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Effect of Cationic Micellar Reaction Field on Reaction Kinetics of Meisenheimer σ -Complex Formation between 1,3,5-Trinitrobenzene and Hydroxide Ion

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Abstract

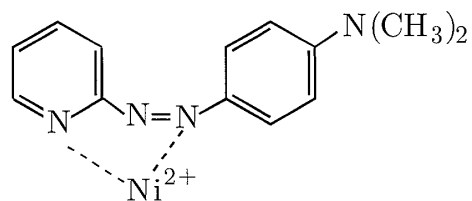
Kinetic studies were done by using stopped-flow method for the Meisenheimer σ -complex formation reaction between 1,3,5-trinitrobenzene (TNB) and hydroxide ion in cationic micellar solutions of dodecyltrimethylammonium bromide (DTAB), myristyltrimethylammonium bromide (MyTAB) and cetyltrimethylammonium bromide (CTAB) dissolved in aqueous solution, for the purpose of elucidating the influence of the microscopic heterogeneity of reaction field. The reaction rate analysis based on a pseudo-phase ion exchange model led us to a conclusion that the partition of reactant molecules between the micelle and water phase, and ion exchange between hydroxide ion and bromide ion existing as counter ions of cationic micellar surface were important. On the activation process, the enthalpy-entropy compensation relationships worked over the wide range of surfactant concentration. The derived isokinetic temperature, T_{iso} , revealed that in CTAB the reaction might be of enthalpy-control, and that in MyTAB be of entropy-control.

Introduction

The feature how chemical reaction rates in solution are influenced by various medium properties such as electric and transport ones has been studied both extensively and intensively^{1,2)}. Historically, the viewpoint to regard solution as a continuum medium has been developed. However, since chemical reactivity in solution is much affected by solvent structure or local structure just around the reactive site, chemical reactions in the microheterogeneous solution systems have attracted much attention^{3,4)}. The microheterogeneous solution system means that

the system under consideration is heterogeneous at the microscopic level such as molecular aggregates composed of surfactants or lipids. The solute distribution can be inhomogeneous throughout the entire volume of the solution. There may be charged interfaces where electrostatic effects can play a dominant role in influencing the solute distribution and their reactions. One of those influences often appears as a "micellar catalysis", which is mainly caused by either environmental effect of the reaction field or increasing local reactant concentration around a micellar particle. The former effect works essentially in analogy with the solvent effect or solvation effect mainly associated with electrostatic properties of micelle phase. The latter effect works remarkably in reactions of highly polar molecules in ionic micellar solutions.⁵⁾

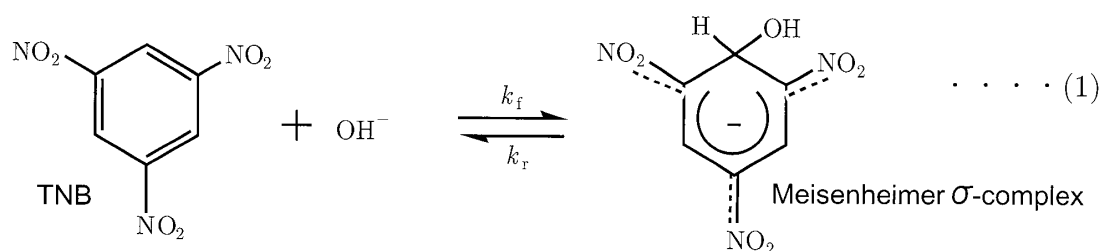
In the previous paper the PADA-Ni²⁺ complex formation reaction between Ni²⁺ and pyridine-2-azo-*p*-dimethylaniline (PADA) in cationic(CTAB), nonionic (hexaethylene glycol monododecylether, C₁₂E₆) and anionic (sodium decylsulfate, SDeS) micellar solutions was studied in detail^{6, 7)}. It was revealed that in CTAB



PADA-Ni²⁺ complex

micellar solution the coulomb repulsion between Ni²⁺ and the cationic micellar surface resulted in increasing separation between PADA which was dissolved in the micelle phase and Ni²⁺ in the water phase so that apparent reaction rate might decrease accordingly. In the nonionic micellar solution, the reaction field was not mainly the hydrophobic core region but the moderately hydrophilic region composed of polyoxyethylene groups. In the anionic micellar solution, the reactant cation was almost completely concentrated on the micellar surface, and rate constant reached a maximum at cmc and decreased slowly with increasing surfactant concentration. That behavior was adequately explained on the basis of the cell model⁸⁾.

In the present paper we have examined micellar effect on a reaction as represented by reaction (1) in which an anion participates, that is, a Meisenheimer σ -complex formation reaction⁹⁾ between 1,3,5-trinitrobenzene(TNB) and hydroxide ion in cationic micellar solutions, for the purposes of not only analyzing the apparent reaction rate on the basis of mixed reaction fields, but considering the activation parameters intrinsic to the respective reaction field. The cationic surfactants used in this study were dodecyltrimethylammonium bromide(DTAB, CH₃(CH₂)₁₁N(CH₃)₃Br), cmc = 16mM at 298K), myristyltrimethylammonium bromide(MyTAB, CH₃(CH₂)₁₃N(CH₃)₃Br), cmc = 3mM at 298K), and cetyltrimethylammonium bromide(CTAB, CH₃(CH₂)₁₅N(CH₃)₃Br), cmc = 1mM at 298K) dissolved in aqueous solution.



Experiment

Materials: 1,3,5-Trinitrobenzene(TNB) obtained commercially(Tokyo Kasei Co. Ltd.) was recrystallized twice from ethanol. Aqueous sodium hydroxide solution prepared commercially for volumetric analysis was used as a source of hydroxide ion. DTAB(AVOCADO Co. Ltd.), MyTAB(Wako Pure Chemical Industries, Ltd.) and CTAB(Nacalai Tesque, Inc.) were used as obtained commercially. Distilled water was used throughout this work.

UV Spectra and Kinetic Measurements: UV spectrum was recorded by a Hitachi U-2000 spectrophotometer. Kinetic measurement was carried out with a RA-2000 stopped-flow spectrophotometer (Otsuka Electronics Co., Ltd.) in which each reaction solution was driven directly by nitrogen gaseous pressure into a mixing chamber. The temperature range was 10–35°C, which was regulated within $\pm 0.1^\circ\text{C}$ by circulating thermostated water around the optical observation cell.

All kinetic and equilibrium runs were performed with hydroxide ion concentration in large excess over substrates. The concentration of TNB was around 4.0×10^{-5} M, and hydroxide ion was in the range $1.0 \times 10^{-3} \sim 1.0 \times 10^{-2}$ M. The ionic strength was controlled, when necessary, by adding potassium bromide. The concentrations of surfactants varied from 1.0×10^{-2} to 1.0×10^{-1} M for DTAB, 1.0×10^{-3} to 1.0×10^{-2} M for MyTAB, and 5.0×10^{-4} to 1.0×10^{-2} M for CTAB, respectively. The pseudo-first order rate constants were determined by fitting to a single exponential function.

Results and Discussions

The electronic absorption spectra of TNB in aqueous micellar solution showed double peaks around 430 and 520nm by addition of OH^- ion, as shown in Fig. 1 which is one of spectroscopic characteristics of Meisenheimer σ -complexes formed from aromatic nitro compounds^{10, 11}). Hereafter, the ionic strength “ $\mu = 0$ ” means that no potassium bromide is added to the solution for controlling ionic strength. The increasing surfactant concentration increased the absorbance of the σ -complex,

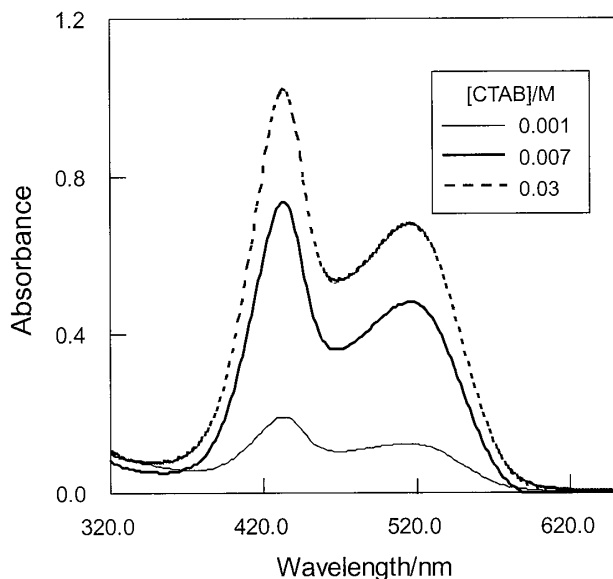


Fig. 1 Absorption Spectra of the Meisenheimer σ -Complex in CTAB Micellar Solution of 10mM OH^- at Room Temperature. $[\text{TNB}]_0 = 4.0 \times 10^{-5}\text{M}$, Ionic Strength $\mu = 0$.

and so the cationic micellar solution enhanced the equilibrium concentration of σ -complex compared to simple aqueous solution. The increases of absorbance monitored by a stopped flow method at those absorption peaks, obeyed a first order kinetics when the $[\text{OH}^-]$ existed in large excess over $[\text{TNB}]$. The pseudo-first order rate constants, k_{obsd} can be represented by eq. (2).

$$k_{\text{obsd}} = k_f[\text{OH}^-]_0 + k_r \cdot \cdot \cdot \cdot (2)$$

Fig. 2 shows the dependence of k_{obsd} on initial hydroxide ion concentration $[\text{OH}^-]_0$ in MyTAB micellar solution, which is well represented by eq. (2) based on reaction (1). “Apparent” forward rate constant k_f was determined from the slope, and “apparent” reverse one k_r was from the intercept. The “apparent” means that, since in micellar solutions forward rate constant determined by eq. (2) is responsible for reaction steps occurring in both micelle and bulk water phases, the apparent rate constant is a composite term of rate constants in the respective phase. Fig. 3 shows that k_f determined by eq. (2) increases with surfactant concentration above cmc, and its magnitude is less remarkable in the solution of higher ionic strength.

Rate Analysis in Cationic Micellar Solution: The feature as shown in Figs. 3 results from the existence of multi reaction fields in a micellar solution, and the distribution of reactants between micelle phase and water one. In the previous

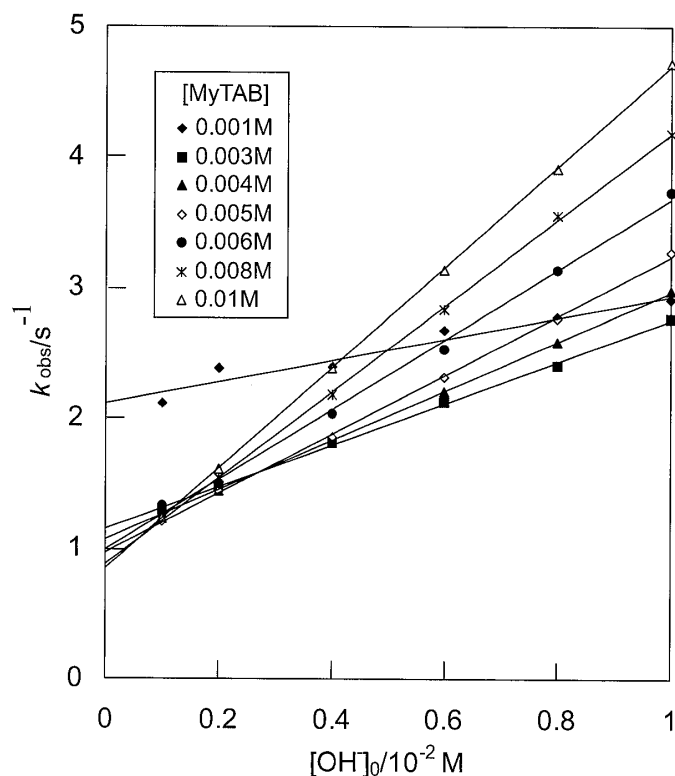


Fig. 2 Pseudo-first Order Plots for TNB-OH⁻ Reaction at 298K in MyTAB Micellar Solution. Ionic Strength $\mu = 0.1$.

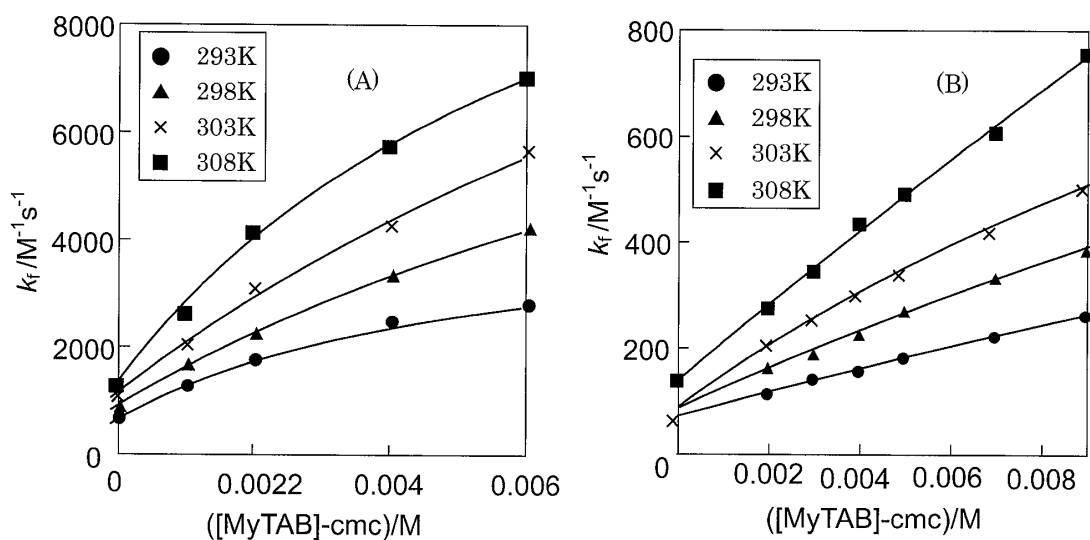


Fig. 3 Change of k_f for TNB-OH⁻ Reaction with [MyTAB]. Ionic Strength, (A) $\mu = 0$, (B) $\mu = 0.1$. The lines were drawn according to eq. (7).

study of PADA-Ni²⁺ complex formation reactions in anionic micellar solutions⁷⁾, the feature that both k_{obsd} and k_f dramatically increased, reaching a maximum around cmc and decreasing slowly with surfactant concentration, was understood by the cell model as described in the followings: The reactants may become initially “concentrated” with increasing micellar concentration even with constant stoichiometric concentration, and beyond cmc the quantity of each reactant molecule contained or solubilized per micelle decreases with increasing surfactant concentration. The decrease of rate constant beyond cmc can be due to such “dilution” of reactant per micelle. In the same PADA-Ni²⁺ complex formation reaction in cationic CTAB and nonionic C₁₂E₆ solutions⁶⁾, the increasing quantity of the surfactants led to reduce monotonously the forward rate constant, and that behavior was satisfactorily understood on the base of pseudo-phase model which took account of the distribution equilibrium of the PADA molecule between water and micelle phases.

The present results, however, are absolutely different from these previous cases. We have to take into account that firstly the increasing ionic strength makes the reaction rate slower, and secondly the increasing surfactant concentration leads to enhancements of the forward rate constant as shown in Fig. 3. So at first a general distribution model^{8, 12)} may be taken into consideration, which is a pseudo-phase model with a modification as reaction (3) on the ionic exchange between micelle and water phases^{13, 14)}.



In reaction (3), subscript m denotes the species in micelle phase, and w denotes the water phase. The ionic exchange equilibrium constants for Br⁻ and OH⁻ with surfactant defined by eq. (4) are represented as K_X and K_{OH} , respectively, and the equilibrium constant K_X^{OH} corresponding to the ionic exchange of reaction (3) is represented by eq. (5). In these equations [S] denotes the surfactant concentration.

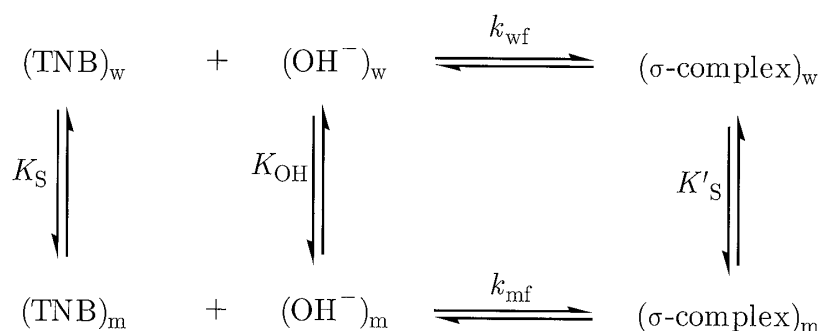
$$K_X = \frac{[\text{Br}^-]_m}{[\text{Br}^-]_w \times [\text{S}]} = \frac{\beta}{[\text{Br}^-]_w} \quad K_{\text{OH}} = \frac{[\text{OH}^-]_m}{[\text{OH}^-]_w \times [\text{S}]} \quad \cdot \cdot \cdot \cdot \quad (4)$$

$$K_X^{\text{OH}} = \frac{[\text{OH}^-]_w}{[\text{OH}^-]_m} \left[\frac{[\text{Br}^-]_m}{[\text{Br}^-]_w} \right] = \frac{K_X}{K_{\text{OH}}} = \text{constant} \quad \cdot \cdot \cdot \cdot \quad (5)$$

The coverage ratio of micellar surface by bromide ion, β , is known to be 0.72 at ionic strength $\mu = 0.1$ ¹⁵⁾. The condensation of both reactant molecules TNB and OH⁻ in or around a micelle due to partition equilibrium will lead to enhancement of reaction rate, and in contrast the ion exchange on a micelle surface as

expressed by reaction (3) will lead to the decrease of reaction rate with increasing $[\text{Br}^-]_w$, that is the increasing ionic strength. Moreover, even if the micellar concentration increases, $[\text{OH}^-]_m$ is not diluted proportionally but controlled according to the ion exchange equilibrium with Br^- , so that the increase of micellar concentration may lead to extension of the reaction field, resulting in the enhancement of reaction rate.

Reaction Scheme: Pseudo-phase Ion Exchange Model



So, the above reaction scheme of pseudo-phase model accompanied with the ion exchange as reaction (3) can be applied to analyze the kinetic data. In this model k_{wf} and k_{mf} are forward rate constants in the water phase and the micelle phase, respectively. Partition of TNB between the two phases is denoted by partition constant K_S as defined by eq. (6).

$$K_S = \frac{[\text{TNB}]_m}{[\text{TNB}]_w[\text{S}]} \cdot \cdot \cdot \cdot (6)$$

Then the apparent rate constant k_f is represented by eq. (7), and the reverse rate constant k_r eq. (8).

$$k_f = \frac{k_{wf} + k_{mf}K_S(K_{\text{OH}})^{-1}K_X([\text{S}] - \text{cmc})}{1 + K_{\text{OH}}([\text{S}] - \text{cmc})} \cdot \cdot \cdot \cdot (7)$$

$$k_r = k_{mr} + k_{wr}/K'([\text{S}] - \text{cmc}) \cdot \cdot \cdot \cdot (8)$$

The observed dependence of k_f on surfactant concentration as shown in Fig. 3 was fitted to eq. (7), and numerical values of k_{wf} and k_{mf} were determined as listed on Table 1. In the course of above calculation, since the partition constant K_S cannot be determined at the same time, we used the literature value¹⁵⁾ of $K_S = \sim 10^2\text{M}^{-1}$ obtained for some aromatic molecules. For the partition equilibria of 1,10-phenanthroline between the cationic micelle and water phases, the values of $K_S = 50 \sim 100\text{M}^{-1}$ were observed for DTAB \sim CTAB micellar solutions¹⁶⁾. The

Table 1 Forward Rate Constants for the Meisenheimer σ -Complex Formation Reaction of TNB-OH⁻ in the Water and the Micelle Phases, Calculated on the Basis of Pseudo-Phase Ion Exchange Model.

Ionic Strength		$\mu = 0.1$		$\mu = 0$	
Surfactant	T/K	$k_{\text{wf}}^{\text{a)}}$ /M ⁻¹ s ⁻¹	$k_{\text{mf}}^{\text{b)}}$ /M ⁻¹ s ⁻¹	$k_{\text{wf}}^{\text{a)}}$ /M ⁻¹ s ⁻¹	$k_{\text{mf}}^{\text{b)}}$ /M ⁻¹ s ⁻¹
CTAB	293	6.92	0.790	—	—
	298	57.8	1.50	1190	11.3
	303	183	2.61	1410	11.7
	308	267	4.71	1880	12.0
MyTAB	293	67.7	2.08	642	4.74
	298	83.6	2.31	906	12.3
	303	86.5	1.71	1120	18.2
	308	137	9.23	1250	14.1
DTAB	293	124	0.81	123	1.94
	298	184	1.36	203	3.01
	303	236	1.77	301	4.47
	308	308	2.33	490	4.92

a) Forward rate constant in the water phase.

b) Forward rate constant in the micelle phase. On calculating k_{mf} from fitting parameters to eq. (7), the partition constant K_s between water and micelle phase was assumed to be $1.0 \times 10^2 \text{ M}^{-1}$ and to be independent of temperature.

values of K_{OH} were $10 \sim 30$ for any surfactant used here, and K_X^{OH} was revealed to be almost constant around $0.4 \sim 0.5$, which agreed almost with the literature values.¹⁵⁾

The adequacy of the ion exchange model can be shown by the dependency of k_f on ionic strength. Eq. (7) is rewritten as eq. (9), which should give a straight line for a plot of k_f vs. $1/\mu$ at constant surfactant concentration, and that trend is really evidenced in Fig. 4.

$$k_f = \frac{k_{\text{wf}}}{1 + K_{\text{OH}}([\text{S}] - \text{cmc})} + \frac{k_{\text{mf}}K_s(K_X^{\text{OH}})^{-1}([\text{S}] - \text{cmc})}{1 + K_{\text{OH}}([\text{S}] - \text{cmc})} \times \frac{\beta}{[\text{Br}^-]_{\text{w}}} \dots \dots (9)$$

Isokinetic Condition: By use of Arrhenius activation energy (E_{af}) and A -factor for k_f , the transition state theory gives, the ‘‘apparent’’ activation parameters (ΔH_f^\ddagger , ΔS_f^\ddagger and ΔG_f^\ddagger)²⁾, which are listed in Table 2 for CTAB micellar solution. The

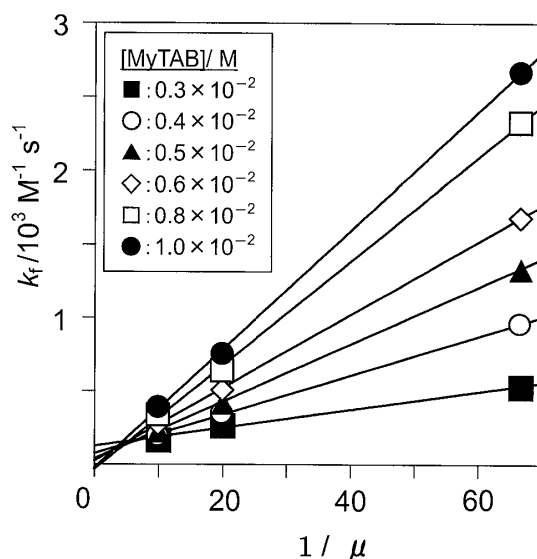


Fig. 4 Change of k_f for TNB-OH⁻ Reaction with Ionic Strength in MyTAB Micellar Solution at 298K.

Table 2 Activation Parameters for the Meisenheimer σ -Complex Formation Reaction of TNB-OH⁻ in the CTAB Micellar Solution at 298K and $\mu = 0.1$.

[CTAB]/mM	E_{af}/kJmol^{-1}	$\Delta H_f^\ddagger/\text{kJmol}^{-1}$	$\Delta S_f^\ddagger/\text{JK}^{-1}\text{mol}^{-1}$	$\Delta G_f^\ddagger/\text{kJmol}^{-1}$
0.5	53.4	51.0	-36.7	61.9
1	54.4	51.9	-31.4	61.2
3	58.1	55.6	-14.3	59.9
4	58.8	56.3	-9.52	59.1
5	55.3	52.8	-20.8	59.0
6	42.7	40.2	-60.8	58.3
8	41.6	39.2	-62.7	57.8
10	43.0	40.5	-56.8	57.5

increase of [CTAB] leads to a little decrease of ΔG_f^\ddagger , however which factor is dominant, ΔH_f^\ddagger or ΔS_f^\ddagger , in controlling the reaction rate, is not clear, because the compensation of these two factors operates just around the experimental temperature¹⁷). In Fig. 5 is given the plot of the compensation effect between ΔH_f^\ddagger and ΔS_f^\ddagger , whose slopes give the isokinetic temperatures (T_{iso}) at which the reaction rate is kept constant^{17, 18}), even if the reaction field is varied by changing surfactant composition. Table 3 lists T_{iso} for the surfactant solutions examined in

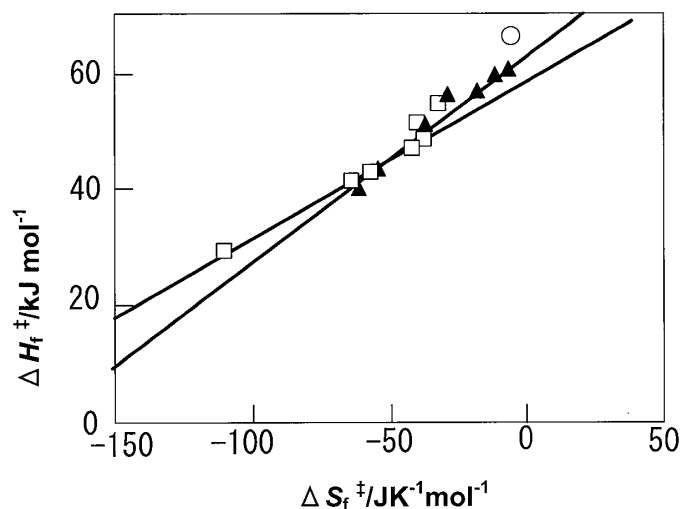


Fig. 5 $\Delta H_f^\ddagger - \Delta S_f^\ddagger$ Compensation Relationships for TNB-OH⁻ Reaction in Aqueous(○), CTAB(▲) and MyTAB(□) Micellar Solutions.

Table 3 Isokinetic Temperatures, T_{iso} , and $\Delta G_{\text{iso}}^\ddagger$ ^{a)} at T_{iso} for the Meisenheimer σ -Complex Formation Reaction of TNB-OH⁻ in the Cationic Micellar Solutions at 298K.

Surfactant	$k_f/\text{M}^{-1}\text{s}^{-1}$				k_f/s^{-1}	
	$\mu = 0.1$		$\mu = 0$		$\mu = 0.1$	
	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$
CTAB	358	61.8	304	52.0	326	72.2
MyTAB	261	58.0	234	50.6	241	73.2
DTAB	202	54.5	254	52.6	353	73.5

^{a)} $\Delta G_{\text{iso}}^\ddagger$ is related to the rate constant at T_{iso} and invariable even with different micellar concentration.

the present study The fact that the enthalpy-entropy compensation relationships work over the wide range of surfactant concentration reveals that the reaction mechanism is unchanged even if the physical properties of the medium near the reactive site change so as to affect thermodynamic quantities of the transition state. In general, if T_{iso} is higher than the temperature at which ΔH_f^\ddagger and ΔS_f^\ddagger are determined (298K in the present study), the reaction at the experimental temperature is controlled mainly by enthalpy of activation rather than entropy,

and *vice versa*¹⁷⁾. T_{iso} 's in Table 3 show that in CTAB the reaction is of enthalpy-control, and in MyTAB is of entropy-control. However, since T_{iso} 's are not so far from the experimental temperature, the present results can't lead to the decisive conclusion either enthalpy-control or entropy-control.

Activation Parameters Intrinsic to Micelle Phase : Contrary to the "apparent" activation parameters as described above, the "intrinsic" activation parameters, assigned to purely micelle phase, were determined by use of k_{mf} . As seen in Table 4 the activation enthalpy is much reduced by transferring from water to micelle phase, $\Delta H_{\text{mf}}^{\ddagger} < \Delta H_{\text{wf}}^{\ddagger}$. That trend reflects often that degree of solvation along the activation process differs dependently on the reaction medium^{1, 6, 7)}.

The reaction (1) is considered to occur *via* the two steps: (i) firstly the dehydration of an OH^- ion, and (ii) secondly a partial bond formation between an OH^- ion and a sp^2 -carbon atom constituting a TNB molecule. The enthalpy change associated with the step (ii) may be almost same for the two phases. So the difference of the dehydration enthalpy with the step (i) causes mostly the difference between $\Delta H_{\text{mf}}^{\ddagger}$ and $\Delta H_{\text{wf}}^{\ddagger}$. Since the degree of hydration of OH^- at the initial state in the micelle phase is less than that in the water phase because of the difference of dielectric constant, the dehydration energy required for the step (i) is less in micelle phase.

The activation entropy is also less, that is of more negative value, in the micelle phase. Entropy of the step (i) increases in general, and the entropy-decrease accompanied with the step (ii), may not differ so much between micelle and water

Table 4 Activation Parameters for the Intrinsic Phases^{a)} of the Meisenheimer σ -Complex Formation of TNB- OH^- in the Cationic Micellar Solutions at 298K.

Ionic Strength	Surfactant	$\Delta H_{\text{mf}}^{\ddagger}$	$\Delta S_{\text{mf}}^{\ddagger}$	$\Delta H_{\text{wf}}^{\ddagger}$	$\Delta S_{\text{wf}}^{\ddagger}$
		kJ mol^{-1}	$\text{J K}^{-1}\text{mol}^{-1}$	kJ mol^{-1}	$\text{J K}^{-1}\text{mol}^{-1}$
$\mu = 0.1$	CTAB	86.6	48.9	90.2	50.7
	MyTAB	76.2	15.2	85.6	35.1
	DTAB	49.4	-77.4	53.5	-60.2
$\mu = 0$	CTAB	7.60	-199	32.0	-78.5
	MyTAB	52.9	-48.9	65.2	38.4
	DTAB	45.7	-82.9	66.0	20.5

^{a)} Subscripts m and w denote micelle phase and water one, respectively, and subscript f the forward process of the Meisenheimer σ -complex formation reaction.

one. Then the activation entropy difference as a whole between the two phases would reflect also the difference of dehydration of OH^- ion. However, the above consideration may explain only a part of the difference. In comparing the activation entropy difference between the two phases the large decrease in the micelle has been found very often in various reactions^{5, 19}). If the reaction (1) takes place just at the surface of the micelle, one reactant(TNB) is inside the boundary, and the other(OH^-) outside. So the movement of a reactant molecule effective to the reaction will be restricted so much: for example, OH^- having net moving velocity directed toward the micelle-core will be only effective to react. Such restriction of direction results in also large decrease of entropy.

Conclusion

The change of the apparent reaction rate of the Meisenheimer σ -complex formation between 1,3,6-trinitrobenzene(TNB) and hydroxide ion in several cationic surfactant solutions was analyzed kinetically, and the followings were elucidated.

1. A number of reactant molecules exist in the inner and on the surface of the cationic micelles. Moreover even if the micellar concentration increases the OH^- concentration on the micellar surface is not diluted proportionally but controlled according to the ion exchange equilibrium with Br^- , so that the increase of micellar concentration may lead to extension of the reaction field, resulting in the enhancement of reaction rate.
2. The activation enthalpy was much reduced by transferring from water to micelle phase, since the degree of hydration of OH^- at the initial state in the micelle phase was less than that in water.
3. The activation entropy was much less in the micellar phase. Such decrease was considered not only due to the difference of degree of dehydration of OH^- but due to the restriction of moving direction of reactants molecules in the reaction field.
4. For the activation process, the enthalpy-entropy compensation relationships worked over the wide concentration range of surfactants. The derived isokinetic temperature, T_{iso} , revealed that in CTAB the reaction might be of enthalpy-control, and that in MyTAB be of entropy-control.

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