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ACKNOWLEDGMENTS AND ADDRESSES

Received February 10, 1970, from the **Department of Biochemistry, School of Medicine, Case-Western Reserve University, Cleveland, OH 44106* and the *† Department of Pharmaceutics, School of Pharmacy, State University of New York at Buffalo, Buffalo, NY 14214*

Accepted for publication April 6, 1970.

Effect of Micelle Formation on Optical Rotatory Dispersion of β-D-Octyl Glucoside

P. MUKERJEE, J. PERRIN, and E. WITZKE

Abstract □ The optical rotatory dispersion of a nonionic surfactant, β-D-octyl glucoside, has been investigated in aqueous solutions in the UV region. The rotatory dispersion curves at any concentration can be represented by a one-term Drude equation. The specific rotation at any wavelength shows an increase at the CMC, which can be determined reliably from this change in specific rotation. The rotatory dispersion curve for the surfactant in micellized form has been derived and compared with that of the nonmicellized surfactant below the CMC. The change is small and can be ascribed to a "medium" effect, arising from the difference in the local refractive index at the micelle surface, as compared to the bulk solvent. This interpretation is compatible with the currently accepted ideas on the fluid nature of the micelle core and suggests a lack of any conformational restraint at the micellar interface.

Keyphrases □ Optical rotatory dispersion, β-D-octyl glucoside—micelle formation effect □ β-D-Octyl glucoside—optical rotatory dispersion, micelle formation effect □ Micelle formation, effect—optical rotatory dispersion, β-D-octyl glucoside

Many chemical and biochemical reactions and interactions of interest occur at interfaces, *e.g.*, monolayers, micelles, enzymes, or membranes. The local molecular environment at an interface and the presence of an asymmetry and other peculiarities in dielectric properties (1) are factors of considerable importance in understanding the properties of molecules at interfaces. It has been pointed out recently that for studying many such interactions, the interface between a micelle and the solution provides a convenient locus whose composition is capable of a considerable controlled variation (2, 3). The use of optically active surfactant monomers or solubilized molecules offers the possibility of using optical activity as a probe for studying properties of interfaces and of understanding the effect of the interface composition on the optical activity itself. The present paper reports what appears to be the first such study on a simple model surfactant system, β-D-octyl glucoside.

β-D-Octyl glucoside has a CMC in aqueous solution of 0.024–0.025 *M* at 25° (4, 5). The micelles probably contain about 30 monomers (6), the hydrocarbon chains forming a spheroidal core. The glucoside head groups presumably remain exposed to water both in the monomeric and micellar forms. This, by itself, would suggest that there should be no change in their optical activity. In fact, however, the packing of the chains produces a high effective concentration of the head groups in the interfacial layer (2), which interact strongly enough with each other to counter the micelle-forming tendency of the aliphatic chain rather substantially. This is apparent from the following comparison.

Recently the CMC of a hypothetical octyl chain, unencumbered by any head group, was estimated to be about 3×10^{-3} *M* (3). The CMC of octyl glucoside is higher by a factor of about 8. The head group self-interaction thus makes the standard free energy of micelle formation for octyl glucoside more positive by $kT \ln 8$ or about $2kT$'s per monomer, where k is the Boltzmann constant and T the absolute temperature (3). The glucoside groups at the micelle surface are thus in a considerably different local environment when compared to the free monomers.

EXPERIMENTAL

Materials—The octanol used was a Baker analyzed reagent, which was purified further by vacuum distillation, the middle one-third portion being collected.

β-D-Octyl Glucoside—Glucose, on acetylation followed by bromination (7), yielded acetobromoglucose, m.p. 89°. The bromo compound was reacted with octanol in dry absolute ether in the presence of silver oxide to give β-tetraacetyl octyl glucoside, m.p. 63–64°. After deacetylation in sodium methylate solutions, β-D-octyl glucoside was obtained. It was recrystallized twice from ethyl acetate, washed with Skelly-A, and dried under vacuum. The compound melts over a wide range, 65–99° (8). The intermediate compounds were purified by recrystallization before proceeding to the next step of the preparation.

Anal.—Calcd. for C, 57.5; H, 9.7. Found: C, 57.8; H, 9.5.

Apparatus and Experimental Procedure—The optical rotatory dispersion (ORD) measurements were carried out in a Cary model 60 spectropolarimeter. The cell compartment was thermostated at 25 ± 0.2°. Five-centimeter cells were used. All solutions were optically clear, and double-distilled water was used. The ORD measurements were made in the 250–370-mμ region.

RESULTS

Figure 1 shows the variation of the observed rotation at 320 mμ as a function of concentration. To magnify the small differences observed, a deviation plot is presented. The data show the usual curvature near the CMC. If the CMC region is excluded, the data

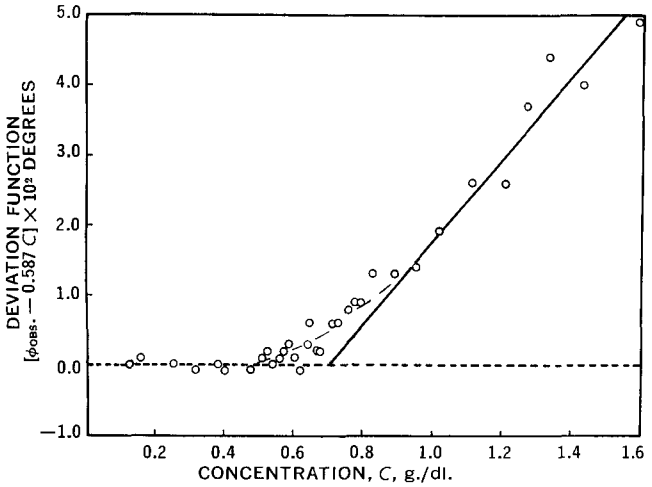

Figure 1—*Variation in optical rotation at 320 mμ with concentration of octyl glucoside at 25°. The ordinate records the difference between the observed rotation, ϕ, and that calculated as 0.587 C, C being the concentration of octyl glucoside in grams per 100 ml.*

can be represented by two straight lines, one below and one above the CMC, whose point of intersection corresponds to the CMC. The value observed, 0.70% or 0.024 mole/l., is in good agreement with the value of 0.024–0.025 *M* obtained from surface-tension measurements (4, 5). ORD measurements are thus capable of determining CMC's for some optically active surfactants. The technique should be of some value for naturally occurring optically active surfactants such as bile salts.

To determine the nature and extent of the change in the ORD curves, the rotation data were analyzed by using the simple Drude equation:

$$[\alpha]_\lambda = A/(\lambda^2 - \lambda_0^2) \qquad \text{(Eq. 1)}$$

n which $[\alpha]_\lambda$ is the specific rotation measured at the wavelength λ. A and λ_0 are constants (9). For exhibiting the changes observed on micelle formation on a magnified scale, Eq. 2, which is a rearranged form of Eq. 1, was used, as suggested by Heller (10):

$$\frac{1}{[\alpha]_\lambda \lambda^2} = \frac{1}{A} - \frac{\lambda_0^2}{A\lambda^2} \qquad \text{(Eq. 2)}$$

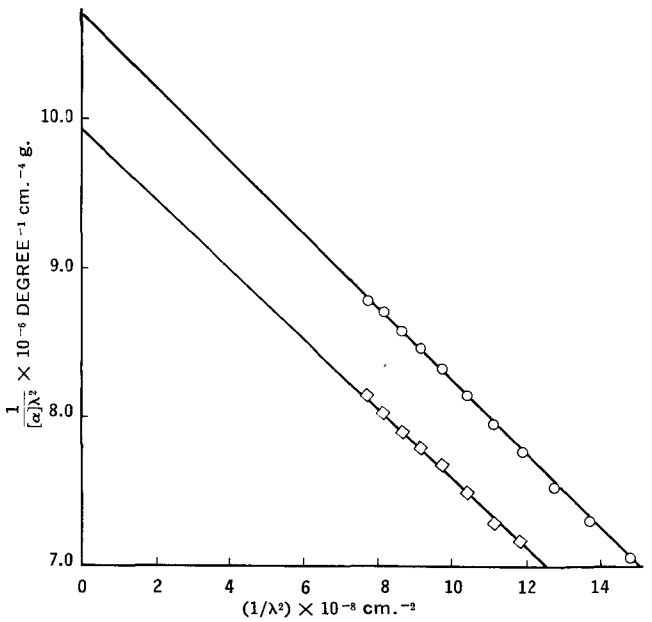

Figure 2—*Plots of specific rotation–wavelength data for octyl glucoside at 25° according to Eq. 2. Key: ○, below the CMC (monomeric); and □, micellar (see text).*

A plot of $1/[\alpha]_\lambda\lambda^2$ *versus* $1/\lambda^2$ should yield a straight line if Drude's equation is obeyed. From the intercept and the slope, A and λ_0 can be determined.

The upper curve in Fig. 2 shows the data below the CMC. Each point is a mean of three measurements at three different concentrations. This curve represents the monomer. To obtain the curve representing the optical rotatory power of octyl glucoside in the micellar form, the change in the observed rotation, $\Delta\phi$, at a particular wavelength was determined from the difference in ϕ between two concentrations, one considerably above and one slightly above the CMC. From this $\Delta\phi$ and the corresponding difference in concentration, ΔC, after a suitable correction for the pathlength of the cell, $[\alpha]_\lambda^m$, the specific rotation of the surfactant in the micellar form was obtained. The rationale behind this method of calculation is the well-founded assumption that above the CMC the monomer concentration changes very little with the total concentration. Here, also, the plotted points are the means of three sets of calculations of $[\alpha]_\lambda^m$, using three different combinations of concentrations. The average variation in the specific rotations estimated at different concentrations was 0.2–0.3%.

Figure 2 shows that the data are linear within experimental error; thus the simple Drude equation is obeyed. The values of A obtained from the least-squares fitted straight lines are 9.32×10^6 and 10.08×10^6 (degree^{-1} cm.$^{-4}$ g.) for the monomeric and micellar forms, respectively, while the corresponding values of λ_0 are 1525 and 1531 Å. Thus, the change in the ORD on micelle formation arises mainly from a change of about 8% in A, the change in λ_0 being barely significant.

DISCUSSION

Although this analysis shows that the simple Drude equation is obeyed and that the primary change on micelle formation is in A rather than λ_0, an unequivocal interpretation is difficult; the apparent simplicity of the Drude equation may be misleading.

For regions far from optically active absorption bands, the specific rotation can be written as (11)

$$[\alpha]_\lambda = \left(\frac{n^2+2}{3}\right)\left(\frac{9600\pi cN}{Mh\lambda^2}\right)\sum_i \frac{R_i}{\nu_i^2 - \nu^2} \qquad \text{(Eq. 3)}$$

where n is the refractive index of the medium, c is the velocity of light, N is Avogadro's number, M is the molecular weight of the substance, h is Planck's constant, ν is the frequency of incident light, ν_i is the frequency characterizing the electronic transition to an excited state, and R_i is the "rotatory strength" of the transition. Replacing the frequencies by the corresponding wavelengths, and condensing several quantities into the new variable A_i, yield

$$[\alpha]_\lambda = \left(\frac{n^2+2}{3}\right)\sum_i \frac{A_i\lambda_i^2}{\lambda^2 - \lambda_i^2} \qquad \text{(Eq. 4)}$$

Although Eq. 4 has the form of the Drude Eq. 1, it clearly shows that λ and A in Eq. 1, where A includes the refractive index factor, are complicated averages.

By considering the physical realities of the situation at a micellar interface, however, it is possible, qualitatively, to ascribe at least a part of the difference in A between free and micellized monomers to the Lorentz correction factor, $(n^2 + 2)/3$. At the micellar interface, the glucose moieties are present at a high concentration, roughly 3 molal or 35% by weight (3), and close to the hydrocarbon core of the micelle. The refractive index, at the sodium D line (5893 Å), of a 35% by weight solution of glucose is estimated to be 1.390 (12),[1] as compared to 1.3330, the value of water. This, by itself, can increase the Lorentz factor by 4%. The actual effect may be substantially higher because of two additional factors. The frequency dependence of the refractive index (dispersion) is expected to be substantially higher for glucose than for water and, therefore, the refractive increment for glucose solutions should be higher at the lower wavelengths at which the ORD measurements were made,

[1] Experimental values of the refractive index of D-glucose solutions at such high concentrations were not available. The refractive increments of D-glucose and sucrose up to 10% concentrations are very similar, however. Therefore, the authors used the value for a 35% solution of sucrose, 1.3902. D-Fructose has a very similar value, also.

2500–3700 Å. The proximity of the hydrocarbon core of the micelle may also be a contributory factor, because of the higher refractive index of octane (n_D = 1.3975) as compared to water. Thus, although no firm conclusion is possible, the change in optical rotation on micelle formation is not incompatible with a "medium" effect, operating through the Lorentz factor, and no conformational restraints at the micelle surface need be invoked. This tentative conclusion is in accord with the accepted fluid nature of the micelle core (3). It should clearly be of some interest to study monomers or solubilized species in micelles containing optically active absorption bands in experimentally accessible wavelength regions.

Finally, note the observed curvature near the CMC in Fig. 1. This is another piece of evidence against the phase-separation model for micellization, the arguments against which have been summarized recently (3).

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ACKNOWLEDGMENTS AND ADDRESSES

Received January 30, 1970, from the *School of Pharmacy, University of Wisconsin, Madison, WI 53706*

Accepted for publication April 23, 1970.

2-Amino-2-oxazoline Formation by Cyclization of 1-(2-Hydroxyethyl)-2-methyl-2-thiopseudoureas

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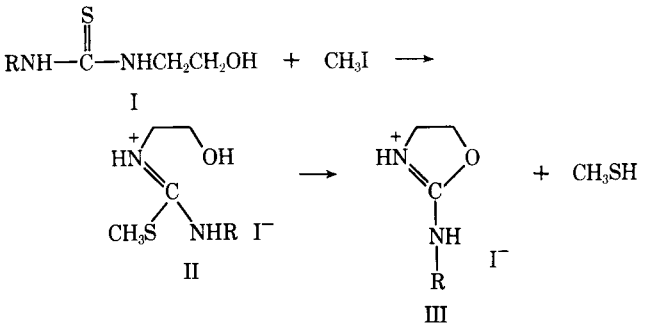
Abstract □ 1-(2-Hydroxyethyl)-3-substituted-2-methyl-2-thiopseudourea hydriodides, when heated in polar solvents, were found in many instances to result in the formation of 2-amino-2-oxazoline derivatives with the simultaneous evolution of methyl mercaptan. The rate of the reaction is apparently influenced by the group substituted in the 3-position of the thiopseudourea. Similarly, the 5,6-dihydro-4*H*-1,3-oxazine ring system could be prepared by starting with a 1-(3-hydroxypropyl)-2-thiourea.

Keyphrases □ 2-Amino-2-oxazoline formation—using thiopseudoureas, cyclization □ Thiopseudoureas—in formation of 2-amino-2-oxazoline □ IR spectrophotometry—identity

An investigation of the influence of the degree of *N*-substitution of *S*-methylthiopseudoureas, which are subjected to alkaline hydrolysis, on the rate of methyl mercaptan evolution was reported earlier (1). In the course of that study the preparation of the *S*-methyl derivative of 1-(2-hydroxyethyl)-3-benzoyl-2-thiourea (I*f*), a potential antiradiation agent, was attempted. It was found that methyl mercaptan was readily evolved when the *S*-methyl derivative (II*f*) was heated in polar organic solvents such as acetonitrile, alcohols, and acetone, even in the absence of base. Methyl mercaptan was formed as a consequence of the intramolecular displacement of the methylthio group by the hydroxyl group to give 2-benzamido-2-oxazoline hydriodide (III*f*) in 73% yield.

To examine further this interesting reaction, a number of other 1-(2-hydroxyalkyl)-2-thioureas were prepared and subsequently treated with methyl iodide (Scheme I).



Scheme I

Simply heating the 2-methyl-2-thiopseudourea hydriodides in polar solvents in several cases led to methyl mercaptan evolution. The rate of this evolution, which reflects the extent of the cyclization reaction, was found to be strongly influenced by the R group of the 1-(2-hydroxyalkyl)-2-thiourea (I). Oxazoline formation proceeds smoothly when there is a benzoyl group in the 3-position of a 1-(2-hydroxyalkyl)-2-thiourea. 1-(2-Hydroxypropyl)-3-benzoyl-2-thiourea (I*l*), on heating with methyl iodide in ethanol, gave 2-benzamido-5-methyl-2-oxazoline hydriodide (III*l*). When 1-(3-hydroxypropyl)-3-benzoyl-2-thiourea was used (I*k*), the cyclization reaction gave the six-membered heterocycle—*viz.*, 2-benzamido-5,6-dihydro-4*H*-1,3-oxazine hydriodide (III*k*), in good yield.

The evolution of methyl mercaptan was slower when the *S*-methyl derivatives of 1-(2-hydroxyethyl)-3-phenyl-2-thiourea (I*d*) and 1-(2-hydroxypropyl)-3-phenyl-2-