Microviscosity and Micellar Phase Diagrams Determined with Fluorescence Probes

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The dependence of microviscosity on salt and surfactant concentrations was determined in micellar solutions of alkyltrimethylammonium bromides by using two fluorescent probes, auramine and 1,3-dipyrenylpropane (P3P). The microviscosity increased with the growth of the micelles, it changed at the sphere to rodlike micelles transition point, and it became constant above the overlap threshold point of rod micelles, that is, the overlapping of micelles did not influence the microviscosity. The transition points of the micellar solutions (the critical micelle concentrations, the sphere-rod transition point, and the micelle overlapping point) determined by the present method were in good agreement with those in the literature. Phase diagrams of the micellar solutions were determined from the above data.

Above the critical micelle concentration (cmc), excess surfactant molecules aggregate to form micelles, whose shape and aggregation number strongly depend on the molecular structure and environment. The dependence of micellar aggregation on salt concentration (C_S) has been investigated in alkyltrimethylammonium halide systems by several groups.[1—9] According to these reports, alkyltrimethylammonium halide micelles grow from a spherical shape to a rigid rod, a flexible rod (stringlike micelle), and then entangle with each other, depending on the salt and surfactant concentrations. The aggregation number of nonionic micelles was found to increase rapidly above a certain temperature.[10—12] Experimentally, the aggregation behavior of micelles has been detected by using light scattering data, small angle neutron scattering data, etc. from a macroscopic point of view. In addition, several researchers have recently focused their attentions on the theoretical investigation of this problem.[13] The environment of a micellar interior might also be affected by the changes in micelle shape, according to the following reports. Broadening line widths in the NMR spectrum[14] and increasing microviscosity[15] were reported at the transition point from a spherical micelle to a rodlike micelle. A time-resolved fluorescence probe method revealed that collisions between micelles can give rise to temporary micelle merging.[11] These reports strongly suggest the possibility that some changes in micelle shape can be detected by measuring the microproperties of a micelle.

The first purpose of this paper is to elucidate the dependence of microviscosity on salt concentration (C_S) and on surfactant concentration (C). The second is to reveal the relationship between the transitions of the micellar aggregation states and microviscosity. In our previous paper,[15] it was reported that auramine is a good probe to determine microviscosity in micelles as it exhibits intense fluorescence in viscous solutions. In addition, we indicated that microviscosity in a micelle depends on its shape and its external environment. Therefore, in the present investigation, auramine was used as one of the microviscosity probes. To allow comparison with the present results, we selected surfactant systems in which knowledge of the relationship between micelle shape and salt concentration is available.

Experimental

Dodecyltrimethylammonium chloride and bromide (DTAC and DTAB, from Tokyo Kasei Ind. Co.) were recrystallized from diethyl ether–ethanol. Tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide (TTAB and CTAB, from Tokyo Kasei Ind. Co.) were recrystallized from acetone.

Auramine (bis[4-(dimethylamino)phenyl]methanimine, guaranteed reagent, Kanto Chemical Co.) and 1,3-dipyrenylpropane (P3P, Wako Pure Chemical Ind. Ltd.) were used as microviscosity probes. The final concentrations of auramine and P3P were 1×10^{-5} and 1×10^{-6} mol dm^{-3}, respectively.

Fluorescence measurements were carried out on a Hitachi fluorescence spectrophotometer F-3010 equipped with a temperature control unit. Excitation and emission wavelengths were 440 and 500 nm for auramine. Their ratio of the fluorescence intensity of auramine in a surfactant solution (I) against its fluorescence intensity in an aqueous solution containing no surfactant (I_0) was used as a measure of microviscosity. The fluorescence intensities of the monomer and excimer states of P3P (I_M and I_E) were measured at 377 and 487 nm, respectively, with excitation light of 348 nm, as a ratio of I_M against I_E can be a measure of microviscosity.[16] The cmcs were determined by use of a

Wilhelmy plate technique (Kyowa Kagaku Model A-3 surface tension meter).

Results and Discussion

Fluorescence Intensity in Cationic Surfactant Solutions: The ratio of the fluorescence intensity in a surfactant solution (I) against the fluorescence intensity in an aqueous solution (I_0) was previously used as a measure of microviscosity for the purpose of detecting only variations in a micelle without perturbations in the bulk phase. Figure 1 shows a comparison of the fluorescence intensity ratio (I/I_0) of auramine between DTAC and DTAB systems. The value of I/I_0 in the DTAC system increased monotonically with increasing concentration of NaCl. While I/I_0 in a DTAB system exhibited behavior similar to that in the DTAC system at low NaBr concentration, it began to deviate upward from a monotonic increasing curve at a certain NaBr concentration (which decreased with an increment of the surfactant concentration, as shown by the arrows in Fig. 1). As seen in Fig. 2, a similar deviation at the same NaBr concentration (1.8 M, 1 M=1 mol dm^{-3}) was observed in the case where P3P was used instead of auramine. Such a deviation might not be observed if there were no changes in the micelles. Upward deviation means increment of microviscosity in DTAB micelles. Upward deviation was also found in a plot of I/I_0 against surfactant concentration at a constant salt concentration. It was found that the point at which the deviation occurred depended on both the salt and sufactant concentrations. In addition, such a deviation was not found in the systems (or regions) where a sphere-rod micelle transition was not observed.

Ikeda and Ozeki[4,5] reported on the effect of salt on

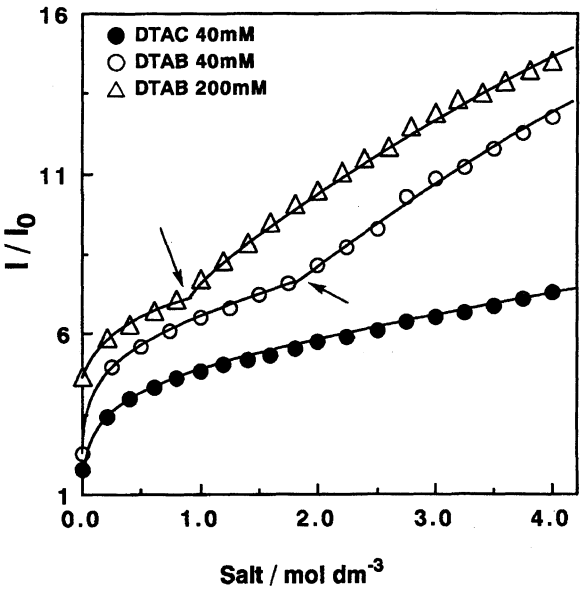

Fig. 1. Dependence of I/I_0 of auramine on salt concentration (NaBr was used for DTAB, NaCl for CTAC) at 25 °C.

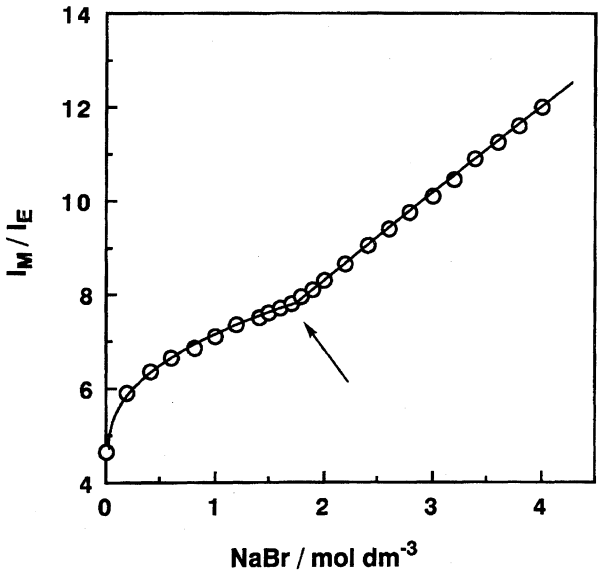

Fig. 2. Dependence of I_M/I_E of P3P on NaBr concentration in 40 mmol dm^{-3} DTAB at 25 °C.

the micelle size of dodecyltrimethylammonium halides. According to their results, DTAC remains in a spherical micelle over a wide concentration range of sodium chloride, although in the corresponding range of sodium bromide, DTAB exhibits a change in the micelle form from a sphere to a rodlike shape. In addition, NMR measurements in DTAB systems indicated that rodlike micelles had a higher microviscosity.[14] Therefore, upward deviation of the fluorescence intensity in the DTAB system must correspond to a transition from a spherical micelle to a rodlike micelle. From this point of view, we examined the effects of surfactant and salt concentrationson fluorescence intensity in more detail.

The values of I/I_0 and I_M/I_E are plotted in Figs. 3 and 4 as a function of NaBr concentration under different CTAB concentrations. Each curve had a similar shape, that is, each curve had two break points except for the systems with low surfactant concentrations. One is a point corresponding to the deviation point in Fig. 1. The other is a point at which the values of I/I_0 or I_M/I_E reached a plateau with increasing salt concentration. This plateau means that the microviscosity in the micelles did not vary in spite of an increment in salt concentration. The salt concentrations at the break points in the case of auramine were always in agreement with those in the case of P3P, unless the solubilized site of each probe was different. This means that the microviscosity varies not only on the micelle surface but also in the micellar interior when the micelle shape changes. Further, it was found that the microviscosity of each surfactant increased with increasing concentrations of salt and surfactant, but it reached a saturated value at high salt concentrations.

Quirion and Magid[9] observed rapid growth of micelles at 0.065—0.07, 0.05, and 0.04 mol kg^{-1} KBr for

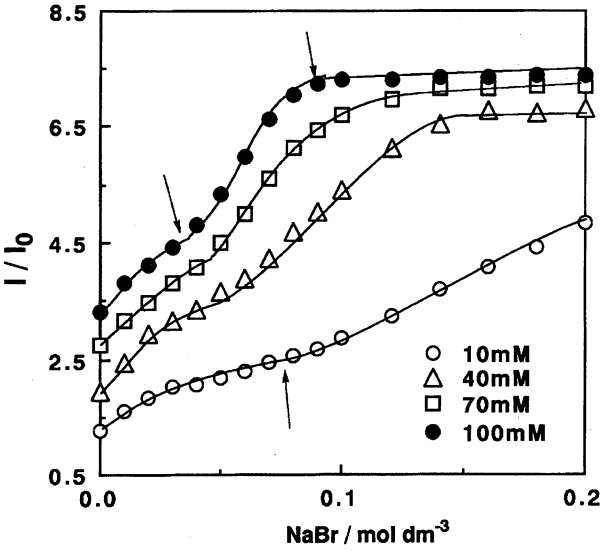

Fig. 3. Dependence of I/I_0 of auramine on NaBr concentration for CTAB at 35 °C.

0.01, 0.03 and 0.05 mol kg^{-1} CTAB, respectively. They pointed out that for 0.03 mol kg^{-1} CTAB plus 0.094 mol kg^{-1} KBr, the hydrodynamic micelle radius was 10.4 nm (corresponding to a cylinder with a radius of 2.32 nm and a length of 48.0 nm). In the present study, rapid increases in the microviscosity occurred at 0.085, 0.06 and 0.05 mol dm^{-3} NaBr for 0.01, 0.04, and 0.05 mol dm^{-3} CTAB, respectively (see Fig. 3). Therefore, the increment of microviscosity at the first break point in Fig. 4 corresponds to a sphere-rod micelle transition. Further, each micelle continues to grow from a rigid rod to a flexible rod and then overlaps with others, as the salt concentration and/or surfactant concentration increases. Corresponding to such micellar growth, the microviscosity in a micelle also increased as seen

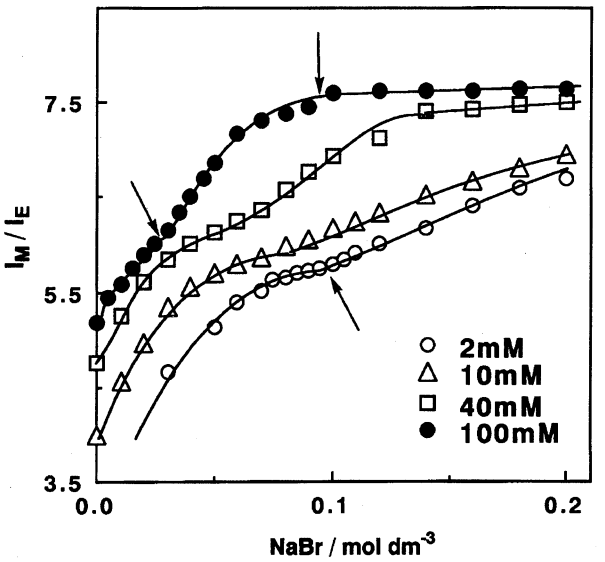

Fig. 4. Dependence of I_M/I_E of P3P on NaBr concentration for CTAB at 35 °C.

in Figs. 3 and 4. Imae, Kamiya, and Ikeda[6] reported the overlap threshold concentration of rodlike micelles is 0.015, 0.01, and 0.007 mol dm^{-3} CTAB for 0.2, 0.3, and 0.5 mol dm^{-3} NaBr, respectively. However, Fig. 3 indicates that the microviscosity in 0.01 mol cm^{-3} CTAB becomes constant above 0.36 mol dm^{-3} NaBr. These concentrations at the second break point are in a similar concentration range with those of the micelle overlapping region. Taking into account that the fluorescence probe method has the essential advantage of being insensitive to intermicellar interactions,[11] the constant values of I/I_0 or I_M/I_E mean that the microviscosity no longer varies in the region where the micelles entangle with each other.

The overlap threshold concentration of rodlike micelles in TTAB systems with the data of the transition points of the DTAB, and CTAB systems were determined by Ikeda et al.[4—8] These data are shown in Table 1 together with the data at the break points. Our data at the first and second break points are in concentration ranges similar to the concentrations at each transition point reported in the literature.

Therefore, the following conclusions were reached: 1) the microviscosity increases with the growth of the micelles, 2) it changes at the transition point from sphere to rodlike micelles, and 3) it becomes constant above the overlap threshold point, that is, the overlapping of micelles does not influence the microviscosity.

Further, based on these conclusions, we tried to determine the boundaries which distinguish different micellar aggregation states. As the next step, the dependence of the cmc on salt concentration was examined.

Critical Micelle Concentrations (cmc) in Alkyltrimethylammonium Bromides: Several cmcs determined in this work are given in Table 2 and are also plotted in Figs. 5, 6, and 7 together with the literature values. Each logarithmic plot gave a straight line at lower salt concentrations and then deviated downward at higher salt concentrations. Generally, a Corrin–Harkins plot gives a straight line in the region of spherical micelles and deviates at the sphere-rod micelle transition point.[4] Such a downward deviation was suggested to result from a decrease in the surface charge density followed by the formation of rodlike micelle.[4] Quirion and Magid[9] pointed out that an increase in a fraction of counterion binding occurs prior to micellar growth. Therefore, this deviation corresponds to the formation of rodlike micelles.

Phase Diagrams of Micellar Solutions: In Figs. 5, 6, and 7, the surfactant concentrations at the break points in Figs. 1, 2, 3, and 4 are plotted against ionic strength. The concentrations corresponding to the sphere-rod transition and the overlap threshold concentrations of rodlike micelles reported in the literature are also shown. The values in the literature are in agreement with the curves drawn from the data at the break points. These curves divided each graph into four re-

Table 1. Threshold Values of Alkyltrimethylammonium Bromide Micelles in Aqueous NaBr Solution

Surfactant	NaBr/mol dm^{-3}			
mmol dm^{-3}	Sphere–rod		Rod–overlapping micelles	
DTAB				
0.42	—	4.0[a]		
8.8	—	3.0[a]		
20.1	2.0	2.0[a]		
40	1.8	—		
200	0.9	—		
TTAB				
8.3	—		—	4.0[b]
8.5	—		—	3.0[b]
10	0.21		3.0	—
15	—		—	2.0[b]
26	—		—	1.0[b]
40	0.17		0.9	—
74	—		—	0.5[b]
100	0.14		0.46	—
200	0.10		0.33	—
CTAB				
2	0.10	—	—	—
7	—	—	—	0.5[e]
10	0.085	0.06—0.07[c]	0.36	0.2[e]
15	—	—	—	0.3[e]
16	—	—	—	0.1[f]
30	—	0.05[c]	—	—
40	0.060	—	0.16	—
50	—	0.04[c]	—	—
60	0.050	—	—	—
70	0.045	—	0.13	—
100	0.035	—	0.09	—
140	—	0[d]	—	—
200	0.01	0[c]	—	—
250	0	—	—	—
910	—	—	—	0.1[e]

a) from Ref. 4. b) from Ref. 7. c) from Ref. 9. d) from Ref. 17. e) from Ref. 6. f) from Ref. 2.

Table 2. NaBr Concentration Dependence of cmc of Alkyltrimethylammonium Bromide

NaBr	TTAB[a]	CTAB[b]
mol dm^{-3}	mmol dm^{-3}	mmol dm^{-3}
0	3.3	0.91
0.01	—	0.19
0.02	0.98	0.11
0.05	0.52	0.059
0.1	0.34	0.036
0.2	—	0.023
0.3	0.19	0.016
0.4	—	—
0.5	0.11	0.0098
0.7	—	—
1.0	0.048	—
2.0	0.029	—

a) 25 °C. b) 35 °C.

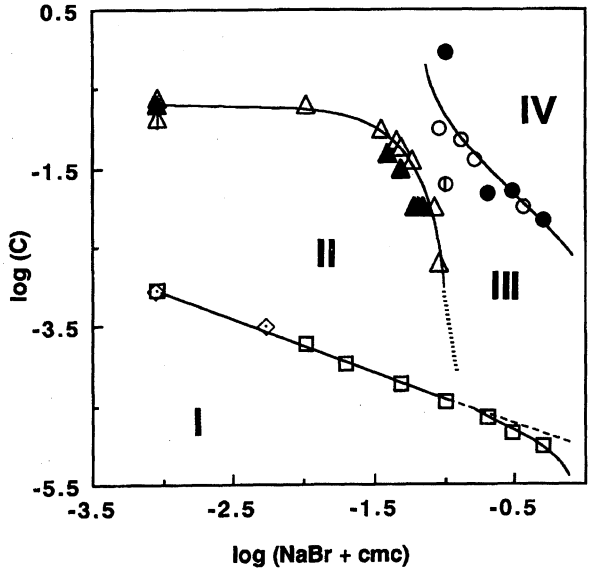

Fig. 5. Micellar phase diagram of CTAB system; □: cmc by surface tension, ◇: cmc by auramine, △: from microviscosity by auramine and P3P, ▲: from Ref. 9, ⚠: from Ref. 17, ○: from microviscosity by auramine and P3P, ●: from Ref. 6, and ⊕: from Ref. 2.

gions. Region I corresponds to a monomer surfactant solution and does not contain micelles as this region exists below a logarithmic plot of cmc and C_S+cmc. Region II, which is located between the cmc and the sphere-rod transition point, is a micellar solution containing globular micelles. As region III exists between the sphere-rod transition point and the overlap threshold point of the rodlike micelles, this region corresponds to a region of rodlike micelles. In region IV, where both surfactant and salt concentrations are high, the micelles entangle with each other.

At the intersection of the cmc curve and the extrapolated curve of the sphere-rod transition, the cmc plot begins to deviate from a straight line. This result supports our conclusion that region III corresponds to a solution phase containing rodlike micelles.

Region II is wide in the DTAB system and narrows as the alkyl chain of the surfactant molecule becomes longer. In the CTAB system, rodlike micelles can exist even at low salt concentrations when the surfactant concentration increases. Reiss–Husson and Luzzati[17] reported that rodlike micelles of CTAB can exist even in the absence of salt. Regions III and IV shift in the direction of lower salt concentration with increasing alkyl chain length.

Much data concerning micelle shape transitions induced by salt concentration or by surfactant concentration have been published, as mentioned above. Such data, however, have not been summarized in a systematic form such as a phase diagram. The phase diagrams given in Figs. 5, 6, and 7 are the first for the alkytri-

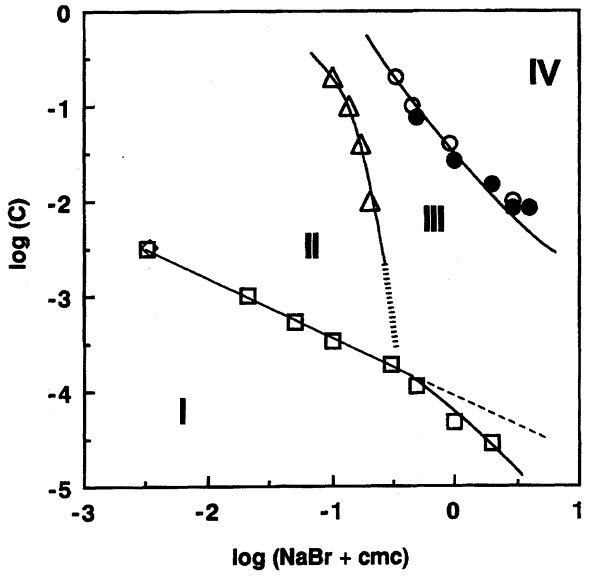

Fig. 6. Micellar phase diagram of TTAB system; □: cmc by surface tension, ◇: cmc by auramine, △: from microviscosity by auramine and P3P, ○: from microviscosity by auramine and P3P, and ●: from Ref. 7.

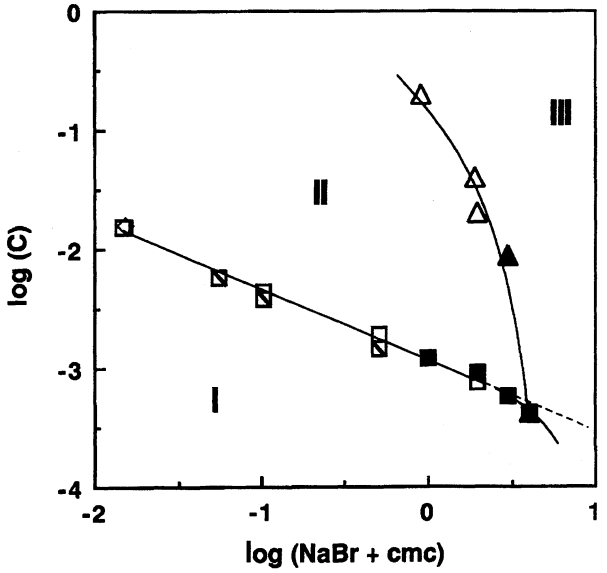

Fig. 7. Micellar phase diagram of DTAB system; □: from Refs. 22 and 23, ◇: cmc by auramine, ⧅: from Ref. 20, ■: from Ref. 4, △: from microviscosity by auramine and P3P, and ▲: from Ref. 4.

methylammonium bromides.

In a previous paper,[18] auramine was reported to be a good probe for the determination of a cmc. The present investigation reveals that auramine is useful for determining sphere-rod transitions and overlap threshold values of rodlike micelles. In conclusion, it was found that by using only a microviscosity probe (auramine), the cmcs and some micelle shape transitions can be detected. The phase diagrams of micellar solutions can also be obtained by combining the fluorescence probe method with other methods.

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