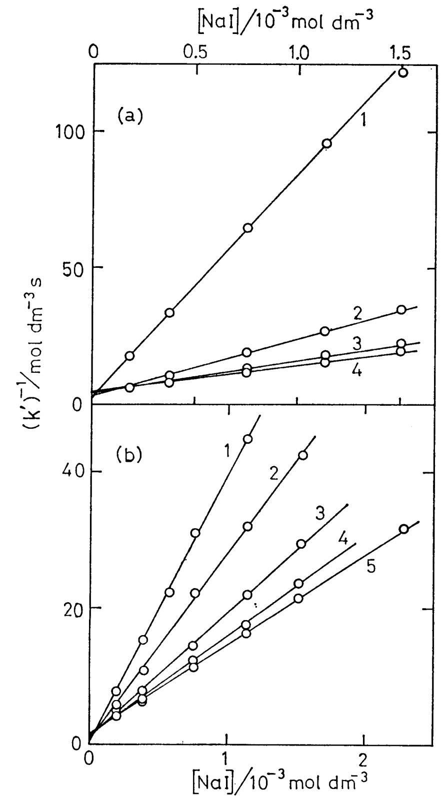

Fig. 3. Plots of $1/k'$ *vs.* sodium iodide concentration at 21 °C.
(a) DeTAC solution. [DeTAC]/mol dm^{-3}: 1; 0.10, 2; 0.20, 3; 0.39, 4; 0.49. (b) DTAC solution. [DTAC]/mol dm^{-3}: 1; 0.03, 2; 0.04, 3; 0.06, 4; 0.08, 5; 0.13.

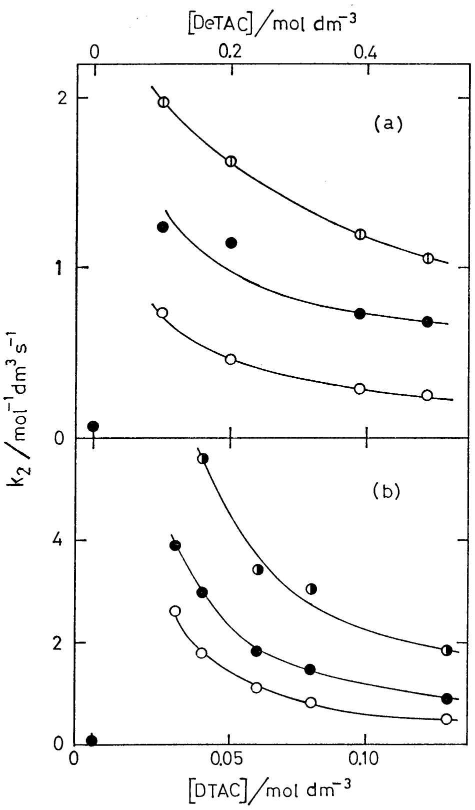

Fig. 4. Effect of the surfactant concentration on the second-order rate constant, k_2.
(a) DeTAC solution. ⦶; 37 °C, ●; 30 °C, ○; 21 °C. (b) DTAC solution. ◑; 40 °C, ●; 30 °C, ○; 21 °C.

Here, the bracket with suffix m or s represents the concentration in moles per dm^3 of the respective phase. Since almost all the triiodide ions are solubilized in the surface region of surfactant micelle as noted above, we have

$$\frac{1}{[I_3^-]_a}\frac{d[I_3^-]_a}{dt} = \frac{1}{[I_3^-]_m}\frac{d[I_3^-]_m}{dt}. \tag{10}$$

It follows, therefore, from Eqs. 3 and 9 that

$$k_a = \frac{k_m[HCO_2^-]_s}{1+K_m[I^-]_s}. \tag{11}$$

It is important to note here that both I_s^- and $I_{3,m}^-$ locate at the micellar surface with virtually uniform electrical potential. This means that the activity coefficient ratio of these ions can safely be ignored without loss of accuracy. With this simplification, K_m may be written as follows:

$$K_m = [I_3^-]_m/[I_2]_m[I^-]_s. \tag{12}$$

By taking into account a relationship, $[I_3^-]_m/[I_2]_m = [I_3^-]_a/[I_2]_a$, $K_m[I^-]_s$ in Eq. 11 can be replaced by $K[I^-]_a$. Equation 11 may accordingly be rewritten as

$$k_a = \frac{k_m[HCO_2^-]_s}{1+K[I^-]_a} = \frac{k_m[HCO_2^-]_a}{1+K[I^-]_a}\frac{[HCO_2^-]_s}{[HCO_2^-]_a}. \tag{13}$$

On converting k'' and K' in Eq. 5 to k_2 and K respectively and comparing it with Eq. 13, we have

$$k_2 = k_m[HCO_2^-]_s/[HCO_2^-]_a. \tag{14}$$

According to Eq. 14, the observed second-order rate constant, k_2, should be a decreasing function of surfactant concentration, since an increase in surfactant concentration is necessarily accompanied by a decrease in surface concentration of formate ion by virtue of surface potential depression. Indeed, the foregoing data shown in Fig. 4 are in accord with the prediction based on Eq. 14, reflecting that the coulombic interaction between formate and micellar ions is of primary importance in determining the rate constant, k_2, in surfactant solutions.

Equation 14 allows us to estimate the true rate constant, k_m, in micellar phase provided that an appropriate information is available for $[HCO_2^-]_s/[HCO_2^-]_a$. According to the common practice in theoretical treatment of the micellar catalysis,4,6,7) it is reasonable to assume that the distribution quilibrium of the formate ion between micellar surface and bulk phase is always established during the course of the reaction. If, therefore, the formate ion has no specific adsorption potential to the micellar surface, the ratio of surface concentration to apparent total concentration of the formate ion may be replaced by that of chloride ion. Thus, noting that $[Cl^-]_a$ is equal to the total surfactant concentration, C, we may write

$$k_2 = k_m C_{1,s}/C, \tag{15}$$

where suffix 1 refers to chloride ion. The usual treatments6,7) of micellar catalysis suppose that the counterion concentration in surface layer (Stern layer), $C_{1,s}$ is independent of total surfactant concentration

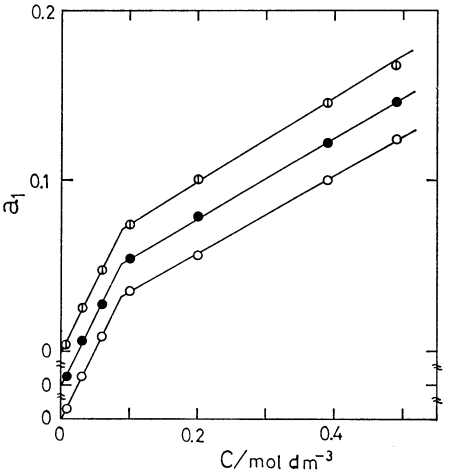

Fig. 5. Change in the chloride ion activity with DeTAC concentration at 37 °C (⦶), 30 °C (●), and 21 °C (○).

and is equal to β/LV, where β represents the degree of counterion association to the micelle, V the volume of Stern layer per micelle forming surfactant molecule in dm^3 and L the Avogadro constant, respectively. We can thus estimate the values of k_m by introducing an appropriate value of $C_{1,s}$ into Eq. 15, provided that the product of k_2 and C remains constant throughout whole surfactant concentration range studied. This is in fact the case for the DTAC solution, *i.e.*, the value of k_2C remains virtually constant and lies around 0.12 s^{-1} at 30 °C. However, the situation is somewhat complicated by the fact that in DeTAC solution the value of k_2C increases slightly but regularly with increasing surfactant concentration. In addition, the determination of k_m based on this treatment requires a knowledge of V which is experimentally rather difficult to estimate. For these reasons, we employed the following approach for the estimation of k_m.

Denoting the surfactant ion by suffix 2, the simple thermodynamic consideration leads immediately to the relations

$$kT\ln(C_{1,s}/\text{mol dm}^{-3}) - e\psi = kT\ln a_1, \tag{16}$$

$$\Delta\mu_2^{\ominus} + e\psi = kT\ln[a_2/(55.5/\text{mol dm}^{-3})] \tag{17}$$

where, ψ is the surface potential of the micelle, a_i the activity of i-th ion ($C^{\ominus}=1$ mol dm^{-3}) and $\Delta\mu_2^{\ominus}$ the standard free energy of transfer of surfactant ion from aqueous medium to micellar phase; other symbols have their usual meanings. Combining Eqs. 16 and 17, we have

$$C_{1,s} = (a_1a_2/55.5)\exp(-\Delta\mu_2^{\ominus}/kT). \tag{18}$$

Although a_1 and a_2 in Eq. 18 can both be measured potentiometrically as a function of surfactant concentration, the determination of the latter is not necessarily required, because the following relationship based on the phase separation theory[8] has been confirmed to hold in various ionic surfactant solutions.[9]

$$a_2a_1^{\beta} = \text{constant} = K_s \tag{19}$$

It follows, therefore, from Eqs. 15, 18, and 19 that

$$a_1^{1-\beta}/k_2 = (55.5C/k_mK_s)\exp(\Delta\mu_2^{\ominus}/kT) \tag{20}$$

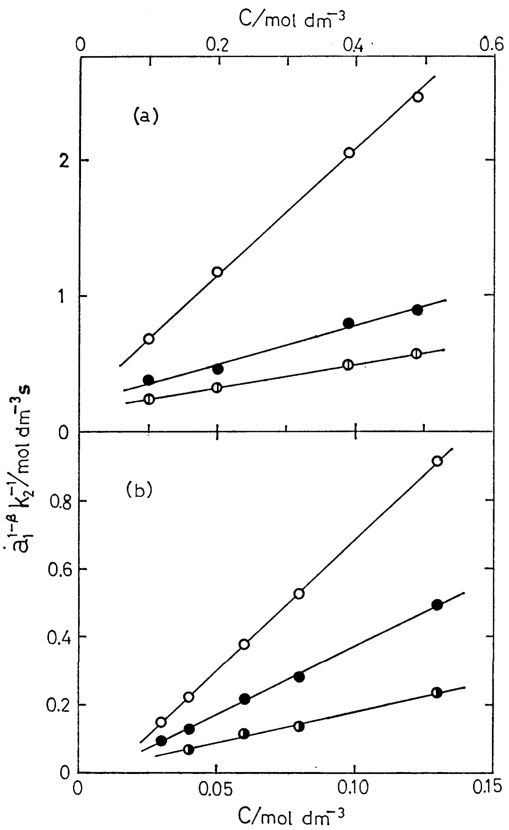

Fig. 6. Plots of the left-hand side of Eq. 20 *vs.* surfactant concentration.
(a) DeTAC solution. ○; 21 °C, ●; 30 °C, ⦶; 37 °C. (b) DTAC solution. ○; 21 °C, ●; 30 °C, ◑; 40 °C.

This implies that the left-hand side of Eq. 20 should be linearly dependent on total surfactant concentration. Information about β can easily be obtained from the concentration dependence of the chloride ion activity. In Fig. 5 is shown the plots of a_1 *vs.* C for DeTAC solution at varying temperatures. According to Botré *et al.*,[10] the slope of the straight line above CMC divided by the activity coefficient at CMC gives $1-\beta$. Using the values of β so determined for DeTAC and DTAC,[5] the left-hand side of Eq. 20 can now be plotted as a function of surfactant concentration. Figure 6 shows such plots at various temperatures. In accordance with Eq. 20, the plot is found to be linear in all cases studied. Since at CMC the surfactant ion activity is virtually identical with the chloride ion activity, a_1°, the value of K_s can safely be set equal to $(a_1^{\circ})^{1+\beta}$ with reasonable accuracy. In addition, the value of $\Delta\mu_2^{\ominus}$ was estimated by Shinoda[11] to be $-1.08\,kT$ per carbon atom in hydrocarbon chain at 25 °C. Introducing these values into Eq. 20 and ignoring the temperature dependence of $\Delta\mu_2^{\ominus}$, we can evaluate approximately the true rate constant, k_m, in micellar phase from the slope of the straight line in Fig. 6. The results are summarized in Table 2 together with the rate constants in various solvents.[1] The values of k_m in DTAC solution can also be obtained by estimating an appropriate value of V as described already. On the basis of geometric considerations for various micelle shapes, Tanford[12] has

TABLE 2. A COMPARISON OF THE ESTIMATED VALUES OF THE SECOND-ORDER RATE CONSTANT AND THE FORMATION CONSTANT IN MICELLAR PHASE WITH THOSE IN WATER AND ALCOHOLS

Solvent	Temp °C	β	k_m mol^{-1} dm^3 s^{-1}	K_m mol^{-1} dm^3
DTAC solution	21	0.76	0.020	230
	30	0.74	0.033	150
	40	0.73	0.061	90
DeTAC solution	21	0.73	0.023	190
	30	0.72	0.073	150
	37	0.72	0.12	140
Water			0.068(30 °C)[a]	730(25 °C)[b]
Methanol			3.2 (30 °C)[a]	10900(31 °C)[b]
Ethanol			7.8 (30 °C)[a]	20700(28 °C)[c]

a) From Ref. 1. b) From Ref. 3.

derived the relationship between the surface area per polar head group of micelle forming surfactant molecules, S, and the micellar aggregation number. According to his calculation for globular micelles, the micellar aggregation number of DTAC of 57[13] corresponds to S of 0.78 nm^2. With an additional assumption that the thickness of the Stern layer is of the order of the diameter of hydrated chloride ion (0.37 nm),[14] the value of $C_{1,s}$ $(=\beta/LV)$ is obtained as 4.3 mol dm^{-3} at 30 °C. Thus the use of Eq. 15 leads immediately to k_m of 0.028 mol^{-1} dm^3 s^{-1} at 30 °C. The result is in good agreement with that given in Table 2, indicating the validity of the present approach.

Apart from the detailed calculation of k_m, it is important to note that the estimated values of k_m are similar in magnitude to those in aqueous medium. This fact is consistent with the foregoing view that the iodine-formate reaction in cationic surfactant solutions will take place at the hydrophilic surface region of the micelle. It may thus be concluded that an increase in surface concentration of the formate ion arising from an electrostatic interaction with polyvalent micellar ion is the principal source of the rate enhancement of the iodine-formate reaction in cationic surfactant solutions. The environmental effect of ionic head groups on k_m seems to be, if any, negligibly small. Unfortunately, the values of k_m given in Table 2 are not of sufficient precision to permit the estimation of the activation parameters in micellar environments, since we ignored the temperature dependence of $\Delta\mu_2^{\ominus}$ in their computation. At the present stage, therefore, it is rather difficult to give any reasonable account of an appreciable dependence of k_m on surfactant chain length at higher temperatures.

Formation Constant in Micellar Phase. Expressions similar to Eqs. 15 and 20 must also hold for the apparent formation constant, K, of triiodide ion. Since $K_m[\mathrm{I}^-]_s$ is equal to $K[\mathrm{I}^-]_a$ as described already, the substitution of the ratio of surface concentration to apparent total concentration of iodide ion by that of chloride ion leads immediately to

$$K = K_m C_{1,s}/C \tag{21}$$

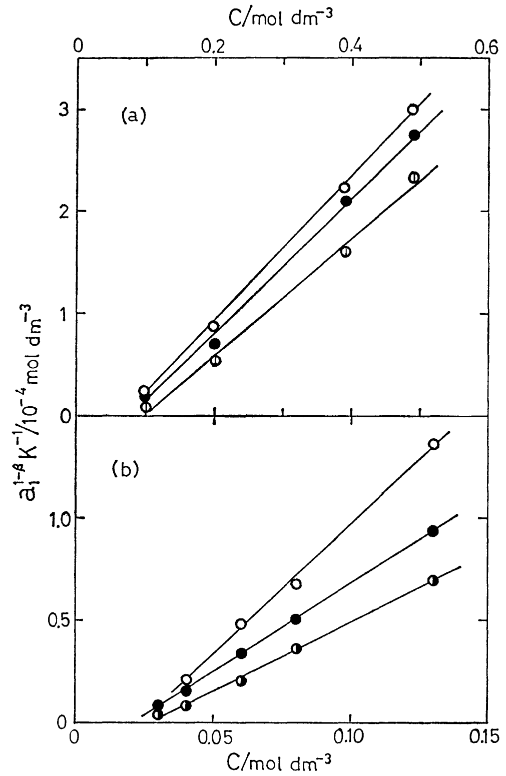

Fig. 7. Plots of the left-hand side of Eq. 22 *vs.* surfactant concentration.
(a) DeTAC solution. ⦶; 21 °C, ●; 30 °C, ○; 37 °C. (b) DTAC solution. ◑; 21 °C, ●; 30 °C, ○; 40 °C.

$$a_1^{1-\beta}/K = (55.5C/K_m K_s)\exp(\Delta\mu_2^{\ominus}/kT). \tag{22}$$

The resulting expression is noted to be identical with Eq. 20, except that k_2 and k_m are replaced respectively by K and K_m. In Fig. 7 is shown the predicted linear relationship between the left-hand side of Eq. 22 and total surfactant concentration. We can thus estimate the true formation constant, K_m, of triiodide ion in micellar phase from the slope of the straight line in Fig. 7. The results are summarized in the last column of Table 2. For the sake of comparison, the formation constants in various solvents[3] are also included in this table. The fact that the true formation constants are comparable with those in water provides an additional evidence for the occurrence of the iodine-formate reaction at the hydrophilic surface region of the micelle. Thus the marked increase in an apparent formation constant shown in Table 1 is concluded to result predominantly from an increase in surface concentration of the iodide ion due to coulombic interaction with the micellar ion.

In a previous study of K_m in DTAC solution,[5] we applied an expression derived by Shinoda[15] for the surface potential of the lamellar micelle. The only drawback of the treatment was the lack of reliable information about S. For example, a tentative calculation based on S=0.78 nm^2 gave K_m of 650 mol^{-1} dm^3 at 30 °C. On the other hand, the use of S=0.30 nm^2 which corresponds to a lamellar micelle model[12] led to K_m of 190 mol^{-1} dm^3 at 30 °C. It is true that the latter value is in fair agreement with K_m estimated above from Eq. 22, but we must keep in mind that small errors in the estimation of $\Delta\mu_2^{\ominus}$ causes an appreciable change in K_m. It is, thus, highly probable that the reliable value of K_m in DTAC solution lies somewhere between 150 and 650 mol^{-1} dm^3 at 30 °C.

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