

Aqueous Solution Properties of a Silicone Surfactant and Its Mixed Surfactant Systems

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The aqueous solution properties of a nonionic silicone surfactant of dimethylpolysiloxane and its mixed surfactant systems were studied. It was found that the silicone surfactant has a high surface activity and forms micelles in two steps: premicelles in dilute concentrations and poly-molecular micelles above 3.7×10^{-7} mol dm⁻³.

In mixed systems of the silicone surfactant with anionic hydrocarbon or fluorocarbon surfactant, weak intermicellar interactions were found. They are due to electrostatic interaction between hydrophilic groups of the respective micelles. Dye solubilization measurements showed that the solubilized amount of Yellow-OB is greater than predicted by ideal systems. Hydrizo-azo tautomerism is observed in fluorocarbon-silicone surfactant systems, while Yellow-OB is solubilized only in the azo-form in the hydrocarbon-silicone surfactant system.

KEY WORDS: Fluorocarbon-silicone surfactant system, fluorocarbon surfactant, hydrizo-azo tautomerism, hydrocarbon-silicone surfactant system, hydrocarbon surfactant, polymolecular micelles, premicelles, silicone surfactant.

Surfactants are classified mainly into hydrocarbon, fluorocarbon, and silicone surfactants based on the type of hydrophobic groups, and these surfactants are very different in properties (1).

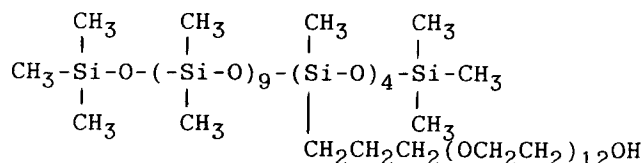
Specifically, fluorocarbon and silicone surfactants show stronger surface activity than hydrocarbon surfactants (2,3). Several workers (4-18) have studied the solution properties of fluorocarbon surfactants and their mixed systems with hydrocarbon surfactants. In mixed systems of fluorocarbon and hydrocarbon surfactants (2,3,19-22), two types of mixed micelles coexist, and the interaction between these two micelles is weak. On the other hand, it is known that a silicone surfactant with a main chain consisting of silicone atoms combined with carbon atoms has a strong surface activity resulting from a high molecular stability, orientation, and flexibility. Generally, silicone surfactants can be classified into polysiloxane, polysilimethylene and polysilane types by the molecular composition of the hydrophobic group. Maki *et al.* (22) reported that a polysiloxane surfactant has the strongest surface activity and lowest surface tension in aqueous solution. However, the length of polysiloxane groups has only a small effect on surface activity (21). Some authors found that there is no difference in surface activity between nonionic surfactants consisting of dimethylpolysiloxane hydrophobic groups in linear, two-chained, or three-chained types (20). However, only a few reports exist about

the solution properties of mixed systems of silicone types with other surfactants. We have synthesized silicone surfactants and characterized their solution properties, but the main part of those studies was limited to nitrobenzene solutions (23-25).

In this work, the aqueous solution properties of a dimethylpolysiloxane surfactant were characterized by many methods. Furthermore, mixed systems such as siloxane-hydrocarbon and siloxane-fluorocarbon surfactant mixtures were also investigated.

EXPERIMENTAL PROCEDURES

Materials. Sodium dodecyl sulfate (SDS) of more than 99.7% purity was obtained from Nihon Surfactant Industries Co., Ltd. (Tokyo, Japan) and purified by extraction with ether, followed by recrystallization from ethanol. Lithium perfluorooctane sulfonate (LiFOS) was synthesized and purified as described earlier (27). A graft polymer of dimethylpolysiloxane and polyoxyethylene nonionic surfactant was kindly supplied by Dow Corning Chemical Co., Midland, MI. Its chemical structure is as follows (Scheme 1):



SCHEME 1

All the surfactants used in this study were confirmed to be highly pure by the absence of a minimum in the surface tension *vs* concentration plots.

α -(*o*-toluylazo)- β -naphthylamine (Yellow-OB) was obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan, and purified by repeated crystallization from ethanol. 1-Anilino-8-naphthalene sulfonate (ANS) was obtained from Wako Pure Chemical Industries (Osaka, Japan) and used as received. Pyrene obtained from Wako Pure Chemical Industries was purified by passing it through silica gel in cyclohexane solution.

Water used in this study was purified by passing it through a Milli-Q system (Nihon Millipore Co., Tokyo, Japan) until its specific conductivity fell below 0.1 $\mu\text{S cm}^{-1}$.

Measurements. Surface tensions were measured with a Wilhelmy plate apparatus (Shimadzu ST1, Kyoto, Japan) at 25°C.

Conductivity measurements were carried out at various concentrations of surfactants by means of a conductivity meter (TOA Electronics Ltd., 30ET, Tokyo, Japan).

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The solubilization measurements were carried out as follows: The surfactant solutions containing an excess amount of Yellow-OB were ultrasonicated for 15 min and then shaken for 24 hr in order to reach saturation. Then, excess Yellow-OB was removed by filtration, and the optical density of the solution at each maximal absorption was measured with a double-beam spectrophotometer (Hitachi, Ltd., 220A, Tokyo, Japan).

Fluorescence emitted by solubilized fluorescence probes (ANS, pyrene) was detected by a fluorescence spectrophotometer (Hitachi Ltd., 650-10S). The concentration of these probes was 2.0×10^{-6} mol dm $^{-3}$.

The viscosity was measured with a Haake Rotovisco RV 100, Karlsruhe, Germany, concentric-cylinder rotational viscometer equipped with a thermostated vessel kept at 25°C. The coaxial cylinder sensor system ME-30 was used.

Static and dynamic light scattering were measured with an Otsuka Densi Light Scattering DLS-700, Osaka, Japan. A 632.8 nm wavelength from a Ne/He ion laser was used for static light scattering and the scattering angle was fixed at 90°. Measurements of specific refractive index increments were carried out at 25°C on an Otsuka Densi Differential Refractometer 12M-102 at the 632.8 nm wavelength. A 488 nm wavelength from an argon ion laser was used for dynamic light scattering, and the normalized correlation function was analyzed by the cumulant method to obtain the average decay rate of the field correlation function. Solvents and solutions were filtered five times through a 0.1 μ m Corning membrane filter, Grand Island, NY.

The nuclear magnetic resonance (NMR) spectra were obtained with a Japan Electron Optics JNM-FX 100 spectrometer at 500 MHz, Tokyo, Japan.

RESULTS AND DISCUSSION

Solution properties of silicone surfactant. Figure 1 shows the surface tension plotted against concentration of the silicone surfactant. The surface tension is lower than that of typical hydrocarbon surfactants, suggesting that the silicone surfactant is strongly surface active. The surface tension at the critical micelle concentration (CMC) was 21 mN m $^{-1}$. This low value is due to high molecular orientation and flexibility of polysiloxane (2,3). Table 1 shows the CMC obtained by means of dye solubilization, iodine method (27,28), fluorescence probing, and surface tension. These results show that the CMC is about 3.7×10^{-7} mol dm $^{-3}$ and is lower than that of typical surfactants. This fact suggests that the silicone surfactant

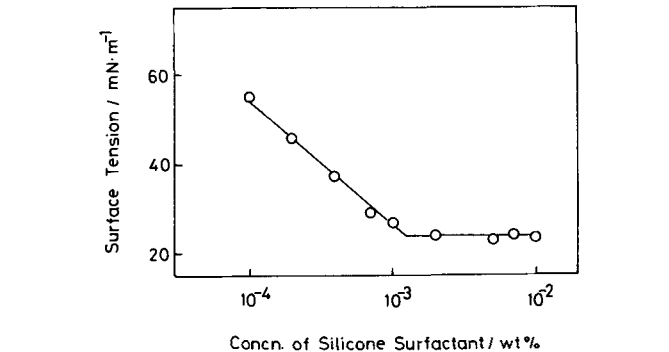


FIG. 1. Surface tension of silicone surfactant as a function of surfactant concentration.

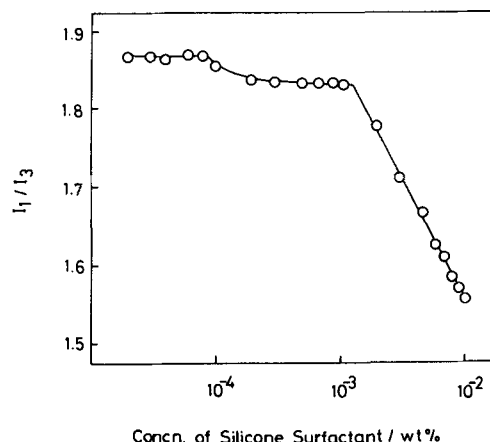


FIG. 2. Change in I_1/I_3 ratio of pyrene with silicone surfactant concentration.

exhibits properties of polymer surfactants (29-34). Figure 2 shows the I_1/I_3 ratio as a function of surfactant concentration, where I_1 and I_3 are the first and third emission maximum intensities of pyrene excited at 335 nm. The I_1/I_3 ratio of pyrene is very sensitive to surrounding media. It is clear that the I_1/I_3 ratio curve has two transition points, one at 2.5×10^{-8} mol dm $^{-3}$ and a second at 3.7×10^{-7} mol dm $^{-3}$. Two transition points were also observed in fluorescence measurements of ANS, and in both cases the second transition point agreed with the CMC obtained by other methods. The existence of the first transition point at lower concentration suggests existence of premicelles (30,31). It has been reported (30) that

TABLE 1

CMC Values of Silicone Surfactant Obtained by Various Methods

	Iodine solubility	Surface tension	Dye solubility	Fluorescence		Viscosity
				Pyrene	ANS	
($\times 10^{-7}$ mol dm $^{-3}$)						
First CMC	—	—	—	0.25	0.24	0.27
Second CMC	3.7	4.0	3.8	3.8	3.1	3.4

water-insoluble block and graft copolymers form a monomolecular micelle at very dilute concentrations and poly-molecular micelles at higher concentrations. Such a change to a polymolecular structure results in a decrease in viscosity. Figure 3 shows that a distinct viscosity change is found at 3.7×10^{-7} mol dm⁻³. This transition point in viscosity coincided to the second transition point detected by fluorescence probing.

The mean micellar hydrodynamic radius R_h of poly-molecular micelles can be obtained directly from the mean diffusion coefficient D in the Stokes-Einstein equation, Equation 1, at infinite dilution:

$$R_h = kT/6\pi\eta D_0 \quad [1]$$

where k is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent. From this equation, the R_h value obtained for the silicone surfactant micelle was 5.4 nm. Furthermore, static light-scattering measurements were performed at an angle of 90°, and the weight-average molecular weight of the micelles, M_w , was obtained from the excess Rayleigh ratio in the Debye equation, Equation 2:

$$H(C-CMC)/R_{VV-90} = 1/M_w + 2A_2C(C-CMC) \quad [2]$$

where $H = 4\pi^2 n_0^2 (dn/dc)^2 / N_A \lambda_0^4$ is the optical constant with N_A, n_0 , and λ_0 being Avogadro's number, refractive index of solvent, and wavelength of light *in vacuo*, respectively. R_{VV-90} is the excess Rayleigh ratio with vertically polarized incident and scattered beams at an angle of 90°, C the concentration in grams per milliliter, CMC the critical micelle concentration in grams per milliliter, and A_2 the second virial coefficient. R_{VV-90} was determined from the measured excess relative scattered intensity by using a known Rayleigh ratio of benzene. Then, the micellar molecular weight M_w can be obtained from this equation and an aggregation number of 30 calculated from M_w for the silicone surfactant.

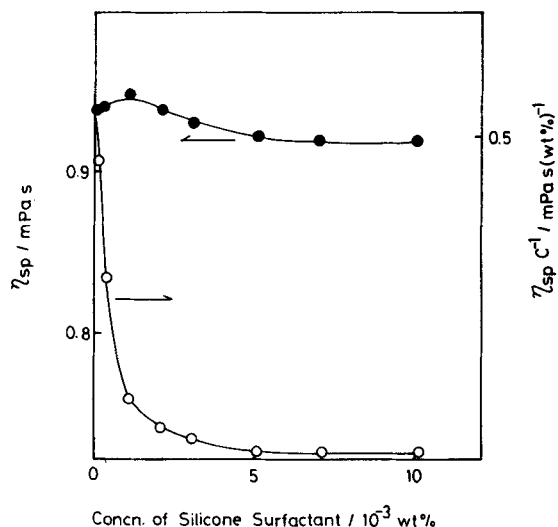


FIG. 3. Relationship between viscosity of silicone surfactant and concentration.

Aqueous solution properties of mixed silicone and anionic surfactants. Figure 4 shows the surface tension curves of SDS as a function of additive concentration of silicone surfactant. The surface tensions of the mixtures were lowered strongly with addition of silicone surfactant, indicating that the silicone surfactant is dominant in surface adsorption due to high flexibility and orientation of polysiloxane. However, the CMC of SDS did not change with addition of the silicone surfactant. To investigate the interaction between SDS and the silicone surfactant, the specific conductivity was measured. Figure 5 shows that the specific conductivity decreases with increasing concentration of silicone surfactant, and the inflection point observed at the CMC of SDS shifts to a lower concentration, suggesting that there is no interaction between SDS and the silicone surfactant at the air/liquid interface, but some interaction occurs in micelles (35–39). The proton resonance signals of SDS were measured at a fixed SDS concentration. The signals of α -protons and β -protons of SDS showed upfield shifts with increasing concentration of silicone surfactant, whereas the signals of methylene protons and ω -protons of SDS showed no shifts (Fig. 6). Since these upfield shifts can be attributed to interaction of the hydrophilic part, it is probably due to a partially

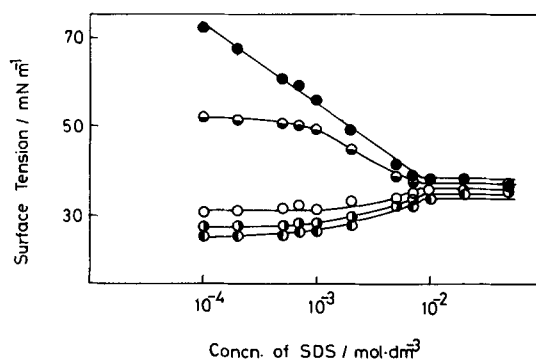


FIG. 4. Surface tension of SDS in presence of various concentrations of silicone surfactant: (●) 0; (○) 1.0×10^{-4} ; (□) 1.0×10^{-3} ; (△) 1.0×10^{-2} ; (◐) 1.0×10^{-1} wt%.

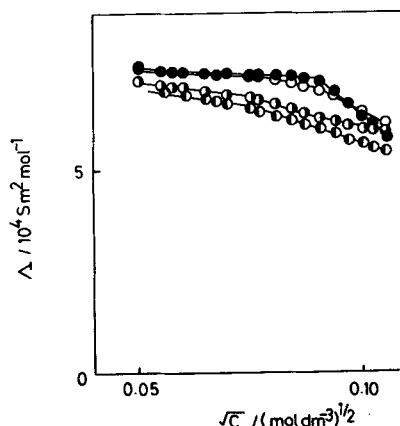


FIG. 5. Specific conductivity of SDS in presence of various concentrations of silicone surfactant: (●) 0; (○) 1.0×10^{-3} ; (□) 1.0×10^{-2} ; (△) 1.0×10^{-1} wt%.

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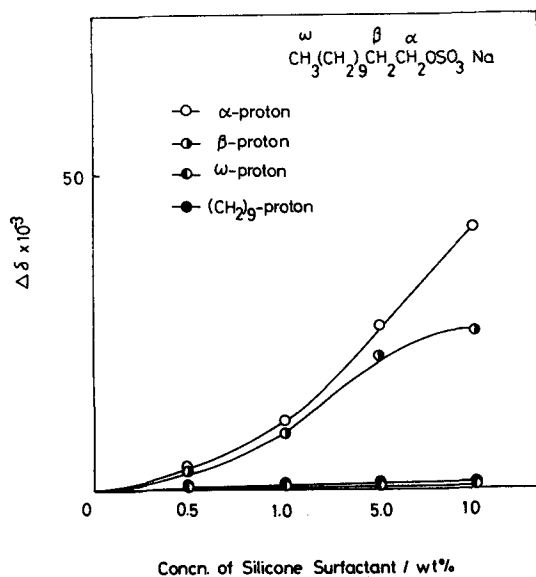


FIG. 6. Change of upfield shift signal of SDS (5.0 wt%) with concentration of silicone surfactant.

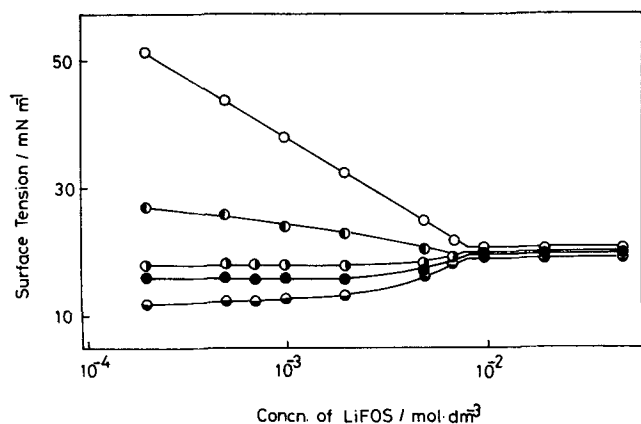


FIG. 7. Surface tension of LiFOS in presence of various concentrations of silicone surfactant: (○) 0; (●) 1.0×10^{-4} ; (◻) 1.0×10^{-3} ; (▲) 1.0×10^{-2} ; (◊) 1.0×10^{-1} .

electrostatic interaction between the positively charged ethylene oxide of the silicone surfactant micelles and the negatively charged hydrophilic groups of SDS micelles (35,36,38).

Similarly, when the surface tension of LiFOS was measured as a function of additive concentration of silicone surfactant (Fig. 7), the CMC of LiFOS hardly changed with addition of silicone surfactant although the surface tension was lowered. Further, the specific conductivity decreased with increasing concentration of silicone surfactant, and the inflection point observed at the CMC of LiFOS shifts downward. Taking into consideration the immiscibility of polysiloxane and fluorocarbon, it is suggested that hydrophilic-hydrophilic interaction occurs in this mixed system similar to that of the SDS-silicone surfactant system.

Solubilization of Yellow-OB was carried out in both mixed systems. Yellow-OB is solubilized as a hydrazo

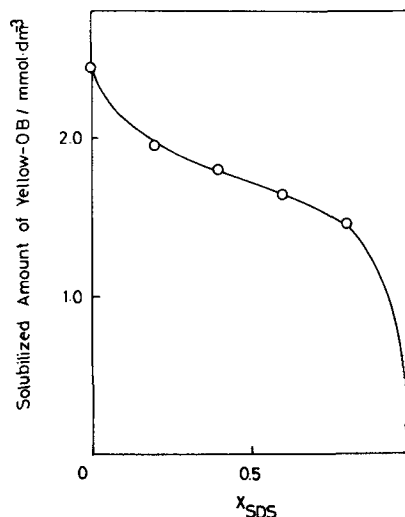


FIG. 8. Solubilized amount of Yellow-OB in SDS-silicone surfactant system with mole fraction of SDS (total concentration = 20 mmol dm^{-3}).

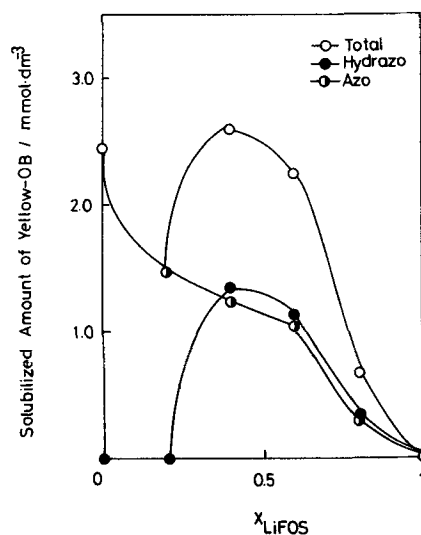


FIG. 9. Solubilized amount of Yellow-OB in LiFOS-silicone surfactant system with mole fraction of LiFOS (total concentration = 20 mmol dm^{-3}).

tautomer (40,41), where the maximal absorption wavelength of the hydrazo-form appears at 480 nm and that of the azo-form at 420 nm.

Figure 8 shows the solubilized amount of Yellow-OB in the SDS-silicone surfactant mixed system (total concentration = $2 \times 10^{-2} \text{ mol dm}^{-3}$). Here, the hydrazo-form of Yellow-OB was not observed. A positive deviation from the ideal additive line increases with increasing mole fraction of SDS and becomes a maximum at SDS mole fraction of 0.8. This deviation may be due to an increase of the sites where the azo-form of Yellow-OB is able to be solubilized by hydrophilic-hydrophilic interaction between SDS and silicone surfactant.

Figure 9 shows the solubilized amount of Yellow-OB in the LiFOS-silicone surfactant mixed system (total concentration = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$). Although Yellow-OB is

not solubilized into the LiFOS micelles, it becomes solubilized into LiFOS micelles in the hydrazo-form with addition of lithium salt. Consequently, Yellow-OB can be solubilized selectively as the hydrazo-azo tautomer in this mixed system. That is, the azo-form is solubilized into the silicone micelle (core) and the hydrazo-form is solubilized into the LiFOS micelle (shell) near the hydrophilic group. An interaction occurs between hydrophilic groups in the respective micelles. It is seen that the solubilized amount of azo-form decreases with increasing LiFOS mole fraction, while the solubilized amount of hydrazo-form increases with the LiFOS mole fraction, has a maximum at about 0.4, and then decreases. The fact that the hydrazo-form exists at low concentration below the CMC of LiFOS indicates that interaction between silicone surfactant micelles and LiFOS monomer occurs. Below the CMC of LiFOS, LiFOS monomer interacts with the silicone surfactant micelle and silicone-rich micelles are formed. Hydrophilic-hydrophilic interaction occurs between LiFOS monomer and silicone surfactant micelles, resulting in penetration of fluorocarbon into the silicone surfactant micelle core. The hydrazo-form becomes solubilized into the silicone surfactant micelle shell. On the other hand, in the silicone surfactant micelle core occupied by fluorocarbon, the solubilized azo-form decreases. Although formation of the hydrazo-form is predominantly due to a property of the fluorocarbon, the hydrazo-form is not formed below a LiFOS mole fraction of 0.2. It seems that the environment does not exist where hydrazo-form can be formed, due to a low ratio of LiFOS/silicone surfactant. While the strongest interaction appears at a LiFOS mole fraction of 0.4 in this mixed system, the formation of hydrazo-form needs a considerable amount of LiFOS. Thus, the above results show that the solubilized amount of Yellow-OB increases for both mixed systems, and the solubilized amount of Yellow-OB is larger for the LiFOS-silicone mixed system than for the SDS-silicone mixed system.

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