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Gel Filtration of Mixtures of Surfactants on Sephadex

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The gel filtrations of mixtures of sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (STS) have been studied for different mole ratios of STS/SDS with varying total concentrations. Above the critical micelle concentration (CMC) of the mixture, two retention volumes V^1_{obs} and V^2_{obs} were obtained from the elution curve, and the difference between V^1_{obs} and V^2_{obs} depends on the total concentrations of the mixture. The initial part of the effluent contains only STS, which means that the separation of STS from the mixture occurs after passing through the column. These results have been discussed by taking into consideration the equilibrium between monomers and micelles for the mixtures of the two surfactants. It is shown that the separation factor is determined by the CMC values of the two surfactants—the greater the ratio $\mathrm{CMC_A/CMC_B}$ ($\mathrm{CMC_A > CMC_B}$), the greater the degree of separation.

In a previous work[1] an attempt was made to apply gel filtration on Sephadex to micellar solutions of single surfactants. The results have been successfully interpreted by taking into account the existence of both micellized and unmicellized species in solution.

In the present work, the gel filtration study has been extended to the micellar solutions of mixed surfactants. The surfactants studied were sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (STS), which were mixed in different ratios. The data obtained were analyzed through equilibrium equations for a two component system containing both monomer and micelle phases.

Experimental

Materials. Sephadex G-50, a cross-linked dextran gel with a particle size of 20—80 microns, and Blue Dextran 2000 with a molecular weight of 2×10^6 were obtained from Pharmacia, Sweden. Sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (STS) were the same samples as used in the previous work.[1]

Gel Filtration. Sephadex G-50 was allowed to swell in distilled water for at least 24 hr and then poured into a jacketed column, 1.3 cm in diameter ×35.5 cm in height, with a sintered glass plate at the bottom. The column was prepared in the same way as that previously described.[1] The void volume of the column was checked on alternated runs using Blue Dextran 2000. The gel filtrations were carried out at 32±0.1°C. Fifty milliliters sample solution (SDS-STS mixture) was applied continuously to the top of the column through a siphon connected to the sample reservoir. An automatic fraction-collector was used and fractions of approximately 1 m*l* were collected. The electrical conductivity of each fraction was measured to obtain the elution curve.

Determination of CMC. The critical micelle concentrations (CMC) of the mixtures of SDS and STS for different mixing ratios were determined at 32°C by an electrical conductivity method[2] using a Toa Dempa Model CM-IDB conductance bridge.

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[1] F. Tokiwa, K. Ohki and I. Kokubo, This Bulletin, **41**, 2285 (1968).

[2] F. Tokiwa, ibid., **36**, 281 (1963).

Gas Chromatography. The SDS and STS present in the fractions of the effluents were hydrolyzed with hydrochloric acid to obtain dodecyl- and tetradecyl-alcohols, which were extracted with *n*-hexane. The mole fractions of dodecyl- and tetradecyl-alcohols were determined by gas chromatography with a Shimadzu Model 4APT apparatus using a Carbowax 20M column at 230°C.

Results and Discussion

Figure 1 shows typical elution curves for mixed solutions of SDS and STS, whose mixing ratio is 1 to 1 in moles, at various total concentrations, C^t. Below the CMC of the mixture, the elution curve is sigmoidal and the retention volume obtained from the curve is independent of C^t. Above the CMC, on the other hand, the elution curve consists of two sigmoidal plots with a plateau between them, as seen in Fig. 1. The curve is characterized by the two retention volumes V^1_{obs} and V^2_{obs} for two shoulders of the curve. The fact that two retention volumes V^1_{obs} and V^2_{obs} are obtained may be explained as due to a continuous change in micelle composition during gel filtration, as will be described later. In Fig. 2, the values of $(V^1_{obs}-V^2_{obs})$ are plotted against C^t for different ratios of STS/SDS. The value of $(V^1_{obs}-V^2_{obs})$ at a given ratio of STS/SDS increases rapidly with C^t and then decreases through a maximum.

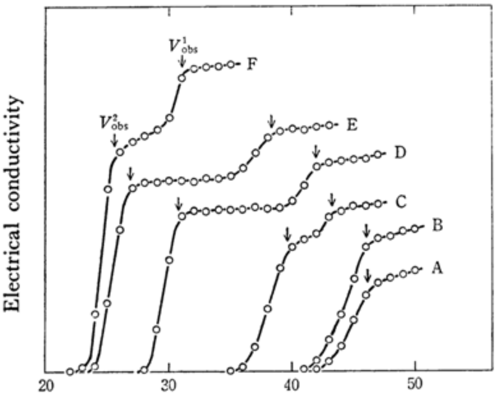

Fig. 1. Elution curves for mixed solutions of SDS and STS at a mixing ratio of 1 to 1 in mole at various total concentrations: A, 0.0020 M; B, 0.0035M; C, 0.0045M; D, 0.0075M; E, 0.011M; F, 0.025M. The arrows indicate the retention volumes of the mixture.

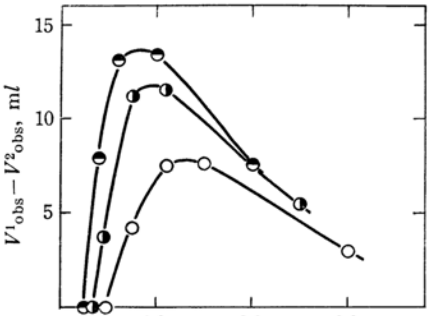

Fig. 2. The values of $(V^1_{obs}-V^2_{obs})$ plotted against C^t at different mixing ratios of STS/SDS: ○, 25/75; ◑, 50/50; ◓, 75/25.

It is reasonable to consider that SDS and STS in aqueous solution form mixed micelles rather than the respective micelles of each surfactant. If we now consider a two component system containing both monomer and micelle phases and assume the system to be ideal, we know that for each component the chemical potentials in the two phases are identical at equilibrium. Under such a condition, the equilibrium between monomers and micelles in the mixed solution of SDS(subscript 1) and STS (subscript 2) may be expressed[3)]

$$y_1C^0_{1,2}=x_1C_1^0 \tag{1}$$

and

$$y_2C^0_{1,2}=x_2C_2^0 \tag{2}$$

or

$$(1-y_1)C^0_{1,2}=(1-x_1)C_2^0 \tag{2'}$$

where x or y is the mole fraction of each surfactant in the micelle or monomer phase, respectively, $C^0_{1,2}$ the CMC of the mixture of the two surfactants and C^0 the CMC of the single surfactant. These equations are analogous to Raoult's equation in the form. From Eqs. (1) and (2′), the CMC value of mixed surfactants $C^0_{1,2}$ is written in the following forms as a function of x_1 or y_1.

$$C^0_{1,2}=\frac{C^0_1-C^0_2}{C^0_1-(C^0_1-C^0_2)y_1} \tag{3}$$

and

$$C^0_{1,2}=(C^0_1-C^0_2)x_1+C^0_2 \tag{4}$$

The relation between x_1 and y_1 is written

$$y_1=\frac{C^0_1}{C^0_1-C^0_2+(C^0_2/x_1)} \tag{5}$$

The curve of $C^0_{1,2}$ *vs.* x_1 or y_1 is shown in Fig. 3, where the values of CMC for SDS and STS (*i. e.*, C^0_1 and C^0_2) were taken to be 8.1×10^{-3} mol/*l* and 2.2×10^{-3} mol/*l*, respectively. At a given CMC, y_1 is always greater than x_1, that is, the fraction of SDS in the monomer phase is always greater than that in the micelle phase. In Fig. 3 the CMC values of the mixtures of SDS and STS are also shown, determined by electrical conductivity measurement for various total mole fractions of SDS, α_1. The $C^0_{1,2}$ values experimentally obtained lie on the $C^0_{1,2}$ *vs.* y_1 curve. This supports

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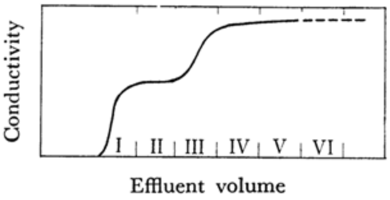
3) F. Daniels and R. A. Alberty, "Physical Chemistry," John Wiley, New York, N. Y. (1966), p. 145.

TABLE 1. MOLE FRACTIONS OF SDS IN EACH REGION OF THE EFFLUENT FOR THE MIXTURES OF SDS AND STS

Mixture		Mole fraction of SDS						
STS/SDS	$C^t\times 10^3$, mol/l	Initial	I	II	III	IV	V	VI
25/75	11.0	0.75	0	0	0.55	0.66	0.76	0.80
50/50	11.0	0.50	0	0	0.38	0.49	0.54	0.52
75/25	10.0	0.25	0	0	0.19	0.23	0.28	0.30



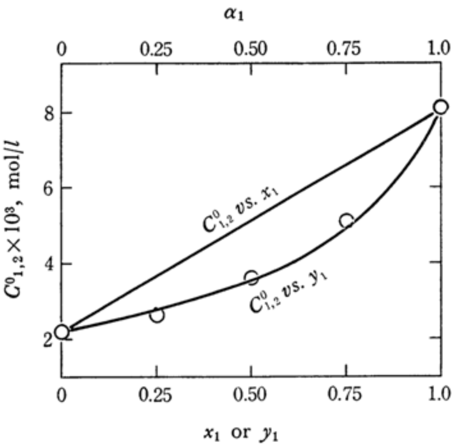


Fig. 3. The relation between $C^0{}_{1,2}$ and x_1 or y_1, where x_1 and y_1 are the mole fractions of SDS in the micelle and monomer phases respectively. The CMC values determined experimentally are also shown by circles as a function of the total mole fraction of SDS α_1.

the use of Eqs. (1) and (2′) for the equilibria between monomers and micelles.

With gel filtration of a surfactant solution, the micelles flow faster down through the column than the monomers, and dissociate into monomers in the frontal region of the solution since micelles can not exist without monomers. The dissociated monomers will flow more slowly, and the concentration of monomers will be increased by similarly dissociated monomers from other micelles. Then, the monomers will again associate to form new micelles when the concentration reaches the CMC. Thus, the processes of dissociation→association, and association → dissociation will be repeated; in other words, the repeated decomposition and formation of micelles occur continuously during gel filtration. With the gel filtration of a mixture of SDS and STS, the fraction of SDS in the micelle decreases with increasing number of steps of decomposition-formation of micelle and ultimately becomes zero when a long gel column is used, since the fraction of SDS in the micelle is always less than that in the monomer phase at the CMC, as shown in Fig. 3. This explains the fact that two shoulders appear in the elution curve of a mixture of SDS and STS. Table 1 shows the mole fractions of SDS, determined through gas chromatography, in the regions of I, II, III,⋯ of the effluent which are indicated schematically below the table. As expected from the above discussion, the frontal parts of the effluent, *i. e.*, the regions I and II, contain only STS after passing through the column. Then, the mole fraction of SDS in the effluent increases with increasing elution volume, but would finally become equal to the initial mole fraction through a maximum value.

Now, one has to explain why the difference between $V^1{}_{\mathrm{obs}}$ and $V^2{}_{\mathrm{obs}}$ becomes smaller at higher concentrations of the mixture of SDS and STS, as seen in Fig. 2. The mole fraction of SDS in the micelle phase, x_1, is defined

$$x_1=\frac{C^M{}_1}{C^M{}_1+C^M{}_2}=\frac{C^t{}_1-C^m{}_1}{C^t-C^0{}_{1,2}} \tag{6}$$

that is,

$$x_1=\frac{\alpha_1 C^t-C^0{}_{1,2}y_1}{C^t-C^0{}_{1,2}} \tag{7}$$

where superscripts m and M refer to monomer and micelle, respectively, and α_1 is the total mole fraction of SDS, *i. e.*, the sum of the mole fractions of SDS in the monomer and micelle phases. Combining Eq. (7) with Eqs. (1) and (4), we have

$$\alpha_1=\frac{1}{n}\cdot x_1\{(1+n)-x_1\},\quad n=C^t/(C^0{}_1-C^0{}_2) \tag{8}$$

The relations between x_1 and α_1 for different values of n are shown in Fig. 4. The relations between y_1 and α_1 at different values of n are similarly obtained by combination of Eq. (8) and Eq. (5), which

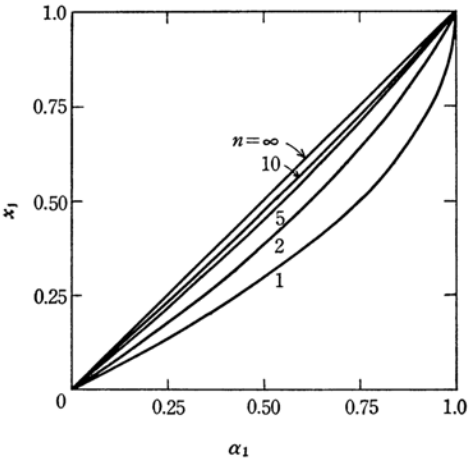


Fig. 4. Curves of x_1 *vs.* α_1 at different values of n, where n is $C^t/(C^0_1-C^0_2)$.

are also shown in Fig. 5. At very high concentrations where $n \gg 1$, *i.e.*, $C^t \gg (C^0_1-C^0_2)$, x_1 approaches α_1. This means that the change in the mole fraction of SDS by repeated micelle formation during gel filtration, which has already been described, is small at high concentrations. Thus, the difference between V^1_{obs} and V^2_{obs} becomes smaller at those concentrations.

The separation factor, β, is generally used as a measure of separation in partition chromatography.[4] In the present case, the β may be defined as $K_{\mathrm{STS}}/K_{\mathrm{SDS}}$, where K is the partition coefficient of the surfactant for micelle and monomer phases; that is,

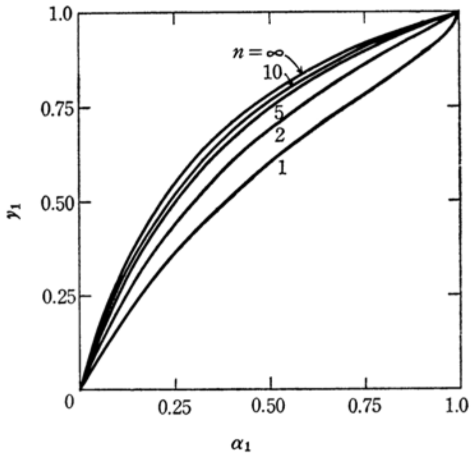


Fig. 5. Curves of y_1 *vs.* α_1 at different values of n, where n is $C^t/(C^0_1-C^0_2)$.

$$\beta = \frac{(C^t - C^0_{1,2})x_2/C^0_{1,2}y_2}{(C^t - C^0_{1,2})x_1/C^0_{1,2}y_1} \tag{9}$$

Using Eqs. (1) and (2), Eq. (9) is rewritten

$$\beta = \frac{(C^t - C^0_{1,2})x_2/C^0_2x_2}{(C^t - C^0_{1,2})x_1/C^0_1x_1} = \frac{C^0_1}{C^0_2} \tag{10}$$

Equation (10) indicates that the separation of two surfactants is governed by the CMC values of each surfactant. The greater the ratio of $\mathrm{CMC_A}/\mathrm{CMC_B}$ where $\mathrm{CMC_A} > \mathrm{CMC_B}$, the greater is the degree of separation of surfactant B from the mixture of surfactants A and B.

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[4] E. Lederer and M. Lederer, "Chromatography," Elsevier, New York, N. Y. (1954).