Ultracentrifugal Determination of Micellar Molecular Weights of Polyoxyethylene Dodecyl Ether

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Several investigations[1-5] of non-ionic detergents in aqueous solutions have shown that the micellar molecular weights are highly dependent on the structures of the detergents. The chain-lengths of the polyoxyethylene of non-ionic detergents are also considered to be one of the factors that affect the micellar molecular weights.

An analytical ultracentrifuge provides a convenient method for the determination of the micellar molecular weights of non-ionic detergents. The transient-state method of determining micellar molecular weights in the analytical ultracentrifuge may be useful in avoiding independent determinations of the diffusion coefficients[6], and the synthetic boundary method may be used to determine relative optical concentrations without independent determinations of specific refractive increments[7]. The treatment of the data obtained from the Schlieren optics of analytical ultracentrifuge has already been given in detail[5,8] and will not be repeated here. The equation required for weight-average micellar molecular weight determination by the transient-state method is:

$$M=\frac{RT}{(1-\bar{V}\rho)\omega^2}\left(\frac{\mathrm{d}c/\mathrm{d}x}{xc}\right)_{\mathrm{m\ or\ b}}$$

Here M is the molecular weight, $\boldsymbol{R}$ the gas constant, T the absolute temperature, $\bar{V}$ the partial specific volume of the solute, ρ the density of the solution, ω the angular velocity, c the solute concentration, and x the distance from the axis of rotation to some point in the

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TABLE I. PROPERTIES OF PODE SOLUTIONS AND MICELLES AS A FUNCTION OF POLYOXYETHYLENE CHAIN-LENGTH

Sample[a)]	Concn. %	Temp. °C	Partial specific volume ml./g.	Micellar molec. wt. $\times 10^{-4}$	Molecules[c)] per micelle
PODE- 7.6	1.08	18	0.931	3.76	72
PODE-10.6	1.09	21	0.910	3.17	49
PODE-20.4	1.06	18	0.890	3.75	35
PODE-38.6	1.10	21	0.866	3.50	19
PODE-67.3	1.03	18	0.825	2.06	6.5
PEG[b)]	1.05	18	0.808	0.41	1

a) Number written after PODE represents the average number of oxyethylene groups per molecule.
b) Approximate molecular weight is 4000 (which is taken from the manufacture's literature).
c) See the text.

solution; the values of c and dc/dx must, on the other hand, be determined. The symbols m and b denote the meniscus and the bottom of the liquid column respectively.

Experimental

The detergents studied were polyoxyethylene dodecyl ether (abbreviated to PODE), $C_{12}H_{25}O\cdot(CH_2CH_2O)_nH$, which were prepared from dodecyl alcohol of high purity. The average degrees of the polymerization of ethylene oxide in these samples used are listed in Table I. The purification of the detergents was carrried out by an extraction method[9)] using water-saturated *n*-butanol and *n*-butanol-saturated water. It was confirmed, by testing through paper chromatography[10)], that the purified samples contained no detectable free polyethyleneglycol (abbreviated to PEG). The molecular weights of the samples (m) were determined by the freezing point depression of their benzene solutions. PEG (Carbowax 4000) was purchased from the Carbide and Carbon Chemicals Co. The detergent solutions were prepared by weight in freshly distilled water and stored for a few days.

The ultracentrifugal experiments were performed in a Hitachi model UGA-1 type ultracentrifuge. Centrifugations were done at 18±0.2°C or 21±0.2°C. In the present work, micellar molecular weights were determined only from the meniscus of the column, because it was found that the detergent solutions gave insufficient refractive-index gradients to permit measurement of the micellar molecular weight at the bottom of the column.

Partial specific volumes were determined from pycnometric measurements of solution densities at the same temperature as centrifugation was performed. The values of partial specific volumes are given in Table I.

Results and Discussion

The results for the micellar molecular weight (M) determination of PODE having various chain-lengths of polyoxyethylene are summarized in Table I. As expected, the micellar molecular weight or the aggregation number (the number of molecules per micelle, M/m) is highly dependent on the chain-length of polyoxyethylene. The aggregation number represented by M/m is used here as a measure of the degree of the aggregation, since the molecular weights of PODE should always have some distribution and the molecular weights obtained from different methods differ from one another. The aggregation number decreased with an increase in the chain-length, and PEG, a high molecular weight condensate composed of hydrophilic ethylene oxide, was found to be dissolved as a single molecule. Concerning the effect of polyoxyethylene chain-lengths on the aggregation numbers, Nakagawa et al.[4)] have obtained similar results from light-scattering and diffusion-viscosity experiments over a relatively limited range of chain-lengths, using methoxy polyoxyethylene decyl and dodecyl ether. It would be desirable to have data for lower concentrations, but even a small error in reading the concentration gradient curves for concentrations lower than about 0.8~1.0 g./100 ml. would introduce much error.

The finding that the aggregation number decreases with the increase in the chain-length of polyoxyethylene indicates that the micelle formation of non-ionic detergents has some relation with the steric effect of the polyoxyethylene chain as well as with the hydrophility of the polyoxyethylene chain. It is a doubtful postulate that ordinary micelles are formed in a solution of such a non-ionic detergent as is encountered in ionic detergent solutions if the polyoxyethylene chain becomes sufficiently long. In the case of PODE of $n=67.3$ the aggregation number is only 6.5, and it is doubtful that a micelle, in the generally accepted meaning of the term, could be formed with

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such an insufficient number of molecules. PEG shows no micelle formation, assuming that the molecular weight reported for the PEG studied is correct. Such behavior is not unexpected since light-scattering(1) and ultracentrifugal(5) experiments have shown that similar compounds, Pluronics, which are high molecular weight condensates of ethylene and propylene oxides, do not form micelles.

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