

negative for *n*-heptane and *n*-hexane. This inverse sense mass effect was first observed for cyclohexane self-diffusion.^{1,3,4}

The largest isotope mass effect is therefore observed in the solvent of lowest viscosity, and the magnitude of (A/D_1) is similar to that obtained for benzene diffusing in that liquid.^{25,28} The variation of the cyclohexane results cannot be rationalized so easily in terms of a simple viscosity dependence, and there is currently no obvious physical explanation of why the mass effects should be in the inverse sense to those observed for benzene.

We can only speculate that the noted variation must reflect the detailed and specific changes in the intermolecular force system between solute and solvent. In this context, we note (Figure 6) that for benzene there is an equally good correlation between the isotope mass effect (A/D_1) and the excess heat of mixing (ΔH_E)²⁹ for benzene

(28) J. G. Albright and K. Aoyagi, *J. Chem. Phys.*, **64**, 81 (1976).

with the solvent. We have made a similar proposal to account for the distinction between benzene and cyclohexane in self-diffusion and noted that, in this case, the small amount of available experimental data (excess heats and volumes of mixing of C_6H_6/C_6D_6 against those for C_6H_{12}/C_6D_{12})³⁰ do provide a reasonable basis for the speculation. In view of this, it would be most interesting to have values of equivalent parameters for the mixing of C_6H_{12} and C_6D_{12} with the solvents used in this experiment. Quite large distinctions might be expected between, for example, the heats of mixing of C_6H_{12} and C_6D_{12} with perfluorobenzene and *n*-hexane. Unfortunately, this data is not available.

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Rodlike Micelles of Sodium Dodecyl Sulfate in Concentrated Sodium Halide Solutions

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Light scattering from aqueous solutions of sodium dodecyl sulfate has been measured in the presence of 0.80 M sodium halides at 35 °C. Sodium dodecyl sulfate forms micelles having a molecular weight of $\sim 50\,000$ or less, at the critical micelle concentration, 0.013 g dL^{-1} , in solutions of all sodium halides except for NaSCN, in which the micelle size is even smaller. The average micelle size increases with increasing concentration of sodium dodecyl sulfate further, and it reaches a maximum around 1 g dL^{-1} . The molecular weight of the large micelle formed at the high concentrations is in the order: NaSCN < NaF < NaCl < NaBr < NaI, and it is 185 000 in NaSCN and 357 000 in NaI solutions. The angular dependence of light scattering indicates that the large micelles are rodlike and have a common structure in NaCl, NaBr, and NaI solutions. It is concluded that the salt-induced sphere-rod transition of ionic micelles is not caused by the change in the structure of water, since the ionic strength for transition is independent of co-ion species of added salt. The dissymmetry and the angular dependence of light scattering in NaF solutions are anomalous at the concentration range just above the critical micelle concentration, and this can be attributed to the formation of trace amounts of microgel particles consisting of spherical micelles, possibly linked by the contaminant polyvalent cations in NaF.

Introduction

In a previous paper¹ we have shown by means of light scattering that the micelle of sodium dodecyl sulfate (SDS) changes its shape from spherical to rodlike when the concentration of added NaCl exceeds 0.45 M and the micelle concentration is $\sim 1\text{ g dL}^{-1}$. Such an effect of added NaCl on the SDS micelle was also observed by Mazer and his co-workers^{2,3} by the measurements of quasi-elastic and total-intensity light scattering. Corti and Degiorgio^{4,5} also observed large values of aggregation number and hydrodynamically equivalent radius of the SDS micelle in 0.6 M NaCl by using the same techniques, but they reserved judgment on the formation of rodlike micelles and considered other possibilities as well.

In a recent work⁶ we have also demonstrated that the micelle of dodecyltrimethylammonium chloride changes its shape from spherical to rodlike when the NaCl concentration is higher than 0.80 M and the micelle concentration is finite. With some other cationic surfactants we can similarly observe definite evidence for the occurrence of sphere-rod transition of micelle shape induced by the change in concentration of added salt.

There are at least two factors responsible for determining such a transition of micelle shape. One is the electrostatic effect of simple salt due to the counterion binding on ionic micelles, and the other is the hydrophobic interaction between surfactant molecules or ions caused by the change in the hydrogen-bonded structure of water. In order to distinguish these two factors for the transition of micelle shape, we have undertaken to measure light scattering from SDS micelles in concentrated salt solutions simply by changing the co-ion species of added salt and to determine the micelle size and shape.

(1) S. Hayashi and S. Ikeda, *J. Phys. Chem.*, **84**, 744 (1980).

(2) N. A. Mazer, G. B. Benedek, and M. C. Carey, *J. Phys. Chem.*, **80**, 1076 (1976).

(3) C. Y. Young, P. J. Missel, N. A. Mazer, G. B. Benedek, and M. C. Carey, *J. Phys. Chem.*, **82**, 1375 (1978).

(4) M. Corti and V. Degiorgio, *Ann. Phys. (Paris)*, **3**, 303 (1978).

(5) M. Corti and V. Degiorgio in "Solution Chemistry of Surfactants", Vol. 1, K. L. Mittal, Ed., Plenum, New York, 1979, p 377.

(6) S. Ikeda, S. Ozeki, and M. Tsunoda, *J. Colloid Interface Sci.*, **73**, 27 (1980).

We have measured light scattering of aqueous solutions of SDS in five different sodium halides of 0.80 M at 35 °C: NaF, NaCl, NaBr, NaI, and NaSCN. The results on SDS solutions in 0.80 M NaCl were published previously.¹ The temperature for the measurements is chosen as 35 °C in order to avoid the possible disturbance of contaminants revealed in anomalous dissymmetry of light scattering.

We have arrived at the conclusion that the sphere-rod transition of the SDS micelle is not influenced by the halide ion species of added salt, and that it is, therefore, mainly caused by the electrostatic effect of counterion binding on the micelle. Nevertheless, we have also found that the sizes of rodlike micelles of SDS differ considerably, dependent on co-ion species of added salt, indicating the effect of hydrophobic interaction on micelle size.

In this series of experiments, we may anticipate the applicability of the theory of Vrij and Overbeek⁷ on the light scattering in a multicomponent solution containing a polyelectrolyte solute. In this application, however, we have to postulate that the micelle molecular weight remains constant, irrespective of the presence of different kinds of added salts. Such an application of this theory was performed by Huisman⁸ on SDS solutions in various sodium halides of 0.01, 0.03, 0.1 and 0.3 M.

Experimental Section

The SDS sample was the same as previously used.¹ NaF was the Merck reagent of suprapur grade, Art. 6450, and NaBr, NaI, and NaSCN were of special grade reagents of Nakarai Chemical Co., Inc., Kyoto. The purities of these sodium halides were examined by following the JIS methods, and they were found to be 99.6, 99.4, and 99.8% for NaF, NaI, and NaSCN, respectively, except for the moisture contents being 0.1, 0.7, and 3.2%, respectively. All of the salts were used without further purification.

Aqueous solutions of SDS in 0.80 M sodium halides were prepared and clarified at 36 °C in the same way as previously done on its solutions in 0.60 and 0.80 M NaCl.¹ They were filtered through a Sartorius membrane filter, SM11311, having a pore size of 10 nm, and directly poured into a cylindrical cell for light-scattering measurements. The cell was immediately put into a cell housing in the photometer.

Light-scattering measurements were carried out on a Shimadzu PG-21 light-scattering photometer using unpolarized light of a mercury lamp at 436 nm. The refractive index increment of the solutions was measured on a Shimadzu DR-3 differential refractometer at 436 nm. The methods of calibration and measurement were described previously.¹ The temperature was kept at 35 ± 0.05 °C by circulating water of constant temperature through the cell housings.

The reduced intensity, R_θ , of light scattered at an angle θ from a solution of concentration c (g cm⁻³), is given by the Debye equation

$$R_\theta = R_\theta^0 + KMP(\theta)(c - c_0) \quad (1)$$

if the external interference is negligible. Here R_θ^0 is the reduced intensity at the critical micelle concentration, c_0 , and K is the optical constant

$$K = 2\pi^2\bar{n}_0^2(\partial\bar{n}/\partial c)_{c_0}^2/N_A\lambda^4 \quad (2)$$

where \bar{n}_0 and $(\partial\bar{n}/\partial c)_{c_0}$ are the refractive index of solvent and the refractive index increment of solution at constant

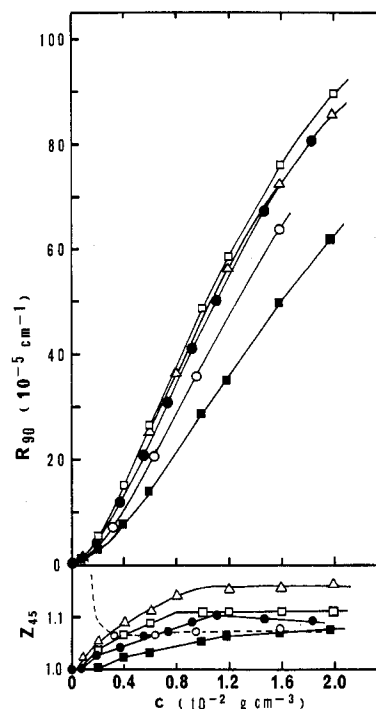


Figure 1. Reduced intensity, R_{90} , and dissymmetry, z_{45} , of light scattering of SDS solutions in 0.80 M sodium halides at 35 °C: (○) NaF; (●) NaCl; (□) NaBr; (△) NaI; (■) NaSCN.

TABLE I: Refractive Index Increment and Light Scattering of SDS Solutions in 0.80 M Sodium Halides at 35 °C

	$(\partial\bar{n}/\partial c)_{c_0}$ cm ³ g ⁻¹	c_0 , 10 ⁻² g cm ⁻³	R_{90}^0 , 10 ⁻⁵ cm ⁻¹	z_{45} (highest value)
NaF	0.108	0.013	3.29	1.07
NaCl	0.103	0.013	3.82	1.10
NaBr	0.103	0.013	4.65	1.11
NaI	0.093	0.013	7.04	1.16
NaSCN	0.103	0.014	7.01	1.08

salt concentration, C_s (M), both at a wavelength λ , and N_A is the Avogadro number. The (apparent) weight-average molecular weight and aggregation number of the micelle are represented by M and $m' = M/M_1$, respectively, where M_1 is the molecular weight of surfactant monomer. The particle scattering factor is represented by $P(\theta)$. From the angular dependence of light scattering, the radius of gyration of the micelle, R_G , can be obtained as the initial slope of the reciprocal envelope plotted against $\sin^2(\theta/2)$. If the micelle is a rigid rod, its length is given by $L = 12^{1/2}R_G$.

Results

Figure 1 shows the variations of reduced intensity at the 90° direction, R_{90} , and dissymmetry at 45°, z_{45} , with SDS concentration for different sodium halide solutions of 0.80 M at 35 °C. The reduced intensity increases above the critical micelle concentration (cmc) around 0.013 g dL⁻¹ or 4.5 × 10⁻⁴ M, first convex downwardly and then convex upwardly. The observed curvature suggests an increase in micelle size with increasing micelle concentration. The cmc is so low that it can be exactly identified with difficulty. It is chosen to give a smooth Debye plot such as shown below. The values of reduced intensity at the cmc are substantially equal to those of the pure salt solution free from SDS, and these values are listed in Table I together with those of cmc and refractive index increment. It is seen that the cmc is scarcely altered by the change

(7) A. Vrij and J. Th. G. Overbeek, *J. Colloid Sci.*, **17**, 570 (1962).

(8) H. F. Huisman, *Proc. K. Ned. Akad. Wet., Ser. B: Phys. Sci.*, **67**, 388 (1964).

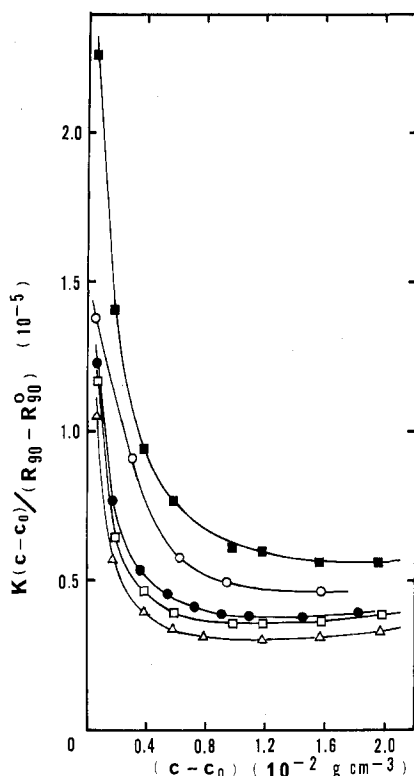


Figure 2. Debye plots for SDS solutions in 0.80 M sodium halides at 35 °C; light scattering in the 90° direction: (O) NaF; (●) NaCl; (□) NaBr; (Δ) NaI; (■) NaSCN.

in the co-ion species of added salt.

The dissymmetry increases gradually above the cmc and reaches a value which is almost constant for each sodium halide solution. This feature indicates that, in addition to the small micelle formed at the cmc, large micelles are formed with increasing micelle concentration and that the equilibrium between these two kinds of micelles shifts with changing total micelle concentration.

It is noticed that the angular dissymmetry is high and anomalous for 0.80 M NaF solutions of SDS when its concentration is close to the cmc. This anomaly will be discussed later in relation to the profile of angular dependence of light scattering.

Figure 2 shows the Debye plots for the 90° direction. They confirm the supposition made above: beyond the cmc, small and large micelles coexist and are in equilibrium, and the amount of the large micelle increases with increasing micelle concentration. Although the extrapolation of these plots to the cmc is not readily possible in such a way as to give the molecular weight of the small micelle, the apparent micelle size of the large micelle can be estimated from the reciprocal values of the ordinate at its minimum. It is clear that the apparent micelle size of SDS at a fixed concentration in 0.80 M sodium halide solutions is in the order: NaSCN < NaF < NaCl < NaBr < NaI.

Figure 3 illustrates the angular dependence of light scattering of SDS micelles in 0.80 M NaBr at 35 °C. When the micelle concentration is low, the angular dependence is different at low angles from that at high angles: at low angles no dependence is observed, but at high angles higher than a certain value a linear dependence having a positive slope is manifest. With increasing micelle concentration the linear part begins to occur at a lower angle. At micelle concentrations higher than $\sim 1 \text{ g dL}^{-1}$, the linear section having a positive slope extends over the whole range of scattering angles. This kind of behavior of angular de-

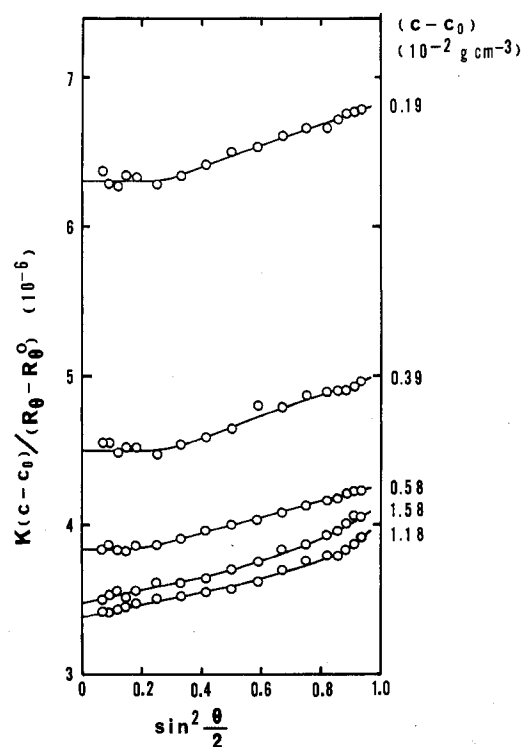


Figure 3. Angular dependence of light scattering of SDS solutions in 0.80 M NaBr at 35 °C.

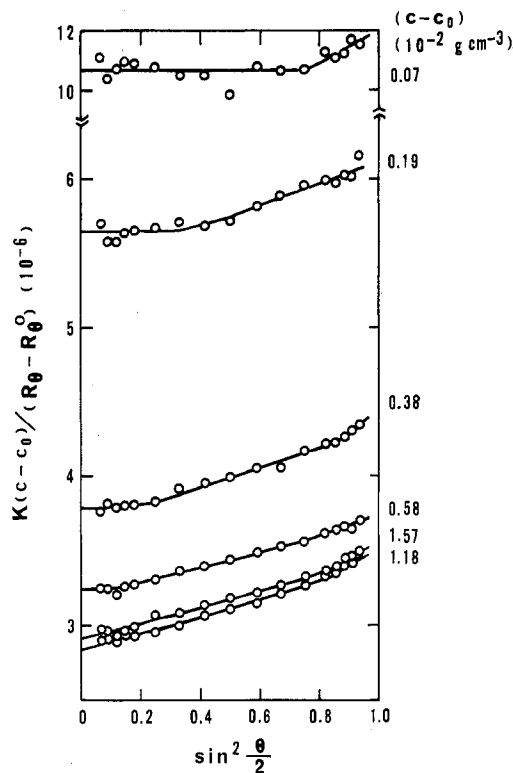


Figure 4. Angular dependence of light scattering of SDS solutions in 0.80 M NaI at 35 °C.

pendence could be attributed to the presence of two kinds of micelles in equilibrium, one being formed at the cmc but small, and the other being formed with increasing micelle concentration and very large.

In all of the sodium halide solutions of SDS except for its NaF solution, similar behavior of angular dependence can be observed. For 0.80 M NaCl solutions the angular dependence was previously measured.¹ For 0.80 M NaI

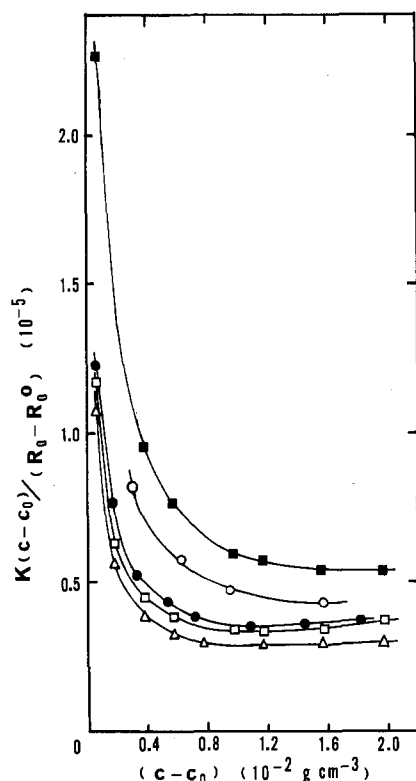


Figure 5. Debye plots for SDS solutions in 0.80 M sodium halides at 35 °C; light scattering extrapolated to the 0° direction: (O) NaF; (●) NaCl; (□) NaBr; (Δ) NaI; (■) NaSCN. For the extrapolation of SDS solutions in 0.80 M NaF, see Figure 8.

solutions at 35 °C, it is illustrated in Figure 4.

By plotting the intercept of angular dependence, we can obtain the Debye plots for the 0° direction, as shown in Figure 5. If we assume no external interference, the reciprocal value of the Debye plot should give the weight-average molecular weight of micelles. At the cmc the SDS micelles have molecular weights around 50 000 or less in all of the sodium halide solutions, except for that in NaSCN solution in which the micelle is even smaller. With increasing micelle concentration, the large micelle is formed and its amount increases. The micelle molecular weight of SDS at a fixed concentration in 0.80 M sodium halide solution is in the order as cited above. At the minimum of the Debye plot, the micelle molecular weight reaches ~185 000–357 000, as listed in Table II. These values can be approximately assigned to the molecular weight of the large micelle, since the amount of large micelle is predominant there.

The presence of two distinct kinds of micelles and their equilibrium may be confirmed by observing the dependence of polydispersity of micelle size on SDS concentration. While the weight-average molecular weight of micelles, M_w , is given by eq 1, their number-average molecular weight, M_n , can be calculated by eq 3, both at a given

$$\bar{M}_n = \frac{c - c_0}{\int_0^{c-c_0} \frac{d(c - c_0)}{M}} \quad (3)$$

concentration, c .⁹ Then we can readily obtain a measure of polydispersity of the micelle size, M_w/\bar{M}_n .

Figure 6 shows the variation of M_w/\bar{M}_n with micelle concentration for SDS in 0.80 M sodium halides at 35 °C.

TABLE II: Molecular Weight and Length of Rodlike Micelles of SDS in 0.80 M Sodium Halide Solutions at 35 °C

	c , 10^{-2} g cm^{-3}	M	m'	R_G , Å	L , Å	L/m' , Å
NaF	1.58	229 000	796	172	596	0.75
NaCl	1.10	284 000	985	172	596	0.61
NaBr	1.19	297 000	1030	176	609	0.59
NaI	1.19	357 000	1240	210	728	0.59
NaSCN	1.97	185 000	641	144	498	0.78

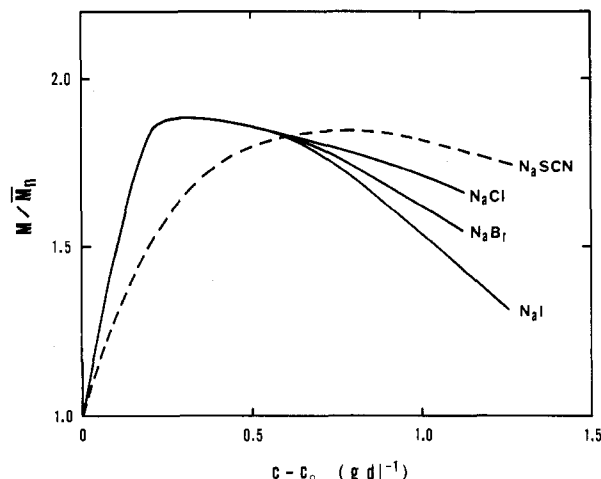


Figure 6. Variation of the degree of polydispersity, M_w/\bar{M}_n , of SDS micelles with total micelle concentration: (—) in 0.80 M NaCl, NaBr, and NaI solutions; (---) in 0.80 M NaSCN solution.

For this calculation it is required to know the value of M at zero micelle concentration, i.e., the molecular weight of the small micelle, but it proves that an approximate value suffices to obtain the general trend of the ratio M_w/\bar{M}_n as a function of concentration. We can see that the ratio M_w/\bar{M}_n increases from unity at the cmc, reaches a maximum having a value less than 2, and then decreases toward unity, as the micelle concentration increases. Such a behavior can be most simply explained as the result of a shift of an association-dissociation equilibrium between two kinds of micelles.

We can also notice that the polydispersity of SDS micelles is common in NaCl, NaBr, and NaI solutions, suggesting similar size distribution of the micelles. Some differences occurring at higher concentrations can be attributed to the effect of different values of the second virial coefficient, which have been neglected and set equal to zero here. On the other hand, the polydispersity of SDS micelles in NaSCN solution is different from that in NaCl, NaBr, and NaI solutions. The equilibrium constant between these two micelles would differ from each other.

The average radius of micelles can be estimated from the slope of the angular dependence of light scattering. At the minimum of the Debye plot, the contribution of the small micelle to the radius of gyration may be safely omitted, since its amount is low. In order for the radius of gyration of the large micelle to conform with the micelle molecular weight, it is readily found that the micelle shape can be best fitted to a rigid rod, as compared with a sphere or a disk. In Table II, the values of the radius of gyration and the length of the rodlike micelles are given. Both the molecular weight and the length of the rodlike micelle vary with the order of the lyotropic series of the co-ion of added salt, except for the SCN^{-1} ion.

If the rodlike micelles formed in different sodium halide solutions have a common structure, independent of co-ion species of added salt, the molecular pitch of a micelle,

(9) E. T. Adams, Jr., *Biochemistry*, 4, 1646 (1965).

(10) M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, 71, 1898 (1967).

L/m' , should be equal for all of these micelles. As can be seen in Table II, its value is equal to ~ 0.6 Å in NaCl, NaBr, and NaI solutions but is larger in NaF and NaSCN solutions. In the former three solutions, the rodlike micelles would have a common structure.

In 0.80 M NaF solutions some effects of contaminants are manifest in light scattering, as will be referred to later. Accordingly, we may expect that the molecular pitch of the SDS micelle in NaF solutions would be equal to those in the above three sodium halide solutions. On the other hand, the smaller size and shorter length of the rodlike micelle in NaSCN solution as well as the deviation of the effect of NaSCN from the lyotropic series suggest that some other interaction different from the lyotropic effect is responsible for the micelle formation of SDS in this solution.

Discussion

Micelle Size Dependent on Co-ion Species of Added Salt. We have shown in this work that SDS associates into rodlike micelles in 0.80 M solutions of various sodium halides at 35 °C, when the SDS concentration exceeds the cmc and the micelle concentration is finite. The molecular weight of the rodlike micelles depends on the co-ion species of added salt and changes in the order of the lyotropic series of halide ions except for SCN⁻ ion: NaSCN < NaF < NaCl < NaBr < NaI. The difference in micelle size must be caused by the effect of co-ion species on hydrophobic interaction in the micelle formation or the extent of destruction of the hydrogen-bonded structure of water.

Huisman⁸ determined the micelle molecular weight of SDS at low concentrations of sodium halide, i.e., in 0.01, 0.03, 0.1, and 0.3 M, in which SDS could form only spherical micelles, and he found that the (apparent weight-average) molecular weight of the spherical micelle was dependent on the co-ion species of added salt but was in the order opposite to that found for the rodlike micelles: NaF > NaCl > NaBr > NaI.

Consequently, the sizes of rodlike micelles at high ionic strengths are enhanced by the hydrophobic effect of added salt or the destruction of the hydrogen-bonded structure of water, while the spherical micelles formed at low ionic strengths are reduced in size by the other effects operating in the opposite direction of the lyotropic series. Figure 7 shows the double logarithmic relation of micelle molecular weight of SDS with ionic strength, both at 25 and 35 °C. We can observe the opposing effects of halide ions on the micelle size above and below ~ 0.45 M sodium halide concentration.

The deviation of the effect of NaSCN on the size of the rodlike micelle from the lyotropic series and the possible different structure of the micelle in NaSCN deserve some comments. In contrast to the spherical shape of genuine halide ions, an SCN⁻ ion is asymmetric and polar, so that it can interact even with nonionic micelles more strongly as well as with anionic micelles.

Some relevant effects of NaSCN on the micelle size can be noticed in the results of light-scattering measurements on a nonionic, poly(oxyethylene) nonylphenyl ether having 50 ethylene oxide residues.¹¹ The molecular weight of the nonionic micelle was found to be 46 000 in 0.86 M NaSCN and 62 000 in 0.86 M NaCl, and this order of micelle size is coincident with that of rodlike SDS micelles. Since SDS in 0.80 M sodium halide solutions is sufficiently shielded from its electrostatic effect by the ionic atmosphere, its micelles in these media would behave like a nonionic

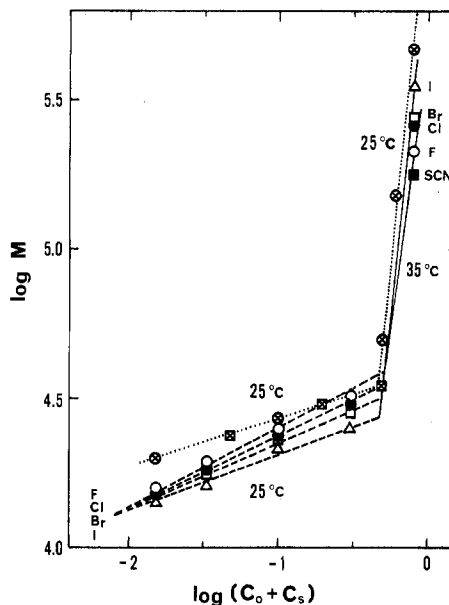


Figure 7. Double logarithmic relations between micelle molecular weight and ionic strength. Added salt: (○) NaF; (●) NaCl; (□) NaBr; (△) NaI; (■) NaSCN. Data at 35 °C in the right (for rodlike micelles) are from the present work, and data at 25 °C in the lower part (for spherical micelles) are from Huisman (ref 8). For comparison, the data in NaCl solutions at 25 °C taken from the previous work (ref 1) (⊙) and from Emerson and Holtzer (ref 10) (⊗) are also given as points and are connected by dotted lines.

micelle, in spite of their different micelle shapes.

It should be noted here, however, that the cmc of SDS micelles in both low⁸ and high ionic strengths is insensitive to the co-ion species of added salt. In contrast, the non-ionic micelles have the cmc sensitively influenced by the halide ion species of added sodium salt or by the added salt species. Poly(oxyethylene) nonylphenyl ether having 50 ethylene oxide residues was found to have a higher cmc in 0.86 M NaSCN than in 0.86 M NaCl.¹¹ Similarly, the nonionic having 15 ethylene oxide residues had a higher cmc in 0.86 M NaSCN, but it also showed a higher cmc in 0.86 M NaI than in 0.86 M NaCl.¹² A similar reversed lyotropic effect on the cmc of the same nonionic micelle had also been published previously.¹³ These effects of salt species on the cmc of nonionics have been attributed to the salting-out effect, i.e., the effects of ionic size and decrease in dielectric constant.

Salt-Induced Sphere-Rod Transition of Ionic Micelles. As can be seen in Figure 7, the rodlike micelle of SDS in NaCl solutions grow very sharply with increasing ionic strength beyond 0.45 M. The ionic strength where the sphere-rod transition occurs is 0.45 M when the ionic strength is mainly given by NaCl. If the transition of micelle shape were sensitively influenced by the co-ion species of added salt, we could expect the micelle molecular weight to be strongly dependent on the co-ion species because the ionic strength for transition would shift. Nevertheless, as shown in Figure 7, we have high molecular weights in 0.80 M sodium halides, all attributable to rodlike micelles. Thus we can conclude that the ionic strength where the transition of micelle shape occurs is not influenced by the co-ion species of added salt.

This conclusion implies that the sphere-rod transition of ionic micelles is induced by the reduced electrostatic interaction between SDS molecules or dodecyl sulfate ions,

(11) M. J. Schick, S. M. Atlas, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1326 (1962).

(12) M. J. Schick, *J. Colloid Sci.*, **17**, 801 (1962).

(13) L. Hsiao, H. N. Dunning, and P. B. Lorentz, *J. Phys. Chem.*, **60**, 657 (1956).

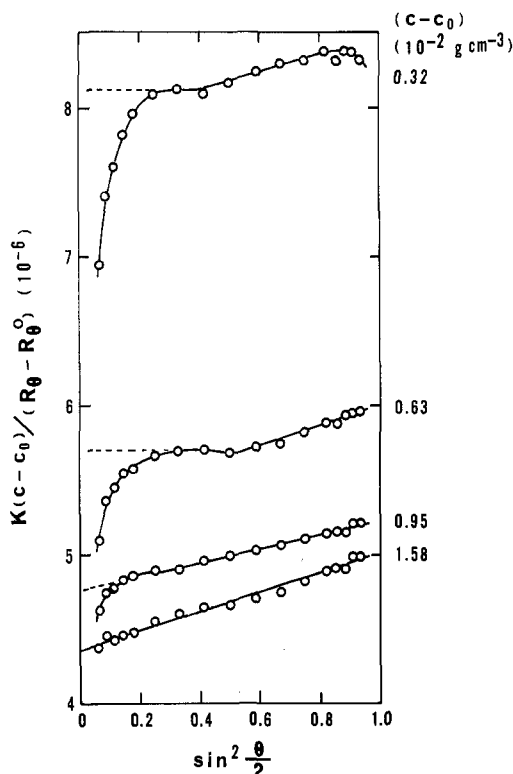


Figure 8. Angular dependence of light scattering of SDS solutions in 0.80 M NaF at 35 °C. The data are extrapolated to 0° in the manner as shown by dashed lines.

mainly caused by the counterion binding on charged micelles. The co-ion species of added salt can alter only the molecular weight of rodlike micelles but does not influence the transition of micelle shape. The importance of counterion species in the sphere-rod transition of ionic micelles can be presumed from the results of light-scattering measurements on the micelle molecular weight of some cationics, such as dodecylpyridinium halides,¹⁴ dodecyltrimethylammonium bromide,¹⁵ and cetylpyridinium bromide,¹⁶ in different salt solutions.

The effect of ionic strength on the aggregation number of ionic micelles was recently discussed by Nagarajan and Ruckenstein¹⁷ as a part of their general and straightforward statistical calculation, and the formation of large micelles at high ionic strengths was derived as the surfactant concentration was increased, while the repulsive electrostatic interaction between ionic surfactants resulted in the formation of small micelles.

Anomalous Dissymmetry Observed in NaF Solutions of SDS. In Figure 1 we have observed an anomaly in dissymmetry of light scattering for SDS solutions in 0.80 M NaF even at 35 °C. The anomaly occurred at concentrations just above the cmc. In order to elucidate the phenomenon in more detail, we show in Figure 8 the results of the angular dependence of light scattering in these solutions.

As can be readily seen, the anomaly occurs only with dilute micellar solutions, and it is attributable to the strong scattering at low angles. This kind of anomalous angular dependence was already observed with SDS solutions in

0.60 and 0.80 M NaCl at 25 °C, and its possible mechanism was discussed previously.¹ Since the anomaly was absent from the solutions of lower NaCl concentrations or at higher temperatures such as 35 °C, its origin was attributed to an effect of some contaminants coming from the added NaCl. With 0.80 M NaF the same kind of anomaly was manifest even at 35 °C. Consequently, our previous supposition that the source of contaminants is in the added salt but not in the SDS sample has been confirmed by the present work.

The anomalous angular dependence of light scattering can be caused by the presence of trace amounts of microgel particles in the solutions as was found in the cases of solutions of linear polymers contaminated with trace amounts of branched chains.¹⁸⁻²⁰ The microgel of SDS would consist of metastable spherical micelles linked by contaminant polyvalent cations, because the anomaly is associated with the concentration range where spherical micelles are just formed and some of them are going to convert into rodlike micelles. Such microgels of SDS could be formed readily in the high salt concentrations and at low temperatures, owing to its high Krafft point or its high critical micelle temperatures and to its molecular shape more adapted to spherical micelles.⁶ A microgel particle would have a network structure consisting of spherical micelles linked by contaminant cations and water occluded in it. Since trace amounts of contaminants are effective for such an anomaly, they could be identified with great difficulty by chemical analysis.

Appendix

Application of the Vrij-Overbeek Theory. So far we have assumed that the light scattering of the micellar solution is brought about by the fluctuation of micelle concentration only, neglecting the contributions from the coexisting small ions, and we have treated the micelle as uncharged. However, the effect of the fluctuation of the concentration of small ions is not necessarily negligibly small, and various methods were proposed to take account of its effect properly and to derive the true molecular weight of the micelle.

The theory and the procedure of Vrij and Overbeek⁷ could be most adequately applied to the micellar solution for this purpose, if the micelle molecular weight were independent of the co-ion species of added salt. Accepting this postulate, we may apply them to our data on light scattering from SDS solutions in 0.80 M sodium halides at 35 °C. Similar application was already performed by Huisman⁸ for SDS solutions in sodium halides of lower concentrations at 25 °C.

Light scattering in micellar solutions can be related to the true molecular weight of an ionic micelle, M_μ , by

$$R_0 = R_0^0 + K_\mu M_\mu (c - c_0) \quad (\text{A-1})$$

if the external interference is omitted, where

$$K_\mu = 2\pi^2 \bar{n}_0^2 (\partial \bar{n} / \partial c)_{\mu_s}^2 / (N_A \lambda^4) \quad (\text{A-2})$$

Here the refractive index increment, $(\partial \bar{n} / \partial c)_{\mu_s}$, of the micellar solutions is referred to the value at constant chemical potential of added salt, μ_s , and it is assumed that the monomeric SDS has a constant chemical potential above the cmc.

The refractive index increment at constant chemical potential of added salt, $(\partial \bar{n} / \partial c)_{\mu_s}$, can be expressed by the

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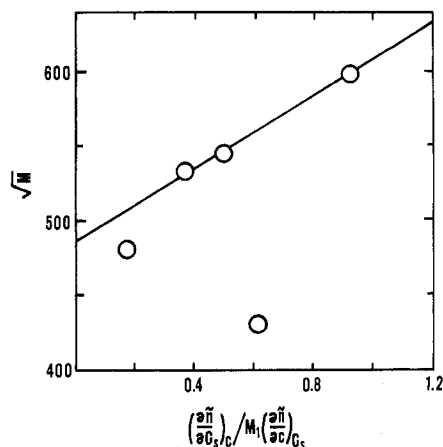


Figure 9. The Vrij-Overbeek plot of micelle molecular weight. The points from left to right are in the following order: NaF, NaCl, NaBr, NaSCN, and NaI.

increment at constant salt concentration directly measurable, $(\partial \bar{n} / \partial c)_{C_s}$, by means of eq A-3. Equation A-3 is

$$(\partial \bar{n} / \partial c)_{\mu_s} = (\partial \bar{n} / \partial c)_{C_s} + (\partial \bar{n} / \partial C_s)_c (\partial C_s / \partial c)_{\mu_s} \quad (\text{A-3})$$

converted into eq A-4, where $\Gamma_s = M_1 (\partial C_s / \partial c)_{\mu_s}$ is the

$$\left(\frac{\partial \bar{n}}{\partial c} \right)_{\mu_s} = \left(\frac{\partial \bar{n}}{\partial c} \right)_{C_s} \left\{ 1 + \frac{(\partial \bar{n} / \partial C_s)_{c=0}}{M_1 (\partial \bar{n} / \partial c)_{C_s}} \Gamma_s \right\} \quad (\text{A-4})$$

amount of preferential adsorption of added salt on SDS micelle, on a molar basis.

Equation A-4 is introduced into eq A-1. Then we have eq A-5, which relates the apparent micelle molecular

$$M^{1/2} = M_{\mu}^{1/2} \left\{ 1 + \Gamma_s (\partial \bar{n} / \partial C_s)_{c=0} / [M_1 (\partial \bar{n} / \partial c)_{C_s}] \right\} \quad (\text{A-5})$$

weight with the true micelle molecular weight.

Figure 9 shows the relation of $M^{1/2}$ with $(\partial \bar{n} / \partial C_s)_c [M_1 (\partial \bar{n} / \partial c)_{C_s}]$ for SDS micelles in 0.80 M sodium halide so-

lutions. It is found that a straight line can be drawn through the three points for NaCl, NaBr, and NaI solutions in such a way as given by eq A-5 with constant adsorption. The deviation of the two points for NaF and NaSCN solutions from this straight line might be related to the reasons as mentioned in the text.

The intercept of the straight line gives the true molecular weight of the rodlike micelle, 236 000, which corresponds to the aggregation number, 819. Its slope leads to the amount of preferential adsorption of the salt, 0.25 mol of salt per mole of SDS, or 205 salt molecules per SDS micelle. That is, ca. four salt molecules are adsorbed on a cross-sectional molecular layer of the rodlike micelle. Then these sodium halide salts are adsorbed on the rodlike micelle positively. On the other hand, in 0.80 M NaSCN solutions the adsorption of the salt is negative, and it amounts to -0.19 mol of NaSCN per mole of SDS, or -156 NaSCN molecules per SDS micelle, if the micelle molecular weight is common to that in the other sodium halide solutions.

Huisman observed negative adsorption of NaF, NaCl, NaBr, and NaI on SDS micelle at lower concentrations of salt, and he ascribed it to the effects of electrostatic repulsion and excluded volume of the spherical micelle. If Huisman's explanation for the negative adsorption is accepted, the actual positive adsorption of salt at the high salt concentration must be even higher than that observed directly, by the amount of the negative adsorption.

However, the conclusion of the large positive adsorption of sodium halides should be considered with severe reservation, since it is based on the postulate of constant molecular weight of the rodlike micelle in 0.80 M sodium salt solutions, irrespective of the co-ion species of salt. We do not have any guarantee for this postulate in the case of the rodlike micelles of SDS in 0.80 M sodium halide solutions, especially because we observe that even the apparent micelle molecular weight changes largely with the halide species of the added salt.

Conductance of Hydrochloric Acid and Potassium Chloride in Supercooled Dilute Aqueous Solution

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Conductance measurements were carried out on dilute aqueous solutions of HCl and KCl at low temperatures; the limiting equivalent conductances were determined at 5, 4, 2, 0, -2, -4, -6, and -8 °C. The excess proton conductance at infinite dilution ($\Lambda^0(\text{HCl}) - \Lambda^0(\text{KCl})$) decreases with decreasing temperature without any anomaly around 0 °C, and its relative contribution to the total proton conductance slightly increases. The decreasing rate of the excess proton conductance is somewhat smaller than that of the inverse of the rotational correlation time in pure water; the difference is ascribed to the effect of the electrostatic field of the H_3O^+ ion on the water rotation controlling the excess proton conductance.

Introduction

The abnormally high conductance of the proton in hydrogen-bonded solvents has attracted many researchers in this century.^{1,2} The mechanism of the anomalous

(excess) conductance of the proton in water was discussed by Conway et al.;^{3,4} rotation of a water molecule in the vicinity of the H_3O^+ ion was concluded to be the rate-determining step. According to this mechanism, the excess

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