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Effect of Surfactant Micelles on the Rate of Reaction of Tetranitromethane with Hydroxide Ion

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The rates of trinitromethanide anion formation by the reaction of tetranitormethane with hydroxide ion were measured in the presence of anionic, cationic and nonionic surfactant micelles in aqueous solutions. Using the analytical approach which takes into consideration the distribution of hydrophobic reactants among micelles,[1] k_1 (a second-order rate constant on micelles associated with one reactant molecule) and K_1/N(K_1: an association constant of the reactant with micelles having no reactant, N: an aggregation number of surfactant molecule in a micelle) were estimated. The anionic surfactant exhibited no effect on the reaction rate. In the case of cationic surfactants, both k_1 and K_1 values increased not only with alkyl chain length but also with hydrophobicity of the surfactants. In the case of nonionic surfactants, an increase of alkyl chain length with a given oxyethylene unit resulted in an increase in the k_1 values, while an increase of oxyethylene group with the fixed alkyl chain length resulted in an appearance of the maximum k_1 value. From temperature dependence of the reaction rate, a stabilization of the activated complex could be explained by an electrostatic interaction of the complex with the charged micellar surface. It was also found from the analytical approach that the distribution of tetranitromethane among micelles used in the present experiment could be approximated by the Poisson distribution.

Surfactant molecules aggregate to form micelles in aqueous solution above a narrow concentration range which is called the critical micelle concentration (CMC).[2] The hydrophobic groups of surfactant form a core of micelle which is liquid hydrocarbon like in character, while the hydrated polar groups constitute an outer shell of micelle and contact with water. Physico-chemical properties of the micelle-bulk interface and an interior of micelles have been really interested not only from the colloid chemistry itself but also from an application of micelles to other fields of chemistry. Especially, the application to a medium or catalyst for organic reactions has been undertaken since the pioneering work by Duynstee and Grundwald in 1959.[3] Then, for more than a decade many studies have been reported on micelle-catalyzed reactions.[4]

The reactions of tri- and tetranitromethane with hydroxide ion were minutely investigated in both aqueous[5–7] and micellar[8] solutions. However, there have been few systematic studies of the effect of surfactant structures, particularly of nonionic surfactant, on the reaction rate. In the present study, the rates of trinitromethanide anion formation by the reaction of tetranitromethane with hydroxide ion were measured in the presence of various surfactants in aqueous solutions. Hereupon, the dependence of the reaction rate on surfactant structure was systematically investigated. Furthermore, in order to find the relationship of stability of the activated complex with kinds of surfactant structures, a temperature effect on the rate was pursued. In addition, the distribution of tetranitromethane among micelles was also examined by applying the random, Poisson, and Gaussian distributions.

Experimental

Materials. Tetranitromethane (TNM) supplied from Tokyo Kasei Ind. was washed three to five times with 0.8 mol dm^{-3}-H_2SO_4, and subsequently five times with double-distilled water. TNM was recrystallized from water below 10 °C and the supernatant was discarded. After these treatments, no absorption of trinitromethanide anion was found at 350 nm in an aqueous solution of TNM. Anionic surfactant, sodium dodecyl sulfate SDS, was synthesized and purified according to the procedure described previously.[9] Cationic surfactants (decyltrimethylammonium chloride DeTAC, dodecyltrimethylammonium chloride DoTAC, hexadecyltrimethylammonium chloride HTAC, hexadecyltrimethylammonium bromide HTAB, *N*-hexadecylpyridinium chloride HPC, benzylhexadecyldimethylammonium chloride BHAC (all obtained from Tokyo Kasei Ind.)) were recrystallized three times from acetone–ethanol mixture in which the volume fraction of ethanol was below 0.1. Hexadecyltrimethylammonium nitrate HTAN was prepared by refluxing HTAB with an excess of silver nitrate in anhydrous methanol for several hours, and the precipitated silver salts were removed by filtration. The above procedure was repeated twice. The HTAN thus prepared was recrystallized three times from acetone. For all cationic surfactants, small amount of residual solvents on recrystallization were eliminated by heating at 100 °C under reduced pressure for more than ten hours. They were always kept in a desiccator because of their hygroscopicity. All nonionic surfactants, poly(oxyethylene) alkyl ether C_mE_n were a gift from Kao Soap Co. and were used without further purification.[10] The details of these surfactants are given in Table 1 together with their CMCs in pure water and in the reaction systems, which were determined by the plots of surface tension against concentrations. Inorganic salts of reagent grade used for adjusting pH, commercial NH_4Cl, NH_4NO_3, and NH_4Br, were purified by recrystallization from water before use.

Method. The reaction of TNM with hydroxide ion was started by injecting an aliquot of aqueous solution of TNM into alkaline surfactant solutions. The reaction rates were followed spectrophotometrically (Beckman-Toshiba DSB-80) by measuring the rate of trinitromethane anion formation at 350 nm ($\varepsilon\{C(NO_2)_3^-\}=1.34\times10^4$ dm^3 mol^{-1} cm^{-1}).[8] The temperature was controlled at 30±0.1 °C by circulating water through the equipment. The initial concentration of TNM (*ca.* 5×10^{-5} mol dm^{-3}) in the individual run was estimated from the optical density at 350 nm at infinite time. The pseudo first-order rate constant k^{obsd} was determined from the slope of linear plots of log(OD_∞—OD_t) against time in the usual manner, where OD_∞ and OD_t represent the optical density due to trinitromethanide anion at infinite time and time t, repectively. The adjustment of pH was made using an NH_3–NH_4^+ buffer whose

Table 1. CMC values of surfactants used in the present study

Surfactant	Abbrev.	CMC/mol dm^{-3} a)	
Cationic		(A)	(B)
$C_{10}H_{21}N^+(CH_3)_3Cl^-$	DeTAC	8.0×10^{-2}	7.7×10^{-2}
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	DoTAC	2.3×10^{-2}	1.7×10^{-2}
$C_{16}H_{33}N^+(CH_3)_3Cl^-$	HTAC	1.3×10^{-3}	9.3×10^{-5}
$C_{16}H_{33}N^+(CH_3)_3Br^-$	HTAB	9.4×10^{-4}	1.0×10^{-4}
$C_{16}H_{33}N^+(CH_3)_3NO_3^-$	HTAN	8.5×10^{-4}	1.0×10^{-4}
$C_{16}H_{33}N^+C_5H_5Cl^-$	HPC	1.0×10^{-3}	8.2×10^{-5}
$C_{16}H_{33}N^+(CH_3)_2CH_2\phi Cl^-$ b)	BHAC	2.5×10^{-4}	1.2×10^{-5}
Nonionic		(C)	(D)
$C_8H_{17}O(C_2H_4O)_6H$	C_8E_6	8.9×10^{-3}	
$C_{10}H_{21}O(C_2H_4O)_6H$	$C_{10}E_6$	7.3×10^{-4}	
$C_{12}H_{25}O(C_2H_4O)_6H$	$C_{12}E_6$	6.7×10^{-5}	6.0×10^{-5}
$C_{12}H_{25}O(C_2H_4O)_{10}H$	$C_{12}E_{10}$	9.0×10^{-5}	9.0×10^{-5}
$C_{12}H_{25}O(C_2H_4O)_{15}H$	$C_{12}E_{15}$	1.3×10^{-4}	1.2×10^{-4}
$C_{12}H_{25}O(C_2H_4O)_{20}H$	$C_{12}E_{20}$	1.8×10^{-4}	1.6×10^{-4}
$C_{12}H_{25}O(C_2H_4O)_{29}H$	$C_{12}E_{29}$	2.6×10^{-4}	2.6×10^{-4}
Anionic			
$C_{12}H_{25}OSO_3^-Na^+$	SDS	8.2×10^{-3}	

a) (A) in pure water at 30 °C, (B) in the reaction system at 30 °C, (C) reference data at 30 °C[23], (D) in pure water at 20 °C. b) ϕ: C_6H_5.

ionic strength was maintained at 0.03; NH_4Cl–aqueous ammonia for anionic and nonionic surfactant solutions, and NH_4X–aqueous ammonia for the micellar solutions of cationic surfactant whose gegenion is X. The pH of the reacting solutions was confirmed not to be changed before and after the reaction.

Results and Discussion

The reaction of TNM with hydroxide ion is represented by:[6]

$$C(NO_2)_4 + OH^- \xrightarrow{k} C(NO_2)_3^- + HNO_3, \qquad (1)$$

where k is the second-order rate constant. The reaction rate is expressed by:

$$-[C(NO_2)_4]/dt = k[C(NO_2)_4][OH^-]. \qquad (2)$$

Since the pH in each solution is kept constant in an alkaline side by a given buffer, $[OH^-]$ remains constant during the course of reactions. Thus, the reaction obeys the following pseudo first-order kinetics:

$$-d[C(NO_2)_4]/dt = k^{obsd}[C(NO_2)_4] \qquad (3)$$

and

$$k = k^{obsd}/[OH^-]. \qquad (4)$$

From Eq. 3 we obtain the following relation:

$$OD_\infty - OD_t \propto [C(NO_2)_4]_t = [C(NO_2)_4]_0 \exp(-k^{obsd}t), \qquad (5)$$

where $[C(NO_2)_4]_0$ and $[C(NO_2)_4]_t$ represent the concentration of TNM at $t=0$ and t, respectively. The rate constant k^{obsd} increases linearly with hydroxide ion concentration and the linearity is very good. Then, the second-order rate constant k is determined from the slope of linear plots of k^{obsd} against $[OH^-]$ whose linearity is good. The second-order rate constant k thus obtained in the absence of surfactant at 30 °C was calculated to be 0.38 dm^3 mol^{-1} s^{-1}, which seems reasonable compared with 0.52 dm^3 mol^{-1} s^{-1} at 30 °C and at ionic strength of 0.1[8] and with 0.65 dm^3 mol^{-1} s^{-1} at 30 °C and at ionic strength 1.0.[7]

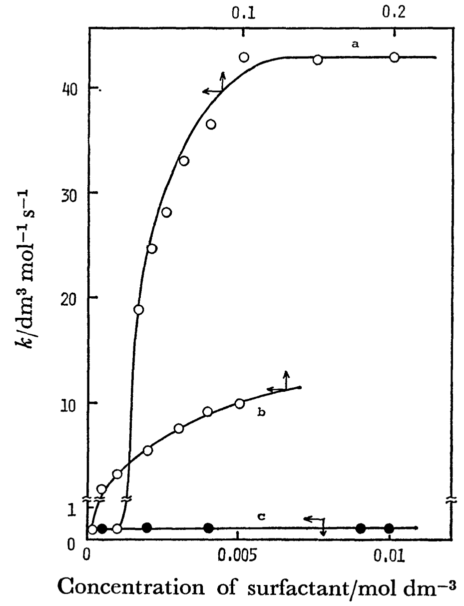


Fig. 1. Effect of surfactant type on the second-order rate constant(k). The variation of k values with surfactant concentrations.
a): DoTAC, b): $C_{12}E_6$, c): SDS.

In the first place, the effect of structure of surfactant on the reaction rate was examined using C_{12} surfactants, DoTAC, SDS, and $C_{12}E_6$ (Fig. 1). SDS had no effect on the reaction rate, while DoTAC and $C_{12}E_6$ brought about an increase in the rate constant with increasing their concentrations.[11–15] From these results, it can be considered that the increase in k

values in the presence of cationic micelles of DoTAC is attributable mainly to the concentration of hydroxide ion in the vicinity of cationic head groups of micelle.

Secondly, in order to understand the above differences on account of surfactant types, further analysis was made using the following reaction mechanism. The reactions take place both in a bulk solution and in micelles. The apparent increase in reaction rate above CMC is mainly due to the presence of micelles. For simplifying the reaction systems, the following assumptions are made; 1) the reactants associate with micelles to form some distribution among micelles and 2) the rate of the association which is of millisecond order is much faster than those of the reactions in both bulk and micellar phases which are of second order. With these assumptions the following reaction scheme which was adopted in the preceeding paper[1] is used to study the present reaction system:

$$\begin{array}{ll} \mathrm{M} + \mathrm{R} \overset{K_1}{\rightleftharpoons} \mathrm{MR}_1 \xrightarrow[\mathrm{OH}^-]{k_1} \mathrm{P} & \\ k_\mathrm{b} \Big\downarrow \mathrm{OH}^- \quad \mathrm{MR}_1 + \mathrm{R} \overset{K_2}{\rightleftharpoons} \mathrm{MR}_2 \xrightarrow[\mathrm{OH}^-]{k_2} \mathrm{P} + \mathrm{MR}_1 & \\ \mathrm{P} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & (6) \\ \quad \mathrm{MR}_{n-1} + \mathrm{R} \overset{K_n}{\rightleftharpoons} \mathrm{MR}_n \xrightarrow[\mathrm{OH}^-]{k_n} \mathrm{P} + \mathrm{MR}_{n-1}. & \end{array}$$

In the above scheme, M, R, MR_i, and P represent micelle, monomer reactant(TNM), micelle with i reactant molecules, and product(trinitromethanide anion), respectively. K_i is the association constant of monomer reactant with MR_{i-1} micelle, and k_b and k_i are the second-order rate constant in the bulk solution and on the MR_i micelle, respectively. The apparent second-order rate constant for the reaction of TNM with hydroxide ion, k^app, is represented in the following way:

$$\begin{aligned} -\mathrm{d}[\mathrm{R_t}]/\mathrm{d}t &= k^\mathrm{app}[\mathrm{R_t}][\mathrm{OH^-}] \\ &= \{k_\mathrm{b}[\mathrm{R}] + \sum_{i=1}^{n} k_i[\mathrm{MR}_i]\}[\mathrm{OH^-}], \end{aligned} \tag{7}$$

where k^app is $k^\mathrm{obsd}/[\mathrm{OH^-}]$ and $[\mathrm{R_t}]$ represents the total equivalent concentration of reactant and is given by:

$$[\mathrm{R_t}] = [\mathrm{R}] + \sum_{i=1}^{n} i[\mathrm{MR}_i]. \tag{8}$$

On the other hand, the total micellar concentration $[\mathrm{M_t}]$ can be expressed by the following equation:

$$[\mathrm{M_t}] = (C_\mathrm{t} - \mathrm{CMC})/N, \tag{9}$$

where C_t and N represent the total equivalent surfactant concentration and an aggregation number per micelle, respectively. Eq. 10 or 11 results from the Poisson distribution of reactants,[1]

$$\frac{1}{k^\mathrm{app} - k_\mathrm{b}} = \frac{1}{k_1 - k_\mathrm{b}} + \frac{N}{K_1(k_1 - k_\mathrm{b})} \times \frac{1}{C_\mathrm{t} - \mathrm{CMC}}, \tag{10}$$

$$\frac{k^\mathrm{app} - k_\mathrm{b}}{k_1 - k^\mathrm{app}} = \frac{K_1}{N} \times (C_\mathrm{t} - \mathrm{CMC}). \tag{11}$$

In this case the plots of $1/(k^\mathrm{app} - k_\mathrm{b})$ against $1/(C_\mathrm{t} - \mathrm{CMC})$ should be linear, and k_1 and k_1/N values can be determined from the intercept and the slope. At the same time some information on reactant distribution among micelles could be also obtained.[1] The k_1 values thus obtained are given in Table 2. From the consideration described in the preceeding paper, it can be said that the k_1 value of DoTAC is much larger than that of $\mathrm{C_{12}E_6}$ and the reactant distribution is very likely to be the Poisson distribution. Further discussion will be given more in detail in the following sections which describe the effect of the cationic and nonionic surfactants and the temperature effect on the reaction rates.

TABLE 2. SECOND-ORDER RATE CONSTANT (k_1) FOR NITROFORM ANION FORMATION, AND THE ASSOCIATION PARAMETER (K_1/N) AND THE ROUGHLY ESTIMATED ASSOCIATION CONSTANT (K_1) OF TNM WITH THE MICELLES

Surfactant	$k_1 \times 10^{-2}$ / $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	$K_1/N \times 10^{-1}$ / $\mathrm{dm^3\,mol^{-1}}$	$K_1 \times 10^{-2}$ / $\mathrm{dm^3\,mol^{-1}}$
Cationic			
DeTAC	0.33	1.17	3
DoTAC	0.56	3.2	12
HTAC	2.28	8.9	54
HTAB	1.76	5.5	44
HTAN	1.27	6.1	48
HPC	1.52	10.9	71
BHAC	2.67	18.3	>150
Nonionic			
$\mathrm{C_8E_6}$	0.044	2.93	9
$\mathrm{C_{10}E_6}$	0.104	1.82	17
$\mathrm{C_{12}E_6}$	0.171	1.03	48
$\mathrm{C_{12}E_{10}}$	0.67	0.70	12
$\mathrm{C_{12}E_{15}}$	0.50	0.83	10
$\mathrm{C_{12}E_{20}}$	0.289	0.55	4
$\mathrm{C_{12}E_{29}}$	0.142	1.60	9

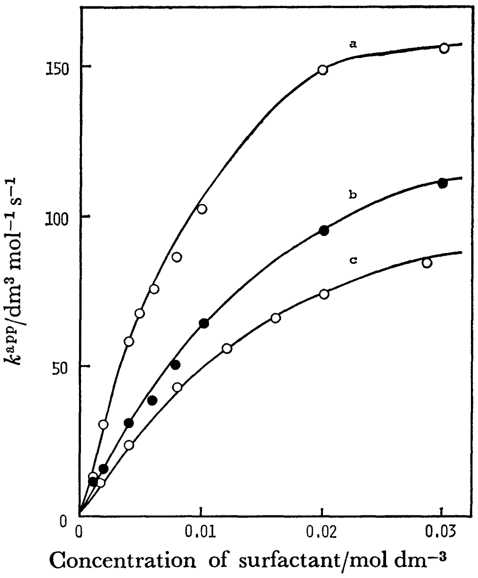


Fig. 2. Effect of the kind of counterion of the cationic surfactants (HTAC(a), HTAB(b), and HTAN(c)) on the apparent second-order rate constant(k^app). Plots of k^app against the surfactant concentrations.

(1) The Reaction Rates in the Presence of Cationic Surfactants: The k^app *vs.* concentration relationship of HTAN, HTAB, and HTAC micelles are plotted in

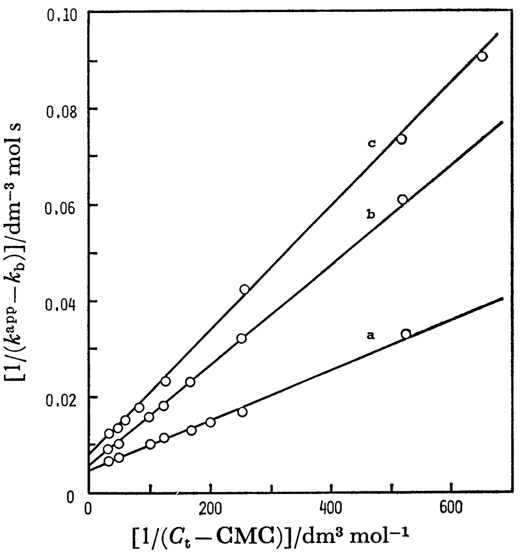


Fig. 3. Determination of the k_1 and K_1/N values from the linearity plots of $1/(k^{\mathrm{app}}-k_{\mathrm{b}})$ against $1/(C_{\mathrm{t}}-\mathrm{CMC})$. a): HTAC, b): HTAB, c): HTAN.

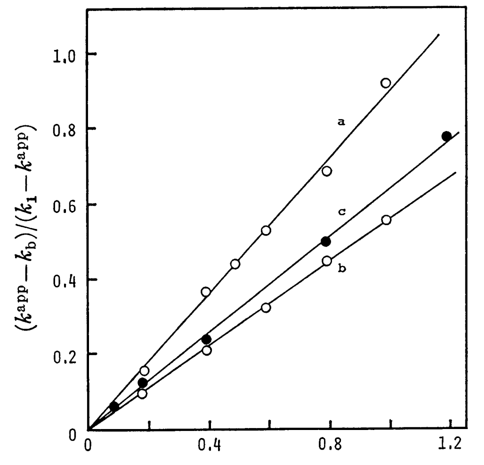


Fig. 4. Determination of the K_1/N vaules from the linearity plots of $(k^{\mathrm{app}}-k_{\mathrm{b}})/(k_1-k^{\mathrm{app}})$ against $(C_{\mathrm{t}}-\mathrm{CMC})$.
a): HTAC, b): HTAB, c): HTAN.

Fig. 2 where some differences owing to counterions are clear. In order to make clear a reason for these differences and to take an insight into the reactant distribution, another plots are given in Fig. 3, relating $1/(k^{\mathrm{app}}-k_{\mathrm{b}})$ to $1/(C_{\mathrm{t}}-\mathrm{CMC})$. Judging from the linearity of these plots shown in Fig. 3, the Poisson distribution is well applicable to these reaction systems within experimental error. The k_1 and K_1/N values obtained in this way are given in Table 2. Equation 11 predicts that the plots of $(k^{\mathrm{app}}-k_{\mathrm{b}})/(k_1-k^{\mathrm{app}})$ against C_{t} should be linear and also determine k_1/N values (Fig. 4). The disadvantage of using Eq. 11 is due to a large uncertainty in the value of either numerator or denomenator when k^{app} is nearly equal to k_{b} or k_1; thus, the useful values are limited to the region of marked increase in k^{app} values. The values of k_1 and K_1/N thus obtained characterize the properties of each micelle.

The k_1 values decrease in the order HTAC>HTAB>HTAN. In these reaction systems, hydroxide ions compete with the surfactant counterions in approaching to charged micellar surface through the electrostatic interaction. In regard to the counterions of surfactants, the hydration radius of the ions decreases in the order $\mathrm{Cl}^->\mathrm{Br}^->\mathrm{NO}^-_3$. That is, the strength of their electrostatic attraction with the charged micelle increases in the order $\mathrm{Cl}^-<\mathrm{Br}^-<\mathrm{NO}^-_3$, which reflects the CMC order (Table 1). In other words, the stronger their electrostatic attraction, the less the electrostatic surface potential of micellar surface. Therefore, it is reasonable to say that the counterions interfere with approach of hydroxide ions to the micellar surface in the order HTAC<HTAB<HTAN. On the other hand, the values of K_1/N decrease slightly in the order HTAC>HTAN>HTAB. For CMC decreases in the order HTAC>HTAB>HTAN, the aggregation number of the micelles may slightly increase in the order HTAC<HTAB<HTAN. Therefore, the large difference is not found in the K_1 values of these cationic surfactants. The K_1 values are about 4—6$\times10^3$ dm^3 mol^{-1}.

Next, the effect of the cationic surfactant micelles with different alkyl chain lengths but with the same head group, DeTAC, DoTAC, and HTAC, is examined in order to see the effect of the aggregation number of micelle. The k_1 values (Table 2) increase with increasing alkyl chain length of the surfactants, *i.e.*, with increasing aggregation number of micelle. This increase in the order is mainly due to the increase in electrical surface potential of the micelle in the above order which can be reasoned by analogy of anionic surfactant micelles[16] and partially due to an increase of hydrophobicity of palisade layer of micelle in the above order. Thus, the hydroxide ion concentration of vicinity of the micellar surface is expected to increase with increasing the aggreagation number. The large difference in the k_1 values, however, can not be explained only with the difference in surface potential of the micelles.[16] This must be considered in relation with the K_1/N values. The K_1/N values, on the other hand, increase in the order DeTAC<DoTAC<HTAC, notwithstanding the same order in the aggregation number (*ca.* 36, 50, and 80 for DeTABr, DoTABr, and HTABr, respectively,[17] and these values do not change so much by replacing Br$^-$ by Cl$^-$; 38 for DoTAC[18]). This means that the K_1 value of TNM for HTAC micelles is about 20 times as large as that of DeTAC. Such a large difference is likely to come from a difference of the location of TNM in the micelles. The roughly estimated K_1 values are given in Table 2. Smaller aggregation number of micelle results in looser palisade layer of micelle, and the hydrophobic reactant is in an innermore part of micelle. Therefore, the effective area for the reactant to sit in micelle becomes less for shorter chain surfactant, which corresponds to a smaller K_1 value. On the other hand, the HTAC micelles have a larger aggregation number as well as a more rigid palisade layer, and the location of TNM must be an outer part of the micelles. This results in a closer contact between TNM and OH$^-$

ion, a higher value of k_1. The larger effective area thus available for the reactant location leads to larger K_1 value. Thus, the large difference in k_1 values between DeTAC and HTAC results from not only the difference in micellar surface potential term but also the difference of the location of TNM in the micelles.

Finally, in order to confirm the above consideration concerning location site of reactants in micelles, the effect of difference of ionic head groups on the reaction rates was examined using HTAC, HPC, and BHAC micelles. Almost the same aggregation number of HTAC and HPC can be deduced from their CMC values (87 for HPBr). The samller k_1 value of HPC, however, results from a large distance between solubilized TNM and OH^- ion in HPC micelles due to interposition of pyridine ring between them. In the case of BHAC micelle both k_1 and K_1/N values are larger than those of the other micelles in spite of the smaller CMC. This result rests on a more hydrophobic nature of outermost part of the micelle. Therefore, the probability for TNM to sit on an outer part of the micelle increases; this should be the main reason for their increase in BHAC micelles.

From these results, we would like to stress that the reaction rate increase in the presence of cationic surfactant micelles is owing mainly to the hydroxide ion concentration near the cationic micellar surface and that the location of reactants in micelle has a strong influence on the reaction rate.

(2) The Reaction Rates in the Presence of Nonionic Surfactants. As is shown in Fig. 1, the nonionic surfactant also increases the reaction rate. Then, in the first place, an effect of alkylchain length on the reaction rate was examined using the surfactants of C_8E_6, $C_{10}E_6$, and $C_{12}E_6$. The k_1 values increase with increasing alkyl-chain length of the nonionic surfactants, or with increasing aggregation number of micelle, in a similar way as the case of cationic surfactants. On the other hand, the K_1/N values decrease with increasing alkyl-chain length. In the case of nonionic surfactants, the aggregation number of micelle in pure water (30, 100, and 460 at 30 °C for C_8E_6, $C_{10}E_6$, and $C_{12}E_6$, respectively[19]) will remain almost unchanged in the buffer solution of such low ionic strength as 0.03.[19] The roughly estimated K_1 values of these surfactants using the above aggregation number are given in Table 2, too. Contrary to the order of the K_1/N values, the K_1 values thus obtained increase with increasing alkyl-chain length of the surfactants. This increase can also be understood from the view point of an available area of the reactant solubilized. From comparison between cationic and nonionic surfactants with an identical alkylchain length, *e.g.* $C_{10}E_6$ and DeTAC or $C_{12}E_6$ and DoTAC, the k_1 values of the cationic surfactants are almost three times as large as those of nonionic surfactants. On the contrary, the K_1 values of the nonionic surfactants are almost four times as large as those of cationic surfactants, which means that the oxyethylene groups connected with alkyl chain probably constitute a palisade layer of the micelles where the hydrophobic reactant locates.[20] This leads to larger available area in the nonionic surfactant micelles than in the cationic micelles.

TABLE 3. RATE PARAMETERS FOR THE REACTION OF TNM WITH HYDROXIDE ION

Surfactant	ΔG^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
None	76.9	65.6	−37.2
DeTAC	66.5	60.2	−20.9
DoTAC	64.8	59.8	−16.7
HTAC	61.9	57.7	−13.8

Next, to see the effect of an oxyethylene chain length the reaction rates were measured in the presence of nonionic surfactants containing different numbers of oxyethylene unit but with the fixed alkyl-chain length, $C_{12}E_6$, $C_{12}E_{10}$, $C_{12}E_{15}$, $C_{12}E_{20}$, and $C_{12}E_{29}$. The k_1 and K_1/N values obtained from the linearity plots are summarized in Table 2. Concerning the decrease in k_1 values with an increase in oxyethylene unit more than ten, it can be expected that the location of TNM goes into an innermore part of the micelles owing to not only loosening of the palisade layer but also their smaller aggregation number with increasing oxyethylene group. Consequently, a separation between TNM and OH^- comes to increase with an increase in oxyethylene unit. Regarding the K_1/N values, on the other hand, even if the decrease in aggregation number of the micelles with increase of oxyethylene group is taken into account (460, 180, 120, 80, and 60 at 30 °C for $C_{12}E_6$, $C_{12}E_{10}$, $C_{12}E_{15}$, $C_{12}E_{20}$, and $C_{12}E_{29}$, respectively, which were estimated by an interpolation or extrapolation from the aggregation numbers in the literature[19]), the K_1 value of $C_{12}E_6$ is almost five times as large as that of $C_{12}E_{29}$. The roughly estimated K_1 values are given in Table 2. This decrease in K_1 values with increasing oxyethylene group is also likely to result from the loose palisade layer caused by less aggregation number with increase of oxyethylene goup. That is, the area for TNM to sit becomes less with increase of the group. The identical explanation should be applicable to the reaction rates on both cationic and nonionic surfactant micelles.

Concerning the distribution of TNM among micelles, the Poisson distribution could be well approximated for both cationic and nonionic surfactant micelles. Namely, regardless of the kinds of surfactants used, the linearity of the plots of $1/(k^{app}-k_b)$ against $1/(C_t-\mathrm{CMC})$ is very good. We may conclude at this point that the Poisson distribution of TNM among micelles can be applied to the present cationic and nonionic surfactant micelles. In other words, the assumption used for this treatment is suitable for these systems.

(3) Temperature Effect on the Reaction Rates. Finally, a dependency of the reaction rates on temperature was examined both in the absence and presence of micelles. The reaction rates were measured over the temperature range of 20—40 °C, and the surfactants used were DeTAC, DoTAC, and HTAC. The reaction rate determination in the presence of these sur-

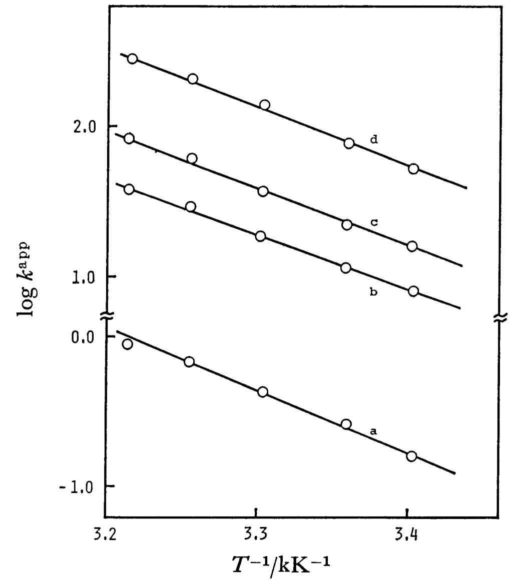
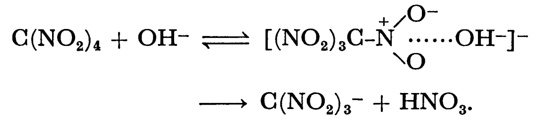


Fig. 5. Arrhenius plots for the reaction of TNM with hydroxide ion.
a): No micelles, b): DeTAC 0.3 mol dm^{-3}, c): DoTAC 0.2 mol dm^{-3}, d): HTAC 0.03 mol dm^{-3}.

factants were made at the higher surfactant concentrations where the second-order rate constant k^{app} is almost equal to the rate constant k_1. The plots of log k^{app} against $1/T$ gives a straight line as shown in Fig. 5, and then the activation energy E_a can be calculated by the Arrhenius equation. The ΔG^* and ΔH^* values decrease and ΔS^* values increase in the presence of these micelles compared with those in the absence of micelles (Table 3). The transition state of the reaction of TNM with hydroxide ion is represented by:[6)]



$$C(NO_2)_4 + OH^- \rightleftharpoons [(NO_2)_3C\text{-}\overset{+}{N}(\text{-}O^-)(\text{=}O)\cdots\cdots OH^-]^- \longrightarrow C(NO_2)_3^- + HNO_3. \quad (12)$$

Therefore, the transition state having a negative charge is electrostatically stabilized by the cationic micelles. In any event, the drastic change of ΔG^* and ΔH^* values could not be found even in the presence of the cationic micelles. This means that the increase in the rate constant in the presence of cationic micelles can be attributed mainly to a local concentration increase of another reactant OH^- ions around the micelles and that the reaction mechanism is not changed much by the presence of these micelles.

References

1) Y. Moroi, *J. Phys. Chem.*, **84**, 2186 (1980).
2) P. Mukerjee and K. J. Mysels, *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand., No. 36* (1971).
3) E. F. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, **81**, 4540, 4542 (1959).
4) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York-San Francisco-London (1975).
5) D. J. Glover, *Tetrahedron*, **19**, 219 (1963).
6) D. J. Glover, *J. Phys. Chem.*, **74**, 21 (1970).
7) S. L. Walters and T. C. Bruice, *J. Am. Chem. Soc.*, **93**, 2269 (1971).
8) J. H. Fendler, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1041.
9) Y. Moroi, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **44**, 2078 (1971).
10) N. Nishikido, Y. Moroi, H. Uehara, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **47**, 2634 (1974).
11) M. T. A. Behme, J. G. Fullington, R. Noel, and E. H. Cordes, *J. Am. Chem. Soc.*, **87**, 266 (1965).
12) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K. Yang, *J. Am. Chem. Soc.*, **90**, 5512 (1968).
13) C. A. Bunton, L. Robinson, and L. Sepulveda, *J. Org. Chem.*, **35**, 108 (1970).
14) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Am. Chem. Soc.*, **95**, 3262 (1975).
15) T. Kunitake, S. Shinkai, and Y. Okahata, *Bull. Chem. Soc. Jpn.*, **49**, 540 (1976).
16) Y. Moroi, N. Nishikido, H. Uehara, and R. Matuura, *J. Colloid Interface Sci.*, **50**, 254 (1975).
17) H. V. Tartar, *J. Phys. Chem.*, **59**, 1195 (1955).
18) L. M. Kushner, W. D. Hubbard, and R. A. Parker, *J. Research Natl. Bur. Stand.*, **59**, 113 (1957).
19) L. Hsiao, H. N. Dunning, and P. B. Lorenz, *J. Phys. Chem.*, **60**, 657 (1956).
20) N. Nishikido, Y. Moroi, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **48**, 1387 (1975).