THE SIZE, SHAPE AND HYDRATION OF CETOMACROGOL 1000 MICELLES

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Cetomacrogol solutions have been studied by three techniques. The micellar weight in water has been found from light-scattering experiments to be 101,000; the micelles appear to be spherical. Viscosity measurements can be interpreted in terms of micellar hydration, and 1·96 g. water appear to hydrate 1 g. of cetomacrogol. A similar amount of hydration (1·92 g. water per g. cetomacrogol) can be calculated from the diffusion coefficient. A check on the micellar weight was obtained from the diffusion and viscosity results, giving 96,000, in good agreement with the result from light-scattering.

NON-IONIC surface-active agents generally consist of a hydrocarbon chain to which is linked a series of water attracting groups. Cetomacrogol 1000 has the structure:

$$Me[CH_2]_{15 \text{ or } 17} [OCH_2CH_2]_{20-24}OH$$

and the chain of ethylene oxide units forms the hydrophilic portion of the molecule.

Few determinations have been made on the micelle size of non-ionic detergents. Triton X100, which has the structure

$$(Me)_3CCH_2C(Me)_2C_6H_4[OCH_2CH_2]_{10}OH$$

has been found by Kushner and Hubbard[1] to have a micellar weight of 90,000, determined by light-scattering; this corresponded to 140 monomers in the micelle. The micelles appeared to be spherical.

As cetomacrogol has a much longer chain of ethylene oxide units than Triton X100, a greater interaction with the solvent would be expected than that given by the latter substance. In this paper results from viscosity, diffusion, and light-scattering experiments have been used to gain an idea of the size, shape, and hydration of cetomacrogol micelles.

EXPERIMENTAL

Materials

A commercial sample of cetomacrogol, based on cetyl alcohol, was dried before use. The molecular weight, determined by freezing point depression in benzene, was 1210.

Organic solvents were Analar materials, and were dried and fractionated. Toluene gave $n_D^{25} = 1·4940$ and benzene $n_D^{25} = 1·4972$; Timmermans[2] gives 1·4941 and 1·4981 respectively.

The sodium dodecyl sulphate was a pure sample kindly given by Dr. I. L. Thomas. (Percentage S found $= 11·10$, percentage S calculated $= 11·12$.)

Diffusion Coefficients

Diffusion measurements were made using the Gouy diffusiometer. Results for cetomacrogol have been reported[3], but their interpretation has not been discussed.

Viscosity Measurements

Viscosities of solutions relative to water were determined in a suspended level dilution viscometer.

Light Scattering

An apparatus was constructed based on that described by Parreira and Ottewill[4], and by Robinson[5].

A modification to the thermostated cell holder has been made (Fig. 1). This consisted of a circular brass tank, with a copper coil sealed in its base. Water from an external thermostat was circulated through the coil.

A block of perspex was used as a secondary light scattering standard.

Clarification of solutions. Solutions were filtered through No. 5 on three sintered glass discs under pressure. The first few ml. were discarded.
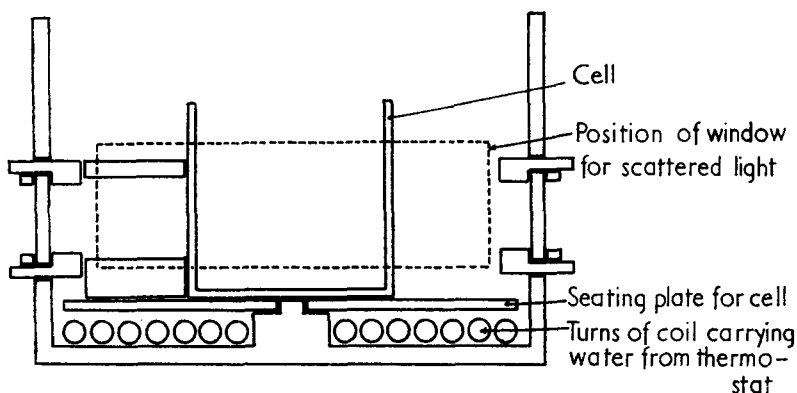

FIG. 1. Thermostated cell holder.

With detergent solutions five or six filtrations were necessary to free the solutions from dust.

Specific refractive index increment. The refractive index difference between solution and solvent was determined using a Hilger-Rayleigh interferometer, and the technique described by Bauer for monochromatic light[6]. The specific refractive index increment could be calculated from the refractive index difference.

Calibration of apparatus. After obtaining regular scattering envelopes for dilute Ludox solutions (a colloidal silica preparation), the calibration constant of the apparatus was determined using Ludox solutions sufficiently dilute to avoid the corrections of Maron and Lou[7]. The calibration constant, C, was determined from the optical density, D, and the amount of light scattered at 90° to the incident beam, S_{90}, by the same solution. S_{90} was measured with reference to the perspex block.

$$T = \frac{16\pi}{3}.R_{90} = \frac{2\cdot303D}{1} = C.S_{90}$$

where T is the turbidity of the solution, R_{90} is Rayleigh's ratio, 1 is the length of the cell of solution. C had the value $4\cdot76 \times 10^{-4}$ cm^{-1}.

Density of Solid Cetomacrogol

Determinations by a displacement technique in a dry light petroleum fraction gave a mean of 1·143 g./ml.

RESULTS

The diffusion coefficient of cetomacrogol in water has been found[3] to be only slightly concentration dependent, and the diffusion was virtually free from charge effects. The extrapolated value of the diffusion coefficient at zero solute concentration was $5·10 \times 10^{-7}$ cm.^{2}sec.$^{-1}$.

TABLE I

RELATIVE VISCOSITIES OF CETOMACROGOL SOLUTIONS AT 25°

Concentration, per cent	0·254	0·313	0·418	0·668	0·928	1·005
ηr	1·018	1·023	1·031	1·050	1·076	1·080
Concentration, per cent	1·256	1·552	1·550	1·669	1·856	2·320
ηr	1·105	1·132	1·135	1·143	1·164	1·209
Concentration, per cent	2·500	2·899	3·868	—	—	—
ηr	1·233	1·280	1·400	—	—	—

The viscosities of cetomacrogol solutions relative to water are given in Table I.

Increasing the cetomacrogol concentration has a fairly large effect on the viscosity of the solutions.

Before studying the light-scattering of cetomacrogol solutions, the apparatus was checked by measuring R_{90} for benzene and toluene. Values of $16·2 \times 10^{-6}$ and $17·7 \times 10^{-6}$ cm.$^{-1}$ respectively were obtained against $16·4 \times 10^{-6}$ and $17·6 \times 10^{-6}$ cm.$^{-1}$ found by Ottewill and Parreira[4]. Depolarisations of 0·42 and 0·43 respectively were found.
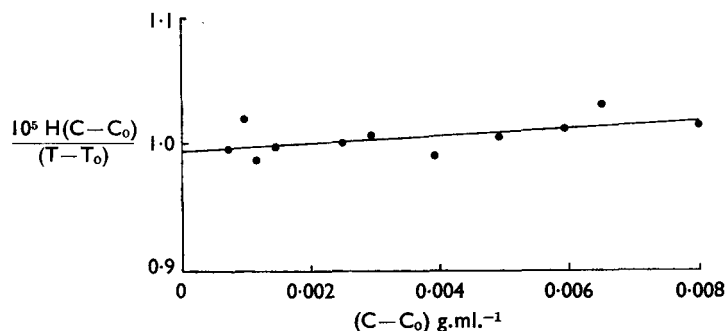

FIG. 2. Graph of $H(C-C_0)/(T-T_0)$ against $(C-C_0)$. For symbols see text.

As a further check the micellar weight of sodium dodecyl sulphate in 0·04N sodium chloride solution was also determined, giving 28,600 at 25°, compared with Phillips and Mysels' value[8] of 29,600 at 22°. The specific refractive index increment, dn/dc for the compound, was found to be 0·116 ml. g.$^{-1}$, compared with 0·115 ml. g.$^{-1}$ by Phillips and Mysels.

Cetomacrogol in water gave dn/dc = 0·133 ml. g.$^{-1}$ ($\pm 0·001$ ml. g.$^{-1}$).

The results of the light-scattering experiments are shown in Figure 2; corrections for depolarisation were applied to the results. A plot of

concentration against turbidity in the low concentration region is shown in Figure 3. At very low concentrations, the turbidity of the solution is scarcely more than that of the solvent, but a point is reached where turbidity begins to increase rapidly with increasing concentration. This is due to micelle formation; as turbidity is proportional to molecular weight of the solute, micelles scatter much more light than single molecules. A crude estimate of the critical micelle concentration, from a large-scale drawing of Figure 3 (including three additional pre-CMC points not
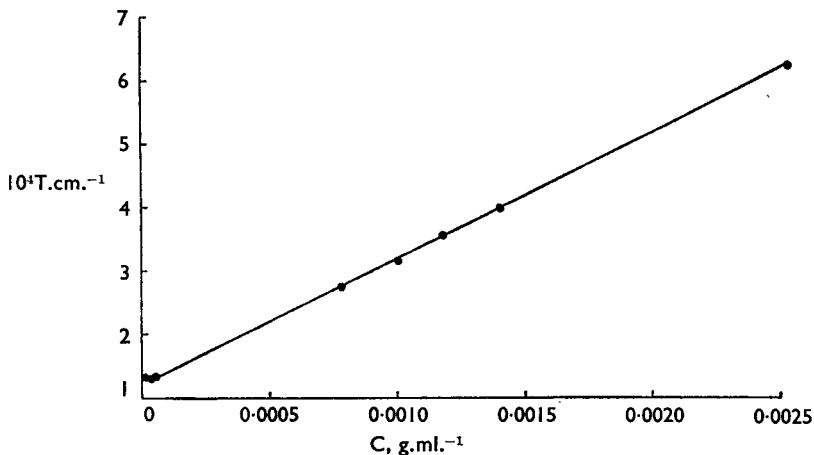

FIG. 3. Graph of turbidity of solutions of cetomacrogol, T, against concentration, C.

shown in the figure) is 0·006 per cent. From surface tension, solubilisation, and the iodine method, it was found[9] that the critical micelle concentration lay in the region 0·006 to 0·008 per cent, in agreement with the value from light scattering.

DISCUSSION

For solutions of small, approximately spherical molecules, the molecular weight, M, is related to the turbidity by

$$\frac{HC}{T} = \frac{1}{M} + 2BC$$

where B is the second virial coefficient, C is the concentration, and

$$H = \frac{32\pi^3 n_0^2 (dn/dc)^2}{3N\lambda^4}$$

where λ is the wavelength of the light used, N is Avogadro's number, and n_0 is the refractive index of the solvent. On plotting HC/T against C, a straight line should be obtained with an intercept of $1/M$ and a slope of 2B.

Following Debye[10,11], for detergents whose solutions give a turbidity T_0 at the critical micelle concentration C_0:

$$\frac{H(C-C_0)}{(T-T_0)}$$ is plotted against $(C-C_0)$ (Fig. 2).

For cetomacrogol the plot is linear, and the molecular weight, determined from the intercept, is 101,000 ± 5 per cent. As the monomer has a molecular weight of 1210, the micelle contained 83 monomers. From the intensity of scattered light measured at two equal angles about 90° to the incident beam, e.g., 60° and 120°, an idea of the micellar shape can be obtained. Spherical micelles should give equal intensities at the two angles, and the ratio of the intensities (the dissymmetry, Z = intensity at 60°/intensity at 120°) should be unity. Dissymmetries varying between 1·02 and 1·05 were observed experimentally, indicating that the micelles are reasonably spherical. Dust in the solutions and the presence of stray light in the apparatus may lead to results suggesting high dissymmetries. The difficulty of completely clarifying detergent solutions, which tend to suspend particles, is probably responsible for the small apparent residual dissymmetry. Soap micelles under normal conditions are generally considered to be spherical; for spherical micelles of dodecyl pyridinium chloride[4], dodecyl pyridinium bromide[4], and sodium dodecyl sulphate[8,12], dissymmetries of the order of 1·01 to 1·3 have been obtained. Stray light or dust are probably responsible where high Z values have been obtained.

The second virial coefficient, B, has the value $1·3 \times 10^{-4}$. Ionised detergents give large values of B, e.g., for sodium dodecyl sulphate B is 122×10^{-4} in water and $4·2 \times 10^{-4}$ in 0·1N sodium chloride solution. Cetomacrogol, being unionised gives a lower value for B, namely $1·3 \times 10^{-4}$.

The interpretation of diffusion and viscosity results is generally complicated by the effects of shape and solvation on the kinetic behaviour of the particle in solution. Assymmetric or solvated particles diffuse slower than spherical or unsolvated particles of the same molecular weight. Similarily, solutions of assymmetric or solvated particles have higher viscosities than those of spherical or unsolvated ones.

The Einstein equation[13] relates the specific viscosity, η_{sp} to the volume fraction of the solute, ϕ.

$$\eta r - 1 = \eta_{SP} = 2·5\phi$$

A plot of η_{sp}/ϕ against ϕ should give a straight line with an intercept of 2·5. An intercept greater than 2·5 suggests that the particle is either solvated or assymmetric. In the present study a value of $8·1_2$ was found (Fig. 4). As the light-scattering results show the micelle to be spherical, the deviation of $(\eta_{sp}/\phi)_{\phi=o}$ from 2·5 can be considered to be due to hydration only. The extent of hydration can be found from equations of the type given by Oncley[14]:

$$\left(\frac{\eta_{SP}}{\phi}\right)_{\phi=o} = 2·5(1 + \frac{w}{\bar{v}\rho})$$

where v = specific volume of the solute, ρ = density of solvent, and w is the number of g. of water hydrating 1 g. of cetomacrogol. In this case w = $1·96$ g. water, which is a large amount of hydration compared with materials like the proteins, where 0·3 g. water per g. protein is a normal figure.

A further idea of the degree of hydration may be gained by using the diffusion coefficient to calculate the radius of the micelle, r. For spherical particles the Stokes-Einstein equation may be applied:

$$r = \frac{RT}{6\pi\eta ND}$$

η is the viscosity of the solvent, D is the diffusion coefficient, and the remaining symbols have their usual significance. The diffusion co-efficient of 5.10×10^{-7} cm.²sec.$^{-1}$ gives a particle radius of 48.1 Å; the volume of the micelle will thus be $466,000$ Å³. This volume will be occupied by both water and cetomacrogol molecules. The 83 monomers of cetomacrogol will occupy a volume of $146,000$ Å³ (83 × monomer volume calculated from molecular weight and density) leaving a volume
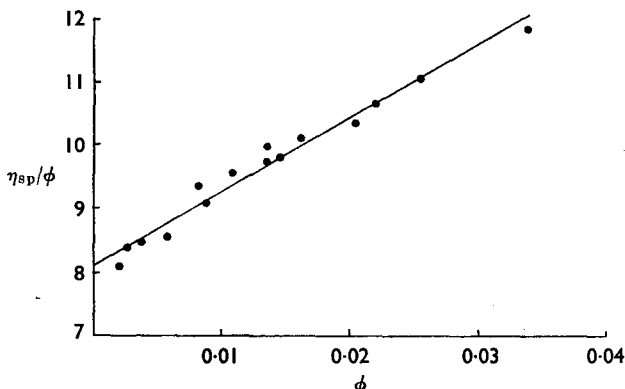

FIG. 4. Graph of η_{sp}/ϕ against ϕ. For symbols see text.

of $320,000$ Å³ for the water. This would allow 10,700 water molecules to be present in the micelle, which corresponds to 129 water molecules per monomer of cetomacrogol, or 1.92 g. water per g. cetomacrogol, in good agreement with the viscosity result. Triton X100 micelles were found to contain 50 water molecules per monomer[1]; but the micelles of this detergent are smaller than those of cetomacrogol. The hydration of Triton X100 corresponds to five water molecules per ethylene oxide unit, while that for cetomacrogol corresponds to six for each —OCH_2CH_2—. This is too large a number to be clustered round each ether linkage, and perhaps the best way of looking at the hydration is to consider that the water molecules are mainly jammed in the interstices of the hydrophilic chains.

A check on the micellar weight can be obtained by combining the diffusion and viscosity results. The hydration of the micelle will make its frictional coefficient, f, larger than that of an unhydrated micelle (f_0) of the same molecular weight. The ratio of the frictional coefficients can be calculated from:

$$\frac{f}{f_0} = \left(1 + \frac{w}{\bar{\nu}\rho}\right)^{\frac{1}{3}}$$

giving $f/f_0 = 1.48_1$.

The diffusion coefficient of the unhydrated micelle (D_0) is obtained from $D/D_0 = f_0/f$
giving $D_0 = 7.55_3 \times 10^{-7}$ cm.^{2}sec.$^{-1}$.
Substitution in that form of the Stokes-Einstein equation for molecular weight yields a result of 96,000 $\pm$ 5 per cent, or a micelle containing 79 monomers, in good agreement with the result from light scattering.

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After the Author presented the paper there was a DISCUSSION.