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The Stability of Spherical Micelles of Dodecyltrimethylammonium Chloride in Aqueous NaCl Solutions

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Light scattering from solutions of dodecyltrimethylammonium chloride in water and 4.00 M (1 M=1 mol dm^{-3}) NaCl has been measured at 25 °C, and the critical micelle concentrations and the micellar molecular weights have been determined. The critical micelle concentration, when combined with the previous data, follows the linear Corrin-Harkins equation over the whole range of NaCl concentrations. The micellar molecular weight remains low, *i.e.*, about 20000 even in the presence of 4.00 M NaCl, and the double-logarithmic relation between the micellar molecular weight and the ionic strength is represented by a straight line over the whole range of NaCl concentrations, when plotted together with the previous data. These results indicate that only spherical micelles are formed by dodecyltrimethylammonium chloride in the presence of added NaCl. The stability of the spherical micelle is attributed to the low degree of binding of Cl$^-$ on the cationic micelles.

In a recent work on light scattering$^{1)}$ we have shown that the micelle of dodecyldimethylammonium chloride is subject to a transition of its shape from spheres to rods when the concentration of added NaCl is increased across 0.80 M (1 M=1 mol dm^{-3}) and when the surfactant concentration considerably exceeds the critical micelle concentration (c.m.c.). By measurements of the viscosity of the micellar solutions,$^{2)}$ we have confirmed such a transition of micelle shape induced by the change in ionic strength.

In another work$^{3)}$ we have also demonstrated that even sodium dodecyl sulfate can form rodlike micelles in concentrated NaCl solutions beyond 0.45 M. The formation of large micelles of sodium dodecyl sulfate in 0.6 M NaCl was observed by Mazer and his coworkers$^{4,5)}$ and by Corti and Degiorgio,$^{6,7)}$ using both quasi-elastic and elastic light scattering, although the latter workers reserved to draw a conclusion for the formation of rodlike micelles and considered other possibilities as well.

Kushner and his co-workers$^{8)}$ measured both the light scattering and intrinsic viscosity of micellar solutions of dodecylammonium chloride in different concentrations of added NaCl. Their data on micellar molecular weight can be interpreted as indicating the formation of rodlike micelles in NaCl solutions more concentrated than 0.07 M.$^{1)}$ The observed intrinsic viscosity of the micellar solutions also suggests the formation of rodlike micelles.$^{2,9)}$

In the previous paper$^{1)}$ we have pointed out that the NaCl concentration or the ionic strength where the sphere-rod transition of an ionic micelle occurs is closely related to the preference of a surfactant molecule to a spherical micelle over a rodlike micelle. This preference is determined by the geometrical ease of packing of surfactant ions in a micelle and by the magnitude of repulsion among polar head groups on a micelle surface. From the geometry of a surfactant molecule we can see that dodecylammonium chloride is more adequately incorporated into a rodlike micelle than dodecyldimethylammonium chloride, and thus, dodecyltrimethylammonium chloride remains to form spherical micelles even in the presence of 0.5 mol kg^{-1} NaCl.$^{10)}$

In order to investigate the nature of the sphere-rod transition of ionic micelles, it is worth observing the light scattering of dodecyltrimethylammonium chloride micelles in more concentrated NaCl solutions and determining the micellar molecular weight as well as the micelle shape. This cationic surfactant has already been studied by Kushner and his co-workers$^{8)}$ and by Emerson and Holtzer,$^{10)}$ using the light-scattering method; they found it to associate into spherical micelles in the presence of NaCl less concentrated than 0.5 mol kg^{-1}.

Experimental

The sample of dodecyltrimethylammonium chloride was purchased from the Tokyo Kasei Kogyo Co., Inc., and was recrystallized from acetone three times. Thermal-decomposition gas chromatography was applied to this sample at the injection temperature of 300 °C and with the column temperature of 240 °C; the results showed that the sample contained 88.2% C_{12}, 9.5% C_{14}, 0.90% C_{10}, 0.86% C_{16}, and 0.55% C_8. The contaminating higher alkyl homologs would not influence the conclusion derived in this work.

NaCl was a special-grade reagent and was used after having been roasted. Water was redistilled from alkaline $KMnO_4$ in a glass still.

The light scattering and the refractive index increment were measured on Shimadzu apparatuses, PG-21 and DR-3, using the unpolarized light of 436 nm of mercury lamps. A cylindrical cell for light scattering was put in a thermostat jacket. The temperature for measurements was kept at 25±0.05 °C by circulating water of a constant temperature through the cell jackets. The procedure for the optical cleaning of the solutions and the methods of measurement and calibration were described previously.$^{1,3)}$

Measurements were carried out on solutions of dodecyltrimethylammonium chloride in water and in 4.00 M NaCl. The reduced intensity of light scattered in the 90° direction, R_{90}, was recorded, and the angular dissymmetry in the 45° direction, z_{45}, was examined. The value of dissymmetry was less than 1.02 above the c.m.c., but it was sometimes higher at lower concentrations. Data showing dissymmetries higher than 1.03 were discarded.

Results

Figure 1 shows the reduced intensity, R_{90}, of the surfactant solutions as a function of the concentration, c (g cm^{-3}). The reduced intensity increases with an

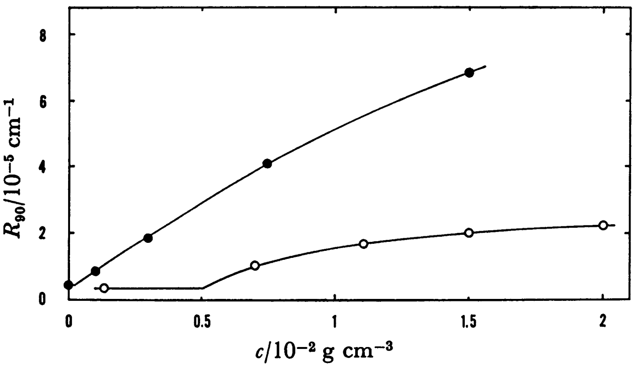

Fig. 1. Reduced intensity of scattered light plotted against surfactant concentration at 25 °C.
○: In water, ●: in 4.00 M NaCl.

Table 1. Refractive index increment and light scattering

C_s/M	$(\partial\tilde{n}/\partial c)_{C_s}$/cm^3 g^{-1}	C_o/10^{-3} M	c_o/10^{-2} g cm^{-3}	R°_{90}/10^{-6} cm^{-1}
0	0.158	19.3	0.51	3.34
4 00	0.123	0.68±0.07	0.018±0.002	4.18

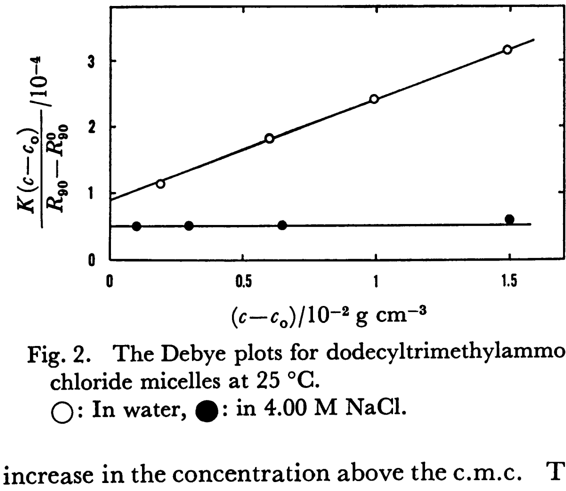

Fig. 2. The Debye plots for dodecyltrimethylammonium chloride micelles at 25 °C.
○: In water, ●: in 4.00 M NaCl.

increase in the concentration above the c.m.c. The values of c.m.c., c_0 (g cm^{-3}) or C_0 (M), and of the reduced intensity there, R°_{90}, are given in Table 1, together with the refractive index increment, $(\partial\tilde{n}/\partial c)_{C_s}$, where C_s is the molar concentration of added NaCl.

Figure 2 shows that the Debye plots both in water and in 4.00 M NaCl are straight lines expressed by

$$\frac{K(c-c_0)}{R_{90}-R^\circ_{90}} = \frac{1}{M} + 2B(c-c_0), \tag{1}$$

where M is the micellar molecular weight and B is the second virial coefficient. The optical constant is

$$K = 2\pi^2\tilde{n}_0^2(\partial\tilde{n}/\partial c)^2_{C_s}/N_A\lambda^4, \tag{2}$$

where $\tilde{n}_0$ is the refractive index of the solvent; λ the wavelength of light, and N_A the Avogadro number.

Table 2. Characteristics of the spherical micelles

C_s/M	M	m'	B/10^{-3} cm^3 g^{-1}	M_m	m	p/m
0	11 500±500	43.6	7.50	13 900	52.8	0.18
4.00	20 000±1 500	75.8	0.05	21 500	81.4	0.2

Table 2 lists the values of the micellar molecular weight, the micellar aggregation number, $m'=M/264$, and the second virial coefficient. The value of the aggregation number indicates that the micelle of dodecyltrimethylammonium chloride is spherical even in 4.00 M NaCl solutions. The positive value of the second virial coefficient also supports the formation of spherical micelles alone, because it has been previously established that rodlike micelles are formed only when the surfactant concentration exceeds the c.m.c.[1,3,6] We have also observed a negative second virial coefficient for a rodlike micelle of *N*,*N*-dimethyldodecylamine oxide half-neutralized by HCl in 0.2 M NaCl.[11] Debye and Anacker[12] reported positive second virial coefficients for the rodlike micelles of hexadecyltrimethylammonium bromide in 0.178 and 0.233 M KBr, but it proves that even for these solutions negative coefficients can be assigned at low micelle concentrations if lower values of c.m.c. are chosen.

To confirm the formation of spherical micelles only and the absence of rodlike micelles for dodecyltrimethylammonium chloride over the whole range of NaCl concentrations, we have performed an experiment to observe the light scattering from a solution of the cationic surfactant in saturated NaCl. To a 0.75 × 10^{-2} g cm^{-3} solution of the cationic in 4.00 M NaCl, solid NaCl was added in such a way as to give a 5.9 M NaCl solution if it dissolved completely. The supernatant was sufficiently clean to permit reliable light-scattering measurements and gave a value of reduced intensity slightly lower than that for the 4.00 M NaCl solution.

Discussion

The Double-logarithmic Relations of the c.m.c. and the Micellar Molecular Weight to the Ionic Strength. Figure 3 shows the Corrin-Harkins plot for dodecyltrimethylammonium chloride in the presence of NaCl. The data of previous workers[8,10] are also plotted. It is seen that the Corrin-Harkins equation

$$\log C_o = -0.631\log(C_o+C_s) - 2.794 \tag{3}$$

proposed by Emerson and Holtzer[10] can be extended up to 4.00 M NaCl. In previous papers[1,13] we have

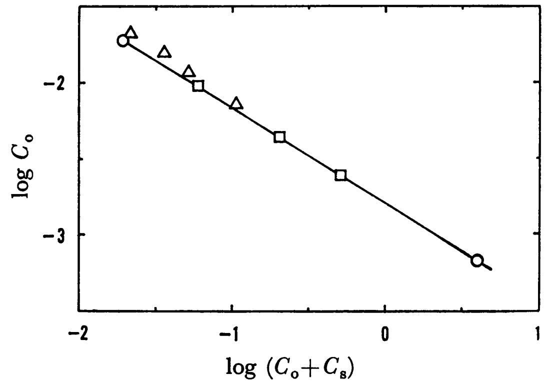

Fig. 3. The Corrin-Harkins plot for the micelles in NaCl solutions.
○: Present results, △: Kushner and his coworkers,[8) □: Emerson and Holtzer.[10)

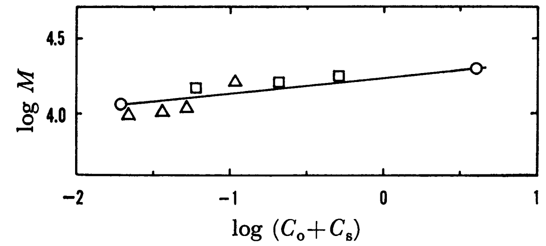

Fig. 4. The double-logarithmic relation of micellar molecular weight with ionic strength in NaCl solutions. ○: Present results, △: Kushner and his coworkers,[8] □: Emerson and Holtzer.[10]

pointed out that the linear Corrin-Harkins relation holds only when spherical micelles are formed; now we have confirmed that proposition. For the stabilization of spherical micelles, the added salt simply serves to shield the electrostatic effect of a charged micelle.

Figure 4 shows the double-logarithmic relation of the micellar molecular weight to the ionic strength. Together with the data of other workers,[8,10] it is represented by a linear relation:

$$\log M = 0.105 \log(C_o + C_s) + 4.26. \qquad (4)$$

The low value of the coefficient of Eq. 4 is consistent with the spherical micelles.

The scatter of the points in Fig. 4 could be partly attributed to different values of the refractive index increment: *e.g.*, the value of Kushner and his coworkers[8] is 0.155 in water, but the value of Emerson and Holtzer,[10] obtained by an extrapolation, is 0.160 in water; while our value is 0.158. But the deviation seems to occur mostly in the opposite direction.

The Factors Determining the Sphere-rod Transition. In the previous paper[1] we proposed a postulate that the salt-induced transition of the micelle shape is controlled by the ratio of the size of the polar head group to the hydrocarbon part of a surfactant molecule and by the degree of counterion binding on the micelle surface. The first factor is related to the geometrical packing of surfactant molecules in a micelle. The ionic strength where the transition occurs should be higher when the head group is more bulky; this was confirmed for the head-group homologs of dodecylammonium chloride in NaCl solutions. That is, the transition occurs at 0.07 M NaCl for dodecylammonium chloride and at 0.80 M NaCl for dodecyldimethylammonium chloride. We can now add an example of dodecyltrimethylammonium chloride, for which the transition NaCl concentration is higher than the saturated NaCl concentration.

The second factor is related to the electrostatic repulsion among polar head groups. The counterion binding on the micelle surface may be examined by changing either the counterion species or the concentration of added salt. The effect of counterion species on the size of dodecyltrimethylammonium micelles in water was investigated by means of light scattering; it was found that only spherical micelles are formed, as suggested by the observed low aggregation numbers.[14–17] The effect of the concentration of added KBr or NaBr on the micelle size of dodecyltrimethylammonium bromide was also investigated by light scattering; it was demonstrated that only spherical micelles are formed in the presence of salt less than 0.5 mol kg^{-1}.[10,15,17]

Anacker and Ghose[18] measured the micellar molecular weight of dodecyltrimethylammonium bromide in 0.500 mol kg^{-1} sodium salt solutions and found that a large micelle with an aggregation number as high as 10 000 is formed in 0.500 mol kg^{-1}NaSCN. The large micelle must be rodlike, and its formation may be attributed to the reduced electrostatic repulsion among surfactant ions caused by the high degree of binding of SCN$^-$ on the cationic. That is, only a strongly hydrophobic ion, SCN$^-$, can bind with the cationic micelle to an amount large enough to stabilize a rodlike micelle.

Consequently, we may conclude that the sphere-rod transition of dodecyltrimethylammonium micelles cannot be induced by the addition of NaCl, because Cl$^-$ does not bind with the surfactant micelle sufficiently.

It is known that the Prins-Hermans-Princen-Mysels theory[19,20] can derive the apparent degree of ionization, p/m, of an ionic micelle, together with its "true" molecular weight, M_m, and its "true" aggregation number, m, based on the assumption of an ideal polyelectrolyte solution. Table 2 also includes these values of the micelles. The low degree of binding of Cl$^-$ would be revealed in the rather large values of the apparent degree of ionization of the micelle, as given in Table 2.

If the hydrocarbon part of alkyltrimethylammonium is longer, the cationic is adapted to a rodlike micelle better than to a spherical micelle. Thus, hexadecyltrimethylammonium bromide can form the rodlike micelles in 0.178 and 0.233 M KBr,[12] while it forms spherical micelles in water and in 0.0130 M KBr.[14,15]

Small-angle X-ray scattering measurements demonstrated that the radius of gyration of an ionic micelle in water suddenly increases with an increase in the surfactant concentration beyond a certain value, and this change was attributed to the transition of the micelle shape from a sphere to a rod.[21,22] We can interpret such a transition as also being caused by the increase in ionic strength given by the surfactant itself.

In this concentration-induced transition of micelle shape, we can still see evidence for the counterion binding. Reiss-Husson and Luzzati[21] determined the surfactant concentration for the sphere-rod transition and tabulated its approximate values as 40×10^{-2} g cm^{-3} for hexadecyltrimethylammonium chloride and as 5×10^{-2} g cm^{-3} for hexadecyltrimethylammonium bromide. This difference in concentration for the transition could be considered to stand for the stronger binding of Br$^-$ than Cl$^-$ to the cationic micelle.

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