Cloud Point Phenomena in Mixtures of Anionic and Cationic Surfactants in Aqueous Solution

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The interaction between anionic and cationic surfactants was investigated by means of surface tension, conductivity, and nuclear magnetic resonance. It was found that a strong interaction exists between anionic and cationic surfactants and the mixed surfactant has a hydrophobic property. The phase diagram has been determined as a function of temperature for the water-stearyltrimethylammonium chloride (STAC)-sodium laurate (NaL). The Krafft point rose remarkably in equimolar mixtures for this system. The phase diagram has been determined as a function of temperature for the STAC-sodium-N-lauroyl-N-methyl-β-alanine (NaLMA) system. The liquid-liquid phase separation phenomenon was observed around an equimolar mixture. It can be identified with the cloud point, which is shown by nonionic surfactants. This phenomenon seemed to be caused by the decreased solute-solvent interaction (i.e., dehydration of the amido group contained in NaLMA molecule) as the temperature is raised. The decreasing effect of protein (ovalbumin) denaturation was observed in the high area of the mole fraction of cationic surfactant in the cationic-anionic system. We believe that this is due to the remarkable lowering of the monomer concentration by the formation of a hydrophobic complex.

KEY WORDS: Cationic-anionic system, cloud point, ion pair.

Recently, there have been many studies on the following mixed systems, anionic-nonionic (1,2), anionic-amphoteric (3-6) and cationic-anionic (7-11) surfactants. Most of these authors have reported that the effect on surface activity of a mixed system was superior to that of a single surfactant system. Interaction between anionic and cationic surfactants especially has become of interest, because the CMC value of their complex salt becomes remarkably low (7,8). But the complex is usually insoluble in water because of a very high Krafft point, so its application is often limited. We found that when surfactants of amino acid type were used as anionic surfactants, the Krafft point of the mixed surfactants did not rise. Therefore, we can expect wide applications of the excellent characteristic of cationic-anionic systems.

In this paper, we report the physicochemical properties and the cloud point phenomena of cationic-anionic systems. The interaction between mixed surfactants and protein is discussed also.

EXPERIMENTAL PROCEDURES

Materials: Anionic surfactant. Sodium laurate (NaL, $C_{11}H_{23}$COONa) was purchased from Tokyo Kawei Kogyo Co., Ltd. (Tokyo, Japan). Sodium-N-lauroyl-N-methyl-β-alanine [NaLMA,$C_{11}H_{23}$CON(CH$_3$)CH$_2$COONa] was obtained from Nikko Chemicals Co., Ltd. (Tokyo, Japan).

Cationic surfactant and protein. Cetyltrimethylammonium-

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chloride [CTAC,$C_{16}H_{33}$N(CH$_3$)$_3$Cl$^-$] and stearyltrimethylammoniumchloride [STAC, $C_{18}H_{37}$N(CH$_3$)$_3$Cl$^-$] were purchased from Tokyo Kasei Kogyo Co., Ltd. Protein used was ovalbumin purchased from Wako Pure Chemical Industries., Ltd. (Osaka, Japan).

Methods. For Krafft points measurements, the samples were dissolved at high temperature and precipitated in order to obtain the hydrated solid agents equilibrated with their solution. Each Krafft point was estimated from solution temperatures on gradual heating (1°C/min) in a water bath under vigorous stirring.

For cloud point measurements, the samples were heated or cooled at the rate of 1°C every min under agitation. Each cloud point was determined by noting the onset of cloudness on heating.

The electrical conductance measurements of the mixtures in varied proportions and concentrations were made by using a TOA Electronics (conductivity) meter model CM-50AT (TOA Electronics Co., Ltd., Tokyo, Japan). Surface tension was measured at 35°C using a Wilhelmy type surface tensiometer, Shimadzu ST-1 (Shimadzu, Kyoto, Japan).

The ^{13}C-NMR measurements of surfactant solutions were made with a PFT-NMR equipment (Japan Electric Optical Co., Ltd., Tokyo, Japan, FX100 type 25 MHz). The heavy water was used as a solvent. The concentration of surfactants was adjusted to 100 mM. The samples were carried out supercooled, so we did not control solution pH.

Protein denaturation was determined by using aqueous gel-permeation chromatography. The eluates were monitored at 220 nm, referring to peptide bonding of proteins, with a Uvidec-100 variable wavelength UV detector (Jasco, Tokyo, Japan). The column used was TSK-G3000SW (Toyo Soda Manufacturing Co., Ltd., Tokyo, Japan). The surfactant solutions of various concentrations were added to an ovalbumin solution buffered to pH 7, so that the sample concentration was 10 mM. The magnitude of protein denaturation was calculated using the following equation: % denaturation (%) = (Ho − Ht) / Ho − 100 where Ho and Ht are the peak heights of protein in the absence and presence of surfactants, respectively.

RESULTS AND DISCUSSION

Physicochemical properties and interaction between the mixed surfactants and protein. Figure 1 shows the relationship between surface tension and the logarithm of total surfactant concentration for STAC, NaL, and the STAC-Nal mixture. The break point in each curve indicates the beginning of micelle formation. The CMC value of the mixture is far lower than that of STAC or NaL alone. This large decrease in the CMC value indicates a strong interaction between two solutes. In other words, the mixed surfactants became more hydrophobic as compared to individual components. Table 1 shows the CMC values of pure and mixed surfactants determined by surface tension and specific conductance measurement for STAC, NaL, NaLMA, STAC-NaL mixture and STAC-NaLMA mixture. The CMC value

of mixed surfactant was found to be far lower than that of individual components. We tried to calculate interaction parameters of anionic and cationic surfactants using Rubingh's non-ideal theory (12) of mixed micelles which can be used to calculate the micelle composition and monomer concentration above the CMC. The interaction parameter refers to the degree of strength of interaction between two surfactants in the micellar phase. Table 2 shows the values of interaction parameter β and monomer concentration calculated according to the theory for these mixtures of STAC-NaL and STAC-NaLMA mixed systems. The application of this theory for these mixed systems leads to $\beta = -12$ -15. Our values were appropriate compared to the literature values (12), and the large negative values of β indicate a strong interaction between NaL, NaLMA, and STAC. In addition, it is clear that the total monomer concentration was decreased markedly (by about one tenth), by mixing NaL or NaLMA with STAC. It has been reported (5) that the decrease of protein denaturation is due to the lowering of monomer concentration in the mixed system of anionic and amphoteric. So, we tried to investigate the interaction between protein and surfactant, that is, the protein denaturation for these mixture systems according to their method (5). Figure 2 shows the relationship between the denaturation rate and mole fraction of STAC in the STAC-NaL and STAC-NaLMA mixture. Denaturation rate decreases with decreasing the mole fraction of STAC and indicates very low values at mole fraction from 0.5 to 0.8 for STAC. This result would be explained by the remarkable lowering of the monomer concentration of STAC due to the formation of a hydrophobic complex, as shown in Table 2. On the other hand, the protein denaturation in the low area of the mole fraction of STAC was approximately the same as that of anionic surfactant in spite of the lowering of monomer concentration of anionic surfactant. We think that the monomer concentration of anionic surfactant decreased by mixing would not be low enough to decrease the protein denaturation. Figure 3 shows the specific conductance as a function of mole fraction of STAC for the STAC-NaLMA system at 25°C. The specific conductance is found to be the smallest in equimolar mixture. This result suggests the formation of a nonconductive equimolar complex, namely, ion pair. In order to confirm the existence of the complex of STAC and NaL, NaLMA, we carried out ^{13}C-NMR measurement. The result is shown in Figure 4. The signal (1) of the nucleus of the carbon atom of the carboxylic group in the NaL molecule shifts to a high field when mixed with STAC. The changes in the chemical shift of the signal (1) indicates that the carboxylic group in the NaL molecule is in a restricted atmosphere, which supports a complex formation between STAC and NaL. The signal of the carboxylic group shifted to a higher field by mixing STAC and NaLMA in a similar manner for the system of STAC-NaL, and this result supported a complex formation between STAC and NaLMA.

Cloud point phenomena of the mixed surfactants. Figure 5 shows the phase diagram of water-stearyltrimethylammoniumchloride-sodium laurate system. Total surfactant concentration is 100 mM. This curve indicates the Krafft point of mixed surfactant solution. Under the Krafft point, surfactant solution separates into two phases. Region (L-S) is a two-phase region consisting of liquid and solid phases. Region (L) is a one-phase region, namely, surfactant solution. In the region indicated by arrows, surfactant solution shows viscoelastic properties. The Krafft point rises remarkably around

TABLE 1

CMC Values

	CMC (mole/L) (35°C)	
	Surface tension	Specific conductance
STAC	3.4×10^{-4}	3.4×10^{-4}
NaL	5.0×10^{-3}	—
NaLMA	—	9.0×10^{-3}
STAC/NaL (molar ratio 3.5/6.5)	4.0×10^{-5}	—
STAC/NaL (molar ratio 6.5/3.5)	2.5×10^{-5}	—
STAC/NaLMA (molar ratio 5/5)	6.0×10^{-5}	5.9×10^{-5}

TABLE 2

CMC, β and Monomer Concentration

	CMC (mole/L) (35°C)	β	Monomer concentration (at 10 mM)	
			Cationic surfactant	Anionic surfactant
STAC	3.4×10^{-4}	—	3.4×10^{4}	—
NaL	5.0×10^{-3}	—	—	5.0×10^{3}
NaLMA	9.0×10^{-3}	—	—	9.0×10^{-3}
STAC/NaL (molar ratio 3.5/6.5)	4.0×10^{-5}	-13.9	8.1×10^{-6}	4.2×10^{-5}
STAC/NaL (molar ratio 6.5/3.5)	2.5×10^{-5}	-14.7 / -15.4	2.6×10^{-5}	7.9×10^{-6}
STAC/NaLMA (molar ratio 5/5)	6.0×10^{-5}	-12.8	2.4×10^{-5}	$3.8\ 10^{-5}$

equimolar composition, which suggests the formation of equimolar complex. Figure 6 shows the phase diagram of water-stearyltrimethylammoniumchloride-sodium-N-lauroyl-N-methyl-β-alanine system. The Krafft point changes monotonously with the change in composition of mixed surfactant. The remarkable rise of the Krafft point was not observed here. On the other hand, mixed surfactant solution around equimolar composition indicated viscoelastic properties and separated into two liquid phases at high temperature. These results suggest that ion pairs are formed in the surfactant solution, but that the complexes are not formed in the solid phase. Imae (13) and Mehreteab (7) have studied the liquid-liquid phase separation for the dimethyloleylamine oxide-salt system and for the alkylpoly (oxyethylene) sulfate or organic alkoxy phosphate ester and tetradecyltrimeth-lammonium bromide system, respectively. We investigated this liquid-liquid phase separation in detail. Figure 7 shows the liquid-liquid phase separation temperature for STAC-NaLMA and CTAC-NaLMA systems in the narrow composition range. The phase separation temperature for CTAC-NaLMA system is higher than that of the STAC-NaLMA system. This is due to a stronger hydrophilic property of CTAC as compared to STAC. These phase separation curves have a minimum at equimolar compositions, and, remarkably, increase with slight deviation from equimolar
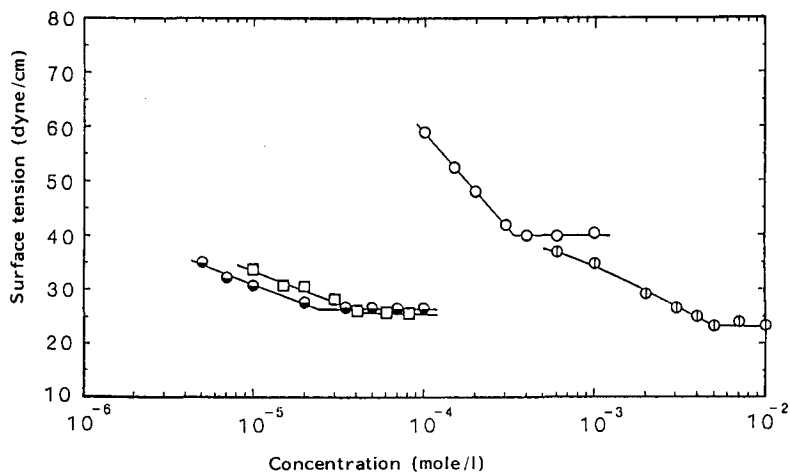
FIG. 1. Relationship between surface tension and log (concentration) of surfactants at 35°C.   , STAC;   , NaL;   , STAC/NaL (molar ratio 3.5:6.5); and   , STAC/NaL (molar ratio 6.5:3.5).
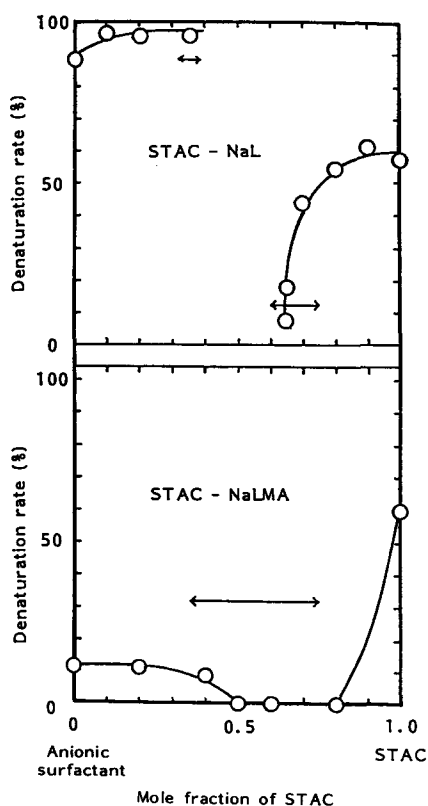

FIG. 2. Relationship between denaturation rate (%) of protein and mole fraction of STAC (total concentration: 10 mM).
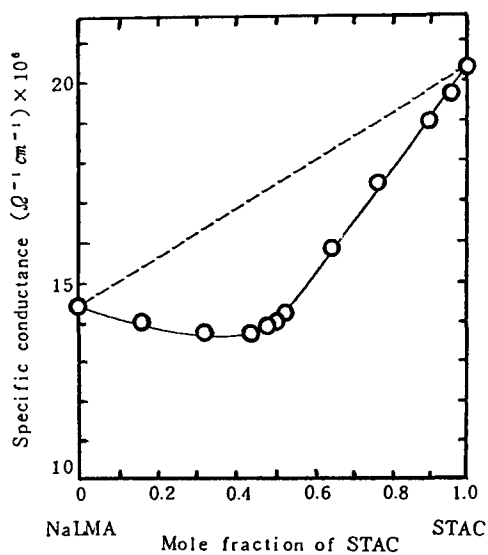

FIG. 3. The specific conductances of the mixture of STAC (2×10^{-4}) and NaLMA (2×10^{-4}) at 25°C.

composition. This indicates a strong interaction between anionic and cationic surfactants in the surfactant solution. Figure 8 shows the phase diagram of water-equimolar mixture of STAC and NaLMA. The Krafft point is almost constant regardless of surfactant concentration, while the curve of the phase separation temperature has a minimum at about 1.6 wt% of surfactant concentration. This curve was similar to the cloud point curve of the nonionic surfactant, which contains ethylene oxide chains as a hydrophilic group (14). The most striking characteristic is that the one-phase region is very wide for STAC-NaLMA system as compared to that of the general nonionic surfactant. From the result of physicochemical properties and interaction of cationic-anionic surfactants systems, this phenomena seemed to be caused by breaking the hydrogen bond between water and both amino group and carboxylic residue contained in NaLMA molecule, as shown by the ion pair model of Figure 9.
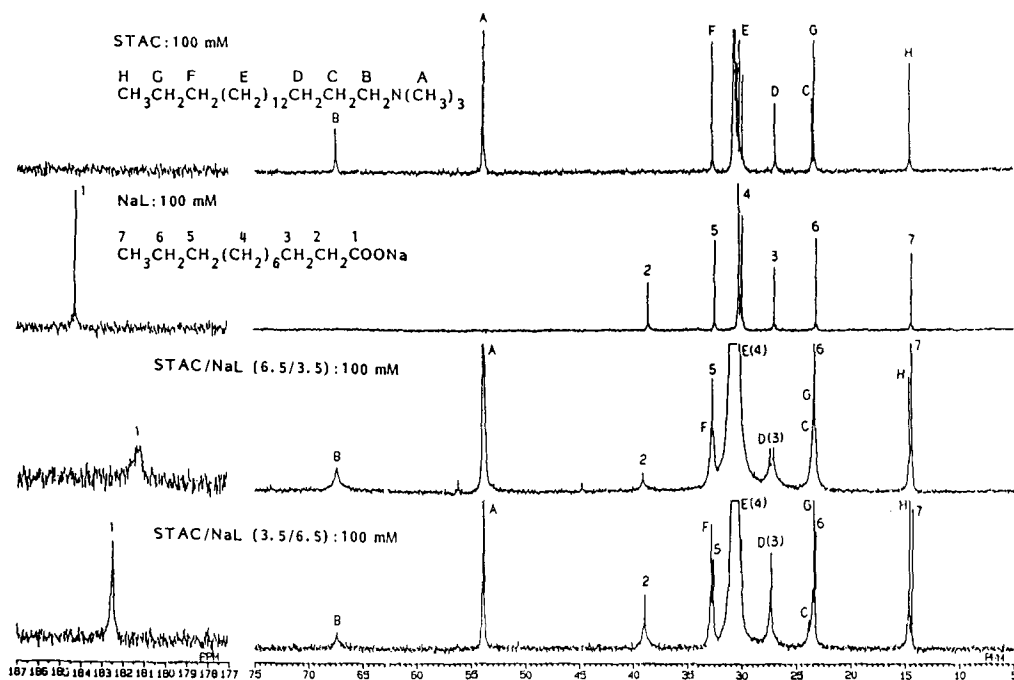
FIG. 4. The ^{13}C-NMR spectrum of STAC, NaL, and mixture of STAC–NaL.
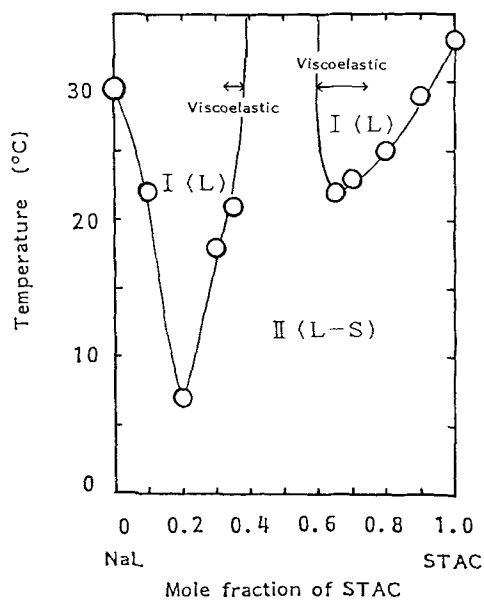

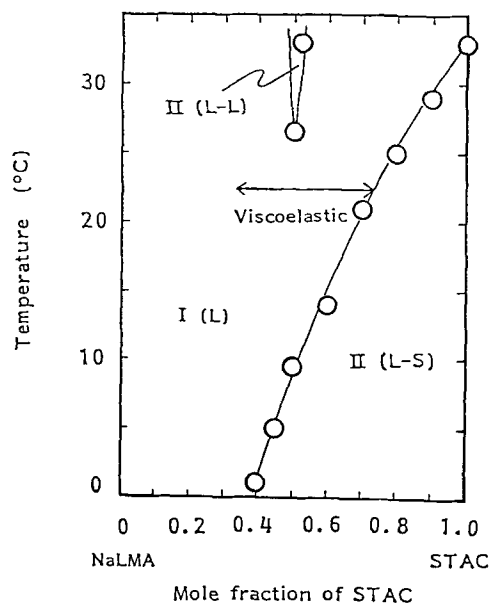FIG. 5. Phase diagram of STAC–NaL mixture system (total concentration: 100 mM).

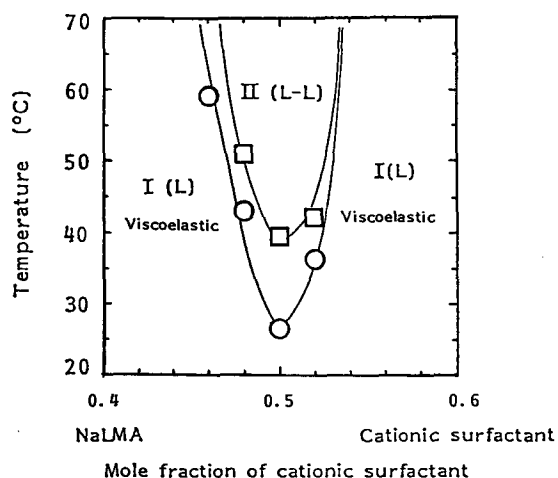FIG. 6. Phase diagram of STAC–NaLMA mixture system (total concentration 100 mM).

FIG. 7. Liquid-liquid phase separation for aqueous solutions of NaLMA/Cationic surfactant mixtures. -O- , STAC; and -□- , CTAC.
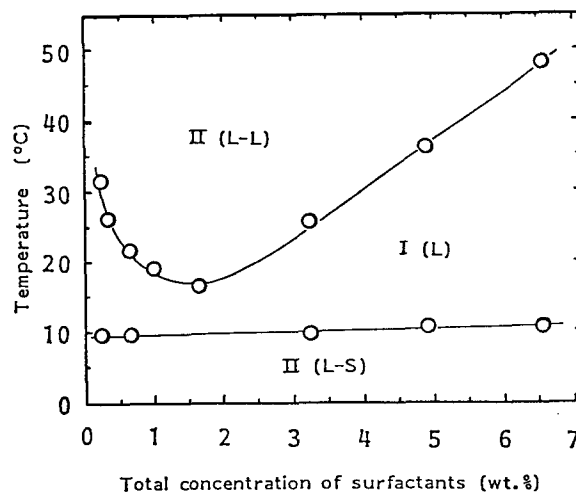

FIG. 8. Phase diagram of the water-STAC/NaLMA (molar ratio 1:1) system.
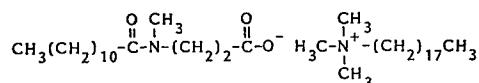

FIG. 9. Ion pair model of STAC–NaLMA system.

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