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# THE VOLUMETRIC BEHAVIOR OF AQUEOUS MIXTURES OF HYDROCARBON AND FLUOROCARBON SURFACTANTS

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The mean partial molal volumes ($\overline{V}$) were determined for *ca.* 1:1 mixtures of sodium pentadecafluorooctanoate (SPFO) and sodium decyl sulfate (SDeS) or sodium dodecyl sulfate (SDS). The concentration dependence of $\overline{V}$ of the SPFO-SDeS mixture was quite similar to that for the respective components, while the $\overline{V}$ of the SPFO-SDS mixture revealed two stages of micelle formation.

Recently, there has been increasing interest in the miscibility or nonideal mixing of hydrocarbon and fluorocarbon surfactants in micelles.[1-3] In order to shed some light on this problem, we have been studying the volumetric behavior: this is a preliminary report dealing with the partial molal volumes of mixtures of SPFO and SDeS or SDS.

The purified material of SDeS was kindly supplied by Dr. Manabe, Niihama Technical College. Sodium dodecyl sulfate (Nakarai Chemicals, 99%) was recrystallized from water, and then twice from ethanol. Pentadecafluorooctanoic acid (PCR Research Chemicals, 99%) was recrystallized three times from $CCl_4$; mp 55.0–57.2°C, lit.[4] mp 56.4–57.6°C. Sodium pentadecafluorooctanoate was prepared by neutralizing the purified acid with aqueous sodium hydroxide, and recrystallized from water.

The solution densities were measured at 25.00±0.002 °C on an oscillating-tube densimeter (Anton Paar DMA 60/602) with an accuracy of $\pm 2\times 10^{-6}$ g cm$^{-3}$. The mean apparent and partial molal volumes ($\phi_V$ and $\overline{V}$) of surfactant mixtures were calculated from the following equations:

$$\phi_V = \frac{1000(d_0-d)}{mdd_0} + \frac{M_1x_1 + M_2x_2}{d} \quad \text{and} \quad \overline{V} = \frac{\partial(m\phi_V)}{\partial m} = \frac{\Delta(m\phi_V)}{\Delta m}$$

where $M_1$ and $M_2$ are the molecular weights, $x_1$ and $x_2$ $(=1-x_1)$ are the mole fractions of surfactants 1 and 2, respectively, $m$ is the total molality of the two surfactants, and $d_0$ and $d$ are the densities of water and the solution, respectively.

Figure 1 shows the $\overline{V}$ and $\phi_V$ of a SPFO-SDeS mixture. Their concentration dependence was quite similar to that for SDeS, SDS, and SPFO. Every $\overline{V}$ was characterized by a sharp increase at the critical micelle concentration (CMC), followed by a slight increase, and then it reached a constant value at concentrations higher than 1.5–2 times the CMC. It is highly probable that this concentration-independent $\overline{V}$ indicates the following factors unchanged; (1) the structure of micelles and/or the mode of aggregation, (2) the concentration of free surfactant in equilibrium with micelles, and in addition, for surfactant mixtures, (3) the composition of mixed micelles and free surfactants. When two surfactants mix ideally in micelles, the

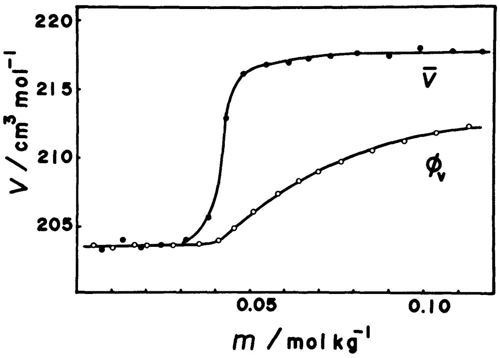

Fig. 1. $\bar{V}$ and $\phi_V$ of SPFO-SDeS mixture. (Mole ratio 0.4770:0.5230)

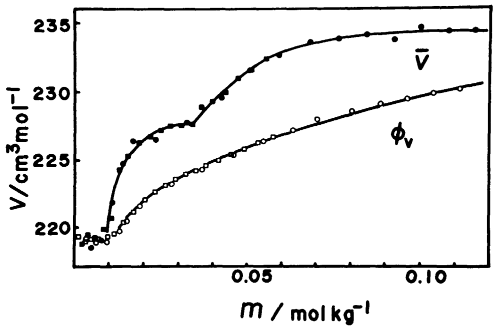

Fig. 2. $\bar{V}$ and $\phi_V$ of SPFO-SDS mixture. (Mole ratio, ● and ○ ; 0.5090:0.4910, ■ and □ ; 0.4974:0.5026)

micellar partial molal volume ($\bar{V}^m$), *i.e.*, the concentration-independent $\bar{V}$ is expressed as the sum of $x_1^m \bar{V}_1^m$ and $x_2^m \bar{V}_2^m$, where $x_i^m$ is the mole fraction of surfactant i in mixed micelles and practically equal to $x_i$ under the condition of constant $\bar{V}^m$. A good example satisfying this relation was the volume of mixed micelles consisting of SDS and SDeS.[5] However, mixing the micellar surfactant of SPFO with that of SDeS caused a volume increase, *i.e.*, $\bar{V}^m_{obsd}$(217.6 cm$^3$ mol$^{-1}$) > $\bar{V}^m_{calcd}$(215.1 cm$^3$ mol$^{-1}$), and the volume change associated with comicellization (14.2 cm$^3$ mol$^{-1}$) was larger than the value (11.2 cm$^3$ mol$^{-1}$) calculated on the assumption of ideal mixed-micelle formation. This finding is attributable to the mutual phobicity between hydrocarbon and fluorocarbon chains in micelles.[3]

A peculiar feature in Fig. 2 is that the $\bar{V}$ continues to increase after the completion of the initial increase until a second plateau is accomplished, indicating two stages of micelle formation. Two possible explanations are as follows.

(1) The mixed micelles initially formed (the first CMC = 0.012 mol kg$^{-1}$) undergo an abrupt structural change at the second CMC (0.034 mol kg$^{-1}$). Subsequently, the micellar composition changes to the overall one in solution; therefore, the constant $\bar{V}^m$ was observed.

(2) As pointed out by Zhu and Zhao,[2] a SDS-rich micelle is formed at the first CMC and another kind of micelle, a SPFO-rich micelle, is formed at the second CMC. Here arises an interesting question whether the two different kinds of micelles *coexist* in the concentration range of the second plateau. The extension of this study is now in progress.

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5) The detailed results will be reported in a forthcoming paper.

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