Studies of the Measurement of the Intermicellar Concentration of Surfactants by Gel Filtration

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Equations are derived which are used to calculate the intermicellar concentration (C_s) of a surfactant from measurements of the elution volumes of micelles, the elution front and the intermicellar monodisperse molecules or ions. These quantities are obtained by the gel filtration of a surfactant charged in band form through a gel column previously filled with the same surfactant at a lower concentration. The C_s values found are not constant, but increase and the increase becomes less pronounced with the concentration (C) of the surfactant, both for sodium dodecyl sulfate and α-dodecyl-ω-hydroxyhexa(oxyethylene). This confirms that the concentration $C-C_s$ of the micelles which move during the gel filtration is smaller than the usually-employed concentration $C-C_m$ of micelles in a stationary state, where C_m denotes the critical micelle concentration.

Many problems remain unsolved regarding the properties of aqueous surfactant solutions, especially the dissolution state of the surfactants.[1] The intermicellar concentration of the aqueous surfactant, for instance, is usually believed to be constant for a solution of concentration C above the critical micelle concentration (CMC), C_m, and the micellar concentration is equated with $C-C_m$.[2,3] Here, constancy of the intermicellar solution is assumed from the constancy of the surface tension of the aqueous surfactant solution above the CMC[4] or from the result of equilibrium dialysis.[5] However, the surface tension of, for instance, a sodium dodecyl sulfate (SDS) solution shows a gradual decrease with increasing concentration of the SDS above the CMC.[1,6] Also, equilibrium dialysis cannot be applied to such a system, consisting of single ions and micelles with rapid equilibrium established between them, since the micelles eventually pass through a semipermeable membrane, if the intermicellar concentration or the activity increases above the CMC.[7]

T. Sasaki *et al.* have studied the dissolution state of aqueous surfactant solutions by gel filtration[8] and have found the method to be suitable also for the study of intermicellar concentrations. The present paper describes studies of the measurements of intermicellar concentrations of the aqueous solutions of SDS and α-dodecyl-ω-hydroxyhexa(oxyethylene) ($D(EO)_6$).

Experimental

Materials. SDS was prepared from 1-dodecanol and chlorosulfuric acid according to the Dreger method[9] and was purified by extraction with diethyl ether and recrystallization from ethanol. $D(EO)_6$ of more than 99% purity, as measured by gas chromatography, was obtained from the Nikko Chemical Company. Both SDS and $D(EO)_6$ were confirmed to be free from surface-active impurities by the absence of a minimum in the surface tension *vs.* concentration curve. Distilled water was used after degassing by boiling.

Apparatus. The gel filtration apparatus is shown in Fig. 1. In this figure, Sephadex G-50 fine gel from Pharmacia

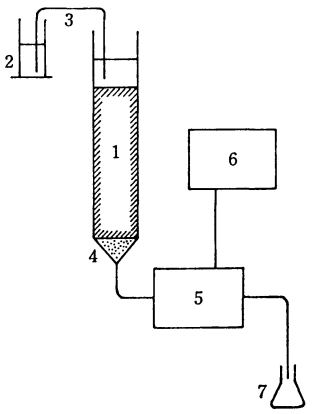

Fig. 1. Gel filtration apparatus.
(1) Gel column, (2) reservoir vessel, (3) siphon, (4) glass wool, (5) differential refractometry monitor, (6) recorder, (7) weighing vessel.

Products was packed in gel column 1 after sufficient swelling in water. The gel beds used were of 1.18 cm inner diameter and 24 and 30 cm in length. For the measurements, a given amount (8 to 30 cm^3) of sample solutions of varying concentrations was placed in vessel 2, from which the solution was introduced through a siphon onto the gel column that had previously been filled with the same solution at a different concentration which is hereafter abbreviated to a preset solution. The sample solution was then eluted by similarly introducing water from vessel 2 through the siphon onto the gel column. This ensures elution under a constant hydrostatic pressure. The rate of liquid flow was 30 and 24 cm^3/h in the cases of SDS and $D(EO)_6$, respectively. The monitor used for the sample flow was a flow-type differential refractometer (LDC-Mitsumi Model 1103 refractomonitor) which detects and records the change of the refractive index at the outlet of the gel column due to the concentration change. The whole apparatus, with the exception of the recorder, was maintained in an air thermostat at 30 ± 1 °C for SDS and 25 ± 1 °C for $D(EO)_6$.

Principle of the Intermicellar Concentration Measurements. Figure 2 shows the elution profile of a surfactant solution of concentration C, which is larger than C_m, charged in band form and eluted with water through a gel column previously swollen with water. As is seen, the tail part of the elution curve forms two steps, corresponding to the fast- and slow-flowing tails of the micelles and the intermicellar single molecules or ions, respectively.

At the elution front, fast-flowing micelles precede the inter-

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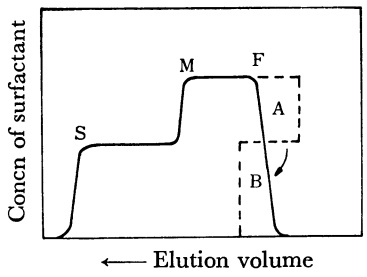

Fig. 2. Elution profile of a surfactant solution.

micellar solution. However, since micelles without the intermicellar solution containing single molecules or ions are unstable, A in Fig. 2 decomposes to form intermicellar molecules or ions, B, with which the rest of the micelles are brought into equilibrium, as is shown in Fig. 2. Because of such a docomposition, the micellar front moves slower than the micelles eluting without decomposition or than the tail of the micelles. Now, if the gel column is previously filled with a preset solution of the same surfactant at concentration C', which is lower than C_m, decomposition of the sample solution at the elution front decreases and the difference in elution rate between the micellar front and tail may become smaller. Then the preset concentration which makes this difference zero is considered to be the intermicellar concentration.

Actually, the concentration of such a preset solution,which contains only single molecules or ions, is not available when the intermicellar concentration C_s is larger than C_m. Therefore, in the present experiment, the concentration of the preset solution, C', was first made slightly lower than C_m. This also avoids the change in structure of the gel due to the change in the solution concentration as elution proceeds. Figure 3 shows the principle of the calculation of C_s. Figure 3(a) shows the state of the preset solution and the sample solution before elution and Fig. 3(b) represents the behavior of the solution during elution. In this figure, R_f, R_m, and R_s denote the elution rates of the solution front, of the tails of micelles, and of the intermicellar molecules or ions, respectively, C is the total concentration of the surfactant, and A_t and A_0 are the cross-sectional area of the gel column through which the

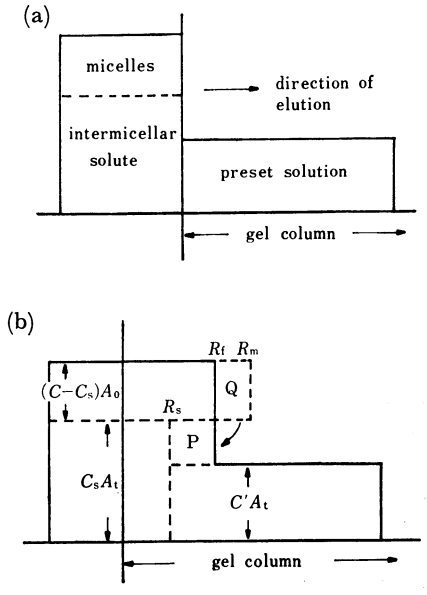

Fig. 3. Gel filtration through a preset solution.
(a) Before elution, (b) during elution.

intermicellar solute and micelles flow, respectively.

In Fig. 3(b), the broken lines indicate the elution profile of each component of solutions of concentrations C and C', the former being assumed to flow without micelle decomposition. Actually, however, as shown by the arrow, part Q of the micellar front of the solution of concentration C decomposes and fills up the solute gap, P. Thus, the entier elution profile assumes the form represented by the solid lines. From this consideration, we obtain

$$(R_m-R_f)(C-C_s)A_0 = (R_f-R_s)(C_s-C')A_t. \quad (1)$$

Taking into account that

elution rate $R \propto$ elution volume V^{-1}

and that

cross sectional area $A \propto$ elution volume V, (2)

Eq. 1 can be rewritten as

$$C_s = \frac{(V_f-V_m)(C-C')}{V_s-V_m} + C', \quad (3)$$

where V_m, V_f, and V_s represent the elution volumes of the micelles, the solution front and the intermicellar single molecules or ions, respectively. Equation 3 enables us to calculate C_s from measurements of V_m, V_f, and V_s for a solution of concentration C eluted through the gel column filled with a preset solution of concentration C'. Here, V_m and V_s can be measured from the elution tail of the corresponding constituent.

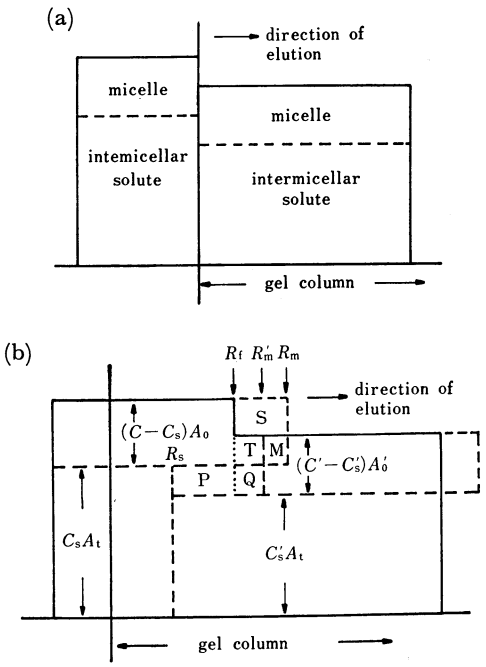

Fig. 4. Gel filtration through a preset solution.
(a) Before elution, (b) during elution.

Furthermore, in case the concentration C' of the preset solution is larger than C_m, so that $C_m<C'<C$, the elution diagram becomes somewhat more complicated, as is shown in Fig. 4. Here, R_m' and C_s' represent the elution rates of the micelles and the intermicellar concentration of the preset solution, respectively, and A_0' denotes the cross-sectional area of the gel column available for micellar flow of the preset solution. The broken lines indicate both the elution tail of the preset solution when eluted alone and the elution front of the solution

of concentration C, assumig that the micelles do not decompose. The solid lines indicate the actual elution front.

From this diagram, it is confirmed that the frontal part of the micelles S+(overlapped)M decomposes to fill up the solute gaps, P and Q, or that the S+M+T part fills up parts P and Q+T. Thus, we obtain

$$(R_m-R_f)(C-C_s)A_o = (R_f-R_s)(C_s-C_s')A_t + (R_m'-R_f)(C'-C_s')A_o'. \quad (4)$$

Again, applying Eq. 2, Eq. 4 can be rewritten as

$$C_s = \frac{C(V_f-V_m)-C'(V_f-V_m')+C_s'(V_s-V_m')}{V_s-V_m}, \quad (5)$$

where the primes indicate preset solution quantities. Equation 5 enables us to calculate the intermicellar concentration, C_s, of the sample solution from measurements of V_f, V_m, and V_s for a solution of concentration C passing through the gel filled with a preset solution of concentration C', intermicellar concentration C_s' and elution volume V_m'. Thus, we can obtain the intermicellar concentration of a surfantant of successively higher concentrations, C.

Results and Discussion

Intermicellar concentration obtained, C_s, is plotted against the total concentration for the aqueous SDS and $D(EO)_6$ solutions in Figs. 5 and 6, respectively. It is seen that C_s increases with increasing concentration of the surfactants both for SDS and $D(EO)_6$, but the increase becomes less marked with the concentration. It is worthwhile to refer to the fact that, according to

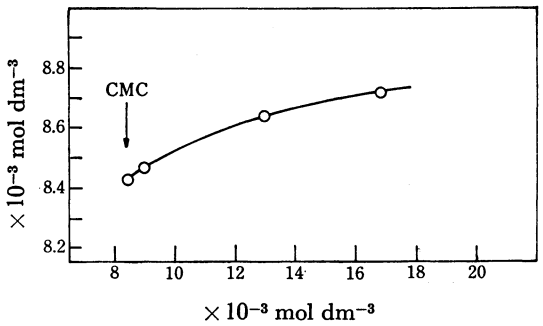

Fig. 5. Intermicellar concentration of SDS.
Abscissa; Concentration of SDS,
ordinate; intermicellar concn of SDS.

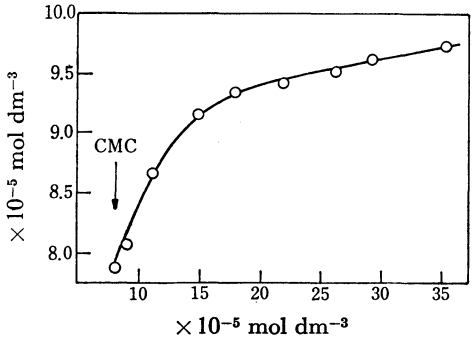

Fig. 6. Intermicellar concentration of $D(EO)_6$.
Abscissa; Concentration of $D(EO)_6$,
ordinate; intermicellar concn of $D(EO)_6$.

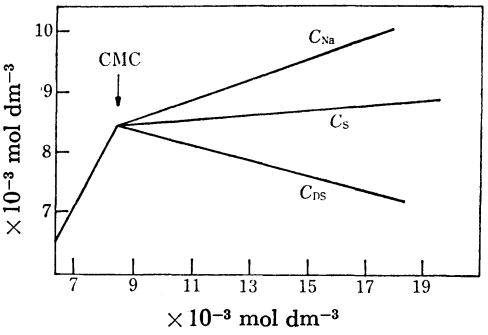

Fig. 7. Intermicellar concentration of SDS at stationary and elution states.
Abscissa; Concentration of SDS,
ordinate; concns of C_{Na}, C_{DS}, and C_s.

the results of EMF measurements,[1] the intermicellar concentration of Na^+ ions increases while that of dodecyl sulfate ions, DS^-, decreases with the total concentration above the CMC as shown in Fig. 7, where the curve for C_s is also depicted. As is seen, the C_s curve is situated between the Na^+ and DS^- curves. This means that the micelles in the stationary state have a net negative charge, but when the micelles precede the intermicellar Na^+ and DS^- ions during elution, they are constrained to move as electrically-neutral units. This requirement is satisfied by the dissociation and the detachment of a part of the excess negative DS^- ions of the micelles and at the same time by the attachment of Na^+ ions to the micelles from the intermicellar solution, thus leaving the solution also electrically neutral.

Actually, Fig. 7 indicates that the amounts of DS^- ion detachment and Na^+ ion attachment are roughly equal and the following relation results,

$$C_{Na} - X = C_{DS} + X = \frac{C_{Na}+C_{DS}}{2} = C_s, \quad (6)$$

where C_{NS} and C_{DS} express the intermicellar concentration of Na^+ and DS^- ions, respectively, and X is the amount of DS^- ions detached from and Na^+ ions attached to micelles. Equation 6 may be the physical meaning of the intermicellar concentration C_s, although the actual intermicellar concentrations in the stationary state are C_{Na} and C_{DS} for Na^+ and DS^- ions, respectively, both of which are different from C_s. Furthermore, the micellar concentration of SDS in the stationary state, or more strictly, the concentration of DS^- ions in the form of micelles is expressed by $C-C_{DS}$, which is larger than the usually-employed value of $C-C_m$,[3] while the concentration of micelles which move during the gel filtration is $C-C_s$ which is considerably smaller than $C-C_{DS}$ and is slightly smaller than $C-C_m$, as is seen from Fig. 7. The difference in concentration of the micelles in the stationary and in the gel filtration states results from the requirement that the micelles be negatively charged in the former case and electrically neutral in the latter case.

The situation may be far simpler in the case of $D(EO)_6$, since it produces no ions. Here also, the micellar concentration is $C-C_s$, and not $C-C_m$. As is seen in Fig. 6, the former is smaller than the latter. It may

also be mentioned that, strictly speaking, $C-C_s$ is the concentration of those micelles which move during gel filtration, while the micellar concentration in the stationary state may differ from $C-C_s$, as in the case of SDS. Although this concentration has not yet been determined experimentally, the value may prove to be close to $C-C_s$, because of the nonionic nature of $D(EO)_6$.

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