Method 2. From the copper complex **12**: To a solution of the copper complex **12** (3.03 g, 5 mmol), and 1,1,3,3-tetramethylguanidine (1.15 g, 10 mmol) in DMF (60 m*l*), was added benzyl bromide (1.71 g, 10 mmol) and the solution was stirred at rt for 24 hr. A solution of EDTA disodium salt (10 g, 20 mmol) in water (300 m*l*) was added and the mixture was stirred for 24 hr. The precipitate was collected by filtration and recrystallized from water. Yield: 83% (2.60 g), mp: 224-226°C, $[\alpha]_D^{20} = +13.5°$ (c = 0.15, 1N HCl). IR (KBr); $\nu = 1740$ cm^{-1} (ester carbonyl). ^{1}H-nmr (CF$_3$COOH); $\delta = 7.30$-7.00 (m, 10H, phenyl), 4.75 (s, 2H, -OCH$_2$-), 4.35-4.00 (m, 3H, -COCH-, -NCH$_2$-) 3.05 ppm (d, J = 5 Hz, 2H, -COCH$_2$-).

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Turbidimetric and Nephelometric Studies on Aggregation of Cationic-Anionic Surfactants[†]

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The aggregation between cationic and anionic surfactants was studied by turbidimetric and nephelometric methods with emphasis on facile analysis of the surfactants and understanding of the mixed micellization. The turbidimetric titration of sodium dodecylsulfate (SDS) with cetyltrimethylammonium bromide (CTAB) or cetylpyridinium bromide (CPB) showed maximum turbidity at equimolar composition in the SDS concentration range of 0.1-0.9mM. The nephelometric titration of the same systems extended the limit of analysis to 0.001mM. The sodium salts of decylsulfate and sulfonate gave similar maxima, but not at equimolar composition. The coexistence of equimolar aggregates and mixed micelles were shown over broad composition range. The aggregation and mixed micellization of the anionic/cationic surfactants mixtures depended sensitively on the hydrophobic character of the surfactants.

Introduction

Ionic surfactants are widely used in both industrial and domestic applications, and drained into neighboring rivers. The analysis of the surfactants in the environmental water can be a mean for monitoring water pollution from domestic waste water.

Two analytical methods are most frequently used for the determination of ionic surfactants. One is "two phase titration" which is based upon stoichiometric reaction between cationic and anionic surfactants.[2-4] The cationic-anionic surfactants aggregates are either insoluble or sparingly soluble in water, but readily soluble in organic solvent. Chlorinated hydrocarbons such as chloroform are typically utilized. Also mixed indicators e.g. dimidium bromide and disulfine blue VN 150 are commonly used for visual end point detection. The other method is spectrophotometric determination after extracting the oppositely charged surfactant-dye complexes with organic solvent.[5-7] These methods can be very precise when they are strictly applied, but they are basically liquid-liquid extraction of cationic/anionic complexes, of which efficiency is effected by experimental manipulation and this has an effect upon the final result. Also the requirement of controlled pH due to the use of dyes and environmental hazard in the laboratory arised from uses of organic solvent are disadvantages of these methods.

The above mentioned analytical methods are based on the aggregation phenomena of surfactant ions with oppositely charged other surfactant ions or dyes. The aggregation can be utilized directly for the analysis of ionic surfactants by turbidimetric and/or nephelometric method. However, little is known on the scope and limitation in analysis.[8] Furthermore, the formation of mixed micelles from surfactant mixtures is of great current interest.[9-11] In this paper, we present the results of the turbidimetric and nephelometric studies on the aggregation of cationic-anionic surfactants in views of facile analysis of ionic surfactants and understanding of mixed micelle formation from cationic-anionic surfactants mixtures.

Experimental

Sodium salts of dodecylsulfate (SDS), decylsulfate (SDeS) and decylsulfonate (SDeSo), and Triton X-100 were obtained
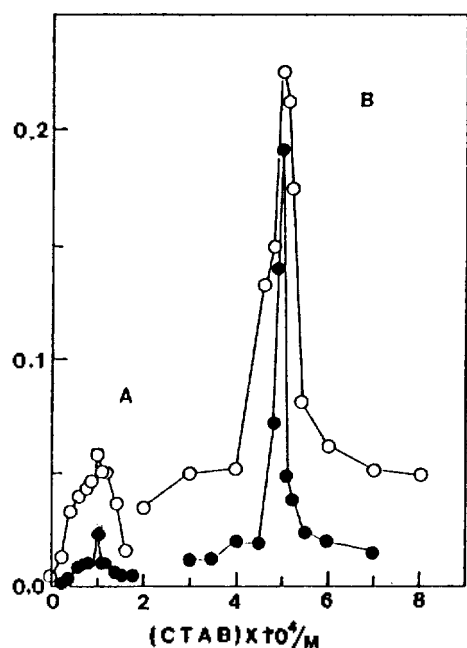
Figure 1. Turbidity of 0.1mM (A) and 0.5mM (B) SDS solutions as functions of CTAB concentration: filled circles are data taken in the presence of 0.01% Triton X-100, and the open circles are those taken in the absence of Triton X-100. The concentrations of SDS were kept constant.

from Aldrich. Cetyltrimethylammonium bromide (CTAB) was purchased from Tokyo Kasei. SDS and CTAB were washed with ether and recrystallized three times from ethanol, and finally dried in a vacuum oven. Other chemicals were used as received. Deionized distilled water was used for preparation of solutions. The solutions of anionic surfactants were prepared on the day measurements were performed.

The stock solutions of surfactants were prepared and thermostated for at least 30 mins. The mixed surfactant solutions were obtained by mixing the stock solutions, and thoroughly mixed with a vortex mixer. The measurements were performed in 5 mins after mixing.

Turbidity was measured at 650 nm from a B/L spectronic 21 spectrometer and read in absorbance scale. Nephelometric measurements were done with a Hitachi 650-10S spectrofluorimeter by scanning the scattered light intensity at 470-530 nm with incident light at 500 nm. The heights of recorder peaks were taken as nephelometric signals. For both measurements, rectangular cells of 1 cm pathlength were used and cell compartments were maintained at 25°C by circulating constant-temperatured water through them.

Results and Discussion

At constant concentration of anionic surfactant SDS, the addition of a cationic surfactant CTAB caused initial turbidity, which became greater and subsequently less as the concentration of CTAB increased. The plots of turbidity against concentration of CTAB are shown in Figure 1. When the concentration of SDS is in the range of 0.1-0.9mM, the plots exhibited turbidity maxima at equimolar compositions. For SDS solutions above 0.9mM, the turbidity near equimolar composition was too high to give reproducible readings. The formation of large aggregates which eventually precipitated
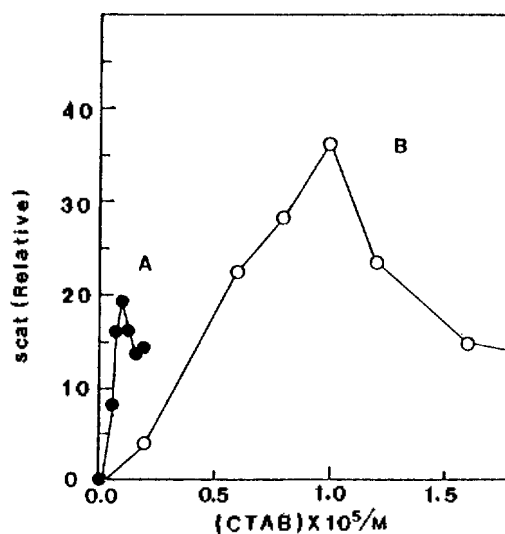

Figure 2. Nephelometric titration of SDS solutions with CTAB keeping SDS concentrations constant at 0.001mM (A) and 0.01mM (B).

also made it difficult to obtain reproducible turbidity. The turbidity of 0.1mM SDS solution with equimolar amounts of CTAB was 0.06 (87% of light transmission), which is about the limit of measurement with reasonable accuracy. This indicated that the turbidimetric titration of SDS with CTAB could be used for the determination of SDS in the concentration range of 0.1 to 0.9mM.

Nephelometric titration of SDS with CTAB also exhibited maxima in light scattering at equimolar composition, i.e., at equivalence points. In this method, the maxima in scattered light intensity with varying concentration of CTAB were easily observed for SDS solution as low as 0.001mM (ca. 0.3ppm) as shown in Figure 2. Thus the limit of SDS analysis by simple titration with CTAB could be extended to this concentration.

The turbidity and light scattering from SDS/CTAB mixtures arise mainly from association of dodecylsulfate (DS⁻) anion with cetyltrimethylammonium (CTA⁺) cation forming CTA⁺-DS⁻ aggregates.

$$CTA^+ + DS^- = CTA^+DS^- \quad Ksp = a_{CTA}a_{DS} \tag{1}$$

This is an example of many interactions between oppositely charged hydrophobic ions. The interaction is primarily affected by the electrostatic factor, but also hydrophobic force contributes. Since we fixed the SDS concentration, the amounts of the CTA⁺DS⁻ aggregates would monotonically increase with CTAB concentration, if no other processes are involved. This is the case observed for SDS concentration below 0.1mM and [CTAB]<[SDS] (Figure 1A and 2).

The enhanced light scattering below the equivalence point and its maximum in SDS solution as low as 1×10^{-6} M by the addition of CTAB indicated the formation of CTA⁺DS⁻ aggregates even in this concentration region. This implies that the solubility product of CTA⁺DS⁻ should be smaller than 1×10^{-12}. Mandel and Moulik[10] reported the solubility product of the same CTA⁺DS⁻ as 1×10^{-9}. This value is too large to explain our observation. On the other hand, Lucassen-Reynders *et al.* gave 2.76×10^{-10} for the solubility product of dodecyltrimethylammonium-dodecylsulfate

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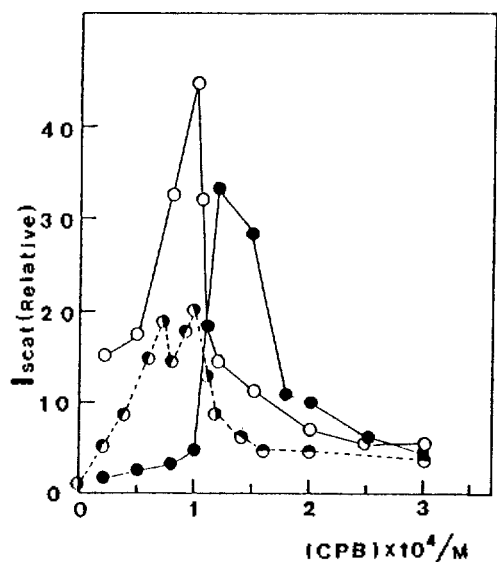**Figure 3.** Nephelometric titration of SDS (o), SDeS (⊙) and SDeSo (●) with CPB. The concentrations of the anionic surfactants are fixed at 0.1mM.

Figure 4. Turbidity or scattered light intensity of SDS-CTAB (o), SDeS-CTAB (⊙) and SDeSo-CTAB (●) mixtures as functions of mole fraction a of anionic surfactants. The total surfactant concentrations are fixed at 0.2mM.

(DTA$^+$ DS$^-$).[11] Considering the difference in alkyl chain length between DTA$^+$ and CTA$^+$ (see below), our result is in reasonable agreement with this report.

In all concentration range of SDS investigated, the plots of turbidity or scattered light intensity vs CTAB concentration showed sharp breaks at equivalence points. This reflects the formation of SDS-CTAB mixed micelles at the expense of the 1:1 aggregates which cause turbidity. The turbidity in 0.5mM SDS solutions remained low and varied little with the concentration of CTAB at [CTAB]<[SDS]. This could be also due to SDS-CTAB mixed micellization. Since the critical micelle concentrations (cmc) of SDS and CTAB are 8.1 and 0.92mM, respectively,[12] the mixed micelles are formed at surfactant concentration far below their cmc's. In the region where the mixed micelles were formed, the solutions were still turbid and scattered light strongly. This indicated the coexistence of the 1:1 aggregates and the mixed micelles over broad composition range.

The presence of non-ionic surfactant Triton X-100 did not interfered the detection of the equivalence point from the turbidity maximum, but rather sharpened it (Figure 1). This is due to the formation of the ternary mixed micelles, SDS-CTAB-Triton X-100, and increased solubility of the CTA$^+$DS$^-$ aggregates into the mixed micelle compared to that into the SDS-CTAB binary mixed micelles. The difference in turbidity in the presence and absence of the non-ionic surfactant reflects the amounts of solubilized CTA$^+$DS$^-$ aggregate forming the mixed micelle. The still large turbidity at equimolar composition of SDS-CTAB indicates limited solubility of the aggregate in Triton X-100, i.e., limited formation of the ternary mixed micelle at [SDS]=[CTAB].

The titration of SDS with cetylpyridinium bromide (CPB) instead of CTAB gave essentially the same result. This can be understood from the similar hydrophobic and micellizing properties of CPB with CTAB.[12] On the other hand, sodium decylsulfate (SDeS) and decylsulfonate (SDeSo), of which alkyl chains are two methylene unit less than SDS, gave much lower turbidity with CTAB as well as with CPB com-
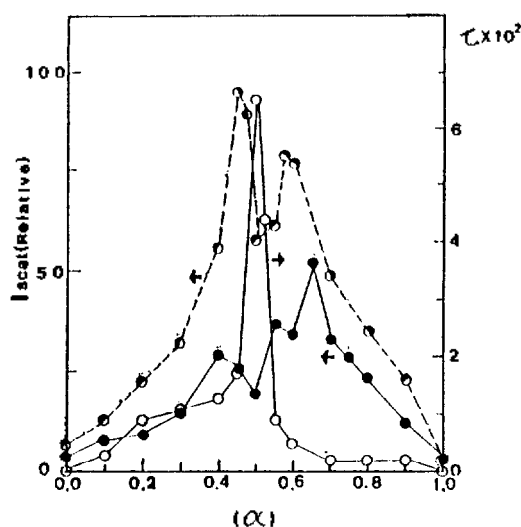
pared to SDS. In fact, the turbidity of 0.1mM SDeS and SDeSo solutions with added CTAB was too low to investigate the cationic/anionic surfactants interaction, even at equimolar compositions. However, the scattered light intensity varied strongly with the concentrations of the cationic surfactants as shown in Figure 3. In the region where the concentration of cationic surfactant is lower than that of the anionic surfactants, the intensities of scattered light were in the increasing order of SDeSo, SDeS and SDS. This is the decreasing order of solubility of the cationic/anionic aggregates.

Alkylsulfonate is less hydrophobic and has higher cmc value than the corresponding alkylsulfate. Also cmc of a surfactant containing linear alkyl chain decreases with increased chain length. The cmc's of SDeS and SDeSo in water were measured to be 29 and 42mM, respectively.[13] These values are much higher than that of SDS, 8.1mM. The difference in hydrophobic character of the anionic surfactants was reflected as the difference in the solubility of the anionic/cationic aggregates. For both SDeS and SDeSo, the maxima in the scattered light intensity deviate from equimolar composition. This points that the turbidimetric or nephelometric titration cannot be used for quantitative analysis, though they can be used for detection, of the surfactants.

Interestingly, the plot of scattered light intensity against the concentration of CPB exhibited two maxima for 0.1mM SDeS solution. Detailed mechanism for this is not certain at this moment, but one possible explanation is as follows. As the concentration of CPB increases in SDeS solution, the CP$^+$DeS$^-$ aggregates are formed and the amounts increase progressively. But, because of considerable solubility of the aggregates, part of added CPB remains as free surfactant. Above certain concentration of CPB, the free CPB and CP$^+$-DeS$^-$ aggregates, possibly with remaining DeS$^-$, form mixed micelles dissolving some of the aggregates. The onset of the micellization appears as the first maximum. Further addition of CPB increases the amounts of both the mixed micelles and the 1:1 CP$^+$DeS$^-$ aggregates. But the formation of the aggregates seems to be more favorable until the onset of the se-
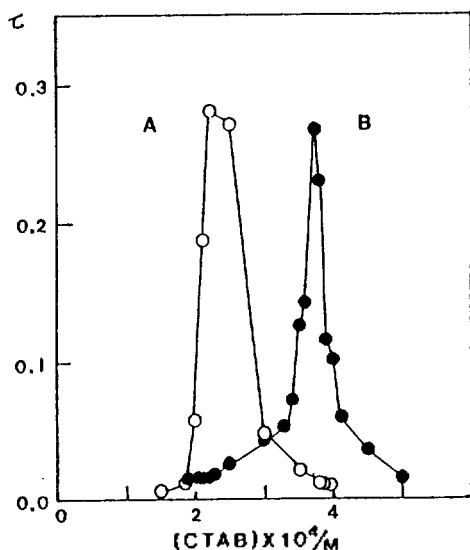
Figure 5. Turbidimetric titration of mixed anionic surfactants with CTAB: A, 0.2mM SDS + 0.2mM SDeSo; B, 0.2mM SDS + 0.2mM SDeS.

cond maximum. Occurence of the two maxima and the compositions at which they are observed are expected to depend sensitively on the aggregate forming and mixed micellizing properties of the surfactants. Under the condition given in Figure 3, well-defined two maxima were not observed for SDS and SDeSo with CPB. However, the similar phenomenon was also shown in SDeSo-CTAB in the other condition shown below.

The turbidity and scattered light intensity maxima were also observed from continuous variation method, that is the ratio of anionic/cationic surfactant is continuously varied while the total concentration of the surfactant is kept constant. The plots of turbidity (for SDS) and scattered light intensity (for both SDeS and SDeSo) against mole fraction of the anionic surfactants in mixtures with CTAB are shown in Figure 4 at a total surfactant concentration of 0.2mM. For SDS, this Figure shows a maximum at mole fraction of 0.5. However, the plots for SDeS and SDeSo show two maxima. This is reminiscent of that observed in the titration result of SDeS-CPB system shown in Figure 3, and the same explanation could be applied.

Figure 5 shows the results of nephelometric titration of 1:1 mixtures of SDS-SDeS and SDS-SDeSo with CTAB at a constant total anionic surfactant concentration of 0.4mM. The maximum light scattering was observed at 0.37mM and 0.23mM CTAB, respectively. These concentrations are lower than equivalent concentration, 0.4mM, and deviation is greater for the mixture containing SDeSo than that with SDeS. This reaffirms us that the CTAB aggregating property of SDeS is much greater than that of SDeSo. Also this indicates that the turbidimetric or nephelometric titration of mixed anionic surfactants containing short alkyl chain (car-

bon number less than 10) with CTAB or CPB could not applied to quantitative analysis of the total surfactant.

In conclusion, the turbidimetric or nephelometric titration of SDS with CTAB or CPB exhibited a sharp break in intensity of scattered light at equimolar composition. This enabled us to determine the surfactant as low as 0.001mM. On the other hand, the anionic surfactants with shorter alkyl chain such as SDeS and SDeSo did not show the break at equivalence point and the titration results displayed complex behaviors. This is due to high solubility of the anionic-cationic 1:1 aggregates and the mixed micellization. The same complications would arise in the conventional "two phase titration" and spectroscopic determination of the surfactants of shorter alkyl chains. Thus, a caution should be exercised to the efficiency of extraction of the cationic-anionic surfactants or surfactant-dye complexes.

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