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# Gel Filtration of Mixtures of Surfactants on Sephadex. II. Estimation of Micellar Molecular Weights of Mixed Surfactants

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It has been shown in previous works[1,2] that gel filtration is useful as a research tool for studying the micellar properties of surfactants and that it also furnishes a simple means of estimating the micellar molecular weight (MMW) of a single surfactant from the retention volume of the micelle ($V_M$).

In the present work, the gel filtration of mixtures of two surfactants at different mixing ratios has been studied, together with the determination of the MMW's of the mixtures, in order to establish the relation between $V_M$ and MMW. The surfactants used were sodium dodecyl sulfate (SDS), $C_{12}H_{25}OSO_3Na$, and dodecyl polyoxyethylene ether (DPE), $C_{12}H_{25}O(CH_2CH_2O)_pH$, with a $p$ value of 12.[3]

TABLE 1. MICELLAR PROPERTIES OF THE MIXTURES OF SDS AND DPE

| Mixing ratio in mole SDS/DPE | in 0.10M NaCl | | | | in water | |
|---|---|---|---|---|---|---|
| | $V_M/V_0$ | $D_M\times10^7$, cm²/sec | $\Phi$, ml/g | MWM[a] $\times10^{-4}$ | $V_M/V_0$ | MMW[b] $\times10^{-4}$ |
| 100/0 | 1.90 | 10.1 | 1.30 | 2.65 | 2.30 | 1.75 |
| 80/20 | 1.77 | 9.36 | 1.44 | 3.00 | 2.24 | 1.90 |
| 60/40 | 1.65 | 8.02 | 1.68 | 4.10 | 2.29 | 1.85 |
| 40/60 | 1.53 | 7.26 | 1.83 | 5.08 | 2.21 | 1.95 |
| 20/80 | 1.35 | 6.59 | 1.94 | 6.14 | 1.95 | 2.70 |
| 0/100 | 1.25 | 6.42 | 2.01 | 6.50 | 1.30 | 6.20 |

a) Calculated from diffusion and viscosity data.
b) Estimated from the log MMW *vs.* $V_M/V_0$ curve.

Table 1 gives the relative retention volumes of the micelles, $V_M/V_0$, at different SDS/DPE ratios in the absence and in the presence of 0.10 M NaCl, where $V_0$ is the void volume of the column used. These values were obtained on Sephadex G-100 by a method previously described.[1] Sephadex G-100 was chosen by taking into account its fractionation range of molecular weight ($1\times10^3$—$1\times10^5$). The $V_M/V_0$ value in 0.10 M NaCl decreases gradually with a decrease in the amount of SDS, while the value in water is almost constant, independently of the SDS/DPE ratio, in the region from 100/0 to 40/60, and then it decreases steeply with an increase in the amount of DPE. The $V_M/V_0$ values in the presence of sodium chloride are, in general, smaller than those in water. It has been found in a previous work that there is a linear relation between log MMW and $V_M/V_0$ for various types of single surfactants, but not for surfactants with a heterocyclic structure.[1] Now, it is of interest and importance to learn whether the linear relation would also be found in the present mixed systems.

The MMW values for the mixed micelles of SDS and DPE at various SDS/DPE ratios are given in Table 1; these values were calculated from the diffusion and viscosity data by the following equation, on the assumption that the micelle is a spherical and rigid particle:[5,6]

$$\text{MMW} = \frac{4\pi r^3}{3} \cdot \frac{N}{\Phi}$$

where:

$$r = kT/6\pi\eta D_M$$

Here, $r$ is the radius of the micelle; $\eta$, the viscosity of the solvent; $D_M$, the diffusion coefficient of the micelle, and $\Phi$, the effective specific volume of the micelle, while $N$, $R$, and $T$ have the conventional meanings. The values of $\Phi$ and $D_M$ are given in Table 1. The $\Phi$ was obtained from the relative viscosity of the solution in terms of the Guth-Simha equation[5,7]; in the present case, it was independent of the concentration of the mixture at relatively high concentrations. The MMW value obtained from $\Phi$ and $D_M$ by Eq. (1) for SDS or DPE alone is in agreement with the

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3) The SDS used was the same sample as that described in Ref. 1; the DPE was prepared from dodecyl alcohol of a high purity by the addition of ethylene oxide.[4]

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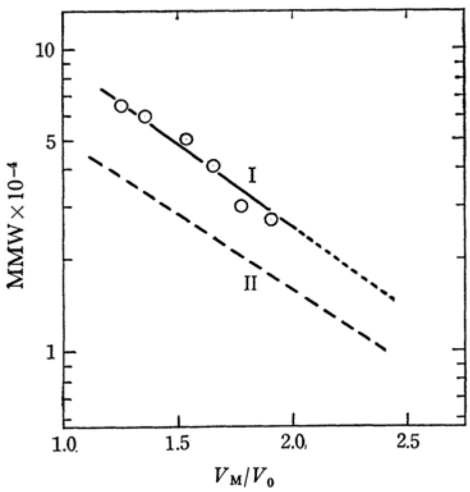


Fig. 1. The relation between log MMW and $V_M/V_0$ for the mixed micelles of SDS and DPE at various mixing ratios using the Sephadex G-100 column at 25°C (I). For reference, the relation for the various types of single surfactants on Sephadex G-75 is also shown by the broken line II.

published value.[8,9]

The MMW values thus obtained at various SDS/DPE ratios are plotted against $V_M/V_0$ in Fig. 1. A linear relation is seen between log MMW and $V_M/V_0$ although the points are somewhat scattered. For reference, the relation for various types of single surfactants obtained in a previous work[1] using Sephadex G-75 is also shown in Fig. 1. From the data presented above, it may be concluded that the gel filtration on Sephadex is a convenient way of roughly estimating the micellar molecular weights of mixed surfactants as well as of single surfactants. The MMW values of the mixed micelles of SDS and DPE in water, estimated from the log MMW *vs.* $V_M/V_0$ curve (I), are given in Table 1.

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9) P. Becher, *J. Colloid Sci.*, **16**, 49 (1961).

**Experimental**

The gel filtration measurements were performed on Sephadex G-100 by a method previously described, (*cf.* Fig. 1 in Ref. 1). The diffusion coefficients of the micelles were determined by the Schlieren method using a Neurath-type cell with the usual precautions.[4] The calculation of the diffusion coefficients was based on the moment method.[10,11] The viscosities of solutions were measured using a Cannon-Fenske-type viscometer with a flow time of 269 sec for pure water. All the experiments were carried out at 25°C.

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