

Membrane osmometry of solubilized systems

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The solubilization of decane, ethyl *p*-hydroxybenzoate, methyl anisate and *p*-hydroxybenzoic acid by aqueous micellar solutions of cetomacrogol 1000 has been examined by membrane osmometry and viscosity techniques. The effect of the solubilizates on the number-average micellar molecular weight, M_n , has been related to their site of incorporation in the micelle. Decane and methyl anisate are solubilized in the hydrocarbon core of the micelles and both compounds produce an increase in M_n up to a maximum value of 2.0×10^5 , at a solubilizate concentration of approximately 80% of the saturation limit for each compound. This increase is shown to result from an increase in the number of molecules of both solubilizate and of surfactant per micelle. Further addition of solubilizate, to produce a saturation level in excess of 80%, results in a decrease in micellar size in both systems. The solubilization of ethyl *p*-hydroxybenzoate and *p*-hydroxybenzoic acid is thought to involve the oxyethylene region of the micelle and both solubilizates cause an increase in M_n owing to the inclusion of solubilizate into the micelle, the number of molecules of surfactant per micelle being unaffected by the solubilization process. Viscosity studies on the decane-cetomacrogol-water system are interpreted as indicating no change in either micellar symmetry or hydration as a result of solubilization. A spherical model for the micelles is shown to be consistent with the experimental data.

The effect of solubilizate on micellar size has been examined in only a few systems. In a light-scattering study of solubilization by hexadecyltrimethylammonium bromide (Hyde & Robb, 1964) it was shown that the incorporation of increasing amounts of the non-polar molecules, decane, octane and cyclohexane, caused a pronounced increase in the micellar molecular weight (mmw). This was due to increases in the numbers of solubilizate and surfactant molecules in each micelle. However, the solubilization of the polar molecule, octanol, although increasing the mmw, caused a decrease in the number of surfactant molecules in each micelle.

Nakagawa, Kuriyama & Inoue (1959, 1960) found the solubilization of decane and decanol by three methoxypolyoxyethylene decyl ethers to result in increases in the micellar weight of the micelles of these non-ionic surfactants. Each weight increase was a consequence of increases in the amount of solubilizate and surfactant per micelle. Viscosity and sedimentation studies of the solubilization of 1,2,4-trichlorobenzene and toluene by cetylpyridinium chloride (Smith & Alexander, 1957) have indicated an increase in mmw and in micellar asymmetry with increase in solubilizate concentration up to a maximum, after which further solubilizate promoted the formation of a more spherical micelle which existed in equilibrium with the rod-like micelles produced initially. In contrast, the solubilization of methyl cyclohexane by the same surfactant resulted in only a small regular increase in mmw and viscosity.

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In most cases, the differences in the effects of the various solubilizates on the micelle size and shape have been attributed to differences in the location of the solubilizate within the micelle. This paper reports an investigation of changes in the mmw of cetomacrogol micelles following the incorporation of four solubilizates for which the site of solubilization is known from previous studies (Corby, 1969, Corby & Elworthy, 1971) and correlates the effects produced with the location of the solubilizate within the micelle.

MATERIALS AND METHODS

Materials. Cetomacrogol 1000 B.P.C. in methanolic solution was deionized by passage through a column of 'Biodeminerolit' mixed bed ion-exchange resin and dried to constant weight over phosphorous pentoxide *in vacuo*.

n-Decane, olefine free (Fluka A.G. Purum grade) was used as received.

p-Hydroxybenzoic acid (BDH Ltd, Laboratory Reagent) was recrystallized from distilled water and dried at 40° over phosphorous pentoxide.

Ethyl *p*-hydroxybenzoate (BDH Ltd, Laboratory Reagent) was recrystallized from distilled water and dried at 40° over phosphorous pentoxide.

Methyl *p*-methoxybenzoate (methyl anisate) was recrystallized from a methanol—water mixture and dried at 30° over phosphorous pentoxide.

Preparation of solutions. Solutions were prepared by melting the solubilizate and cetomacrogol together at 40° then adding sufficient warm distilled water to produce the required total concentration. The weight of each solubilizate necessary to produce the required degree of saturation of the micelles was calculated from the solubility data of Corby (1969, Corby & Elworthy, 1971). All solutions were allowed to equilibrate at 30° (24 h) before measurements were made. Preliminary experiments indicated no measurable difference in the osmotic pressure of solutions prepared in this way and of corresponding solutions prepared by shaking for a period of three days. Hence it was concluded that the above procedure produced solutions in which solubilization to the required extent was complete.

Membrane osmometry. Measurements were made on a Hewlett-Packard 503 high-speed membrane osmometer at $30^{\circ} \pm 0.1^{\circ}$. B.19 cellulose acetate membranes (Schleicher and Schuell) were used since these had previously been shown to retain the micelles of cetomacrogol (Attwood, Elworthy & Kayne, 1969). Since the membranes are freely permeable to monomers and to free solubilizate it was necessary to achieve, as far as possible, an equal concentration of these species on either side of the membrane to reduce to a minimum their contribution to the osmotic pressure. Consequently a solution of cetomacrogol above the critical micelle concentration (cmc) and containing sufficient solubilizate to give the required degree of saturation was placed in the solvent compartment of the osmometer.

Viscosity measurements. Measurements were made at $30^{\circ} \pm 0.01^{\circ}$ using a suspended-level dilution viscometer with a solvent flow time of approximately 200 s.

Density measurements. A Lipkin pycnometer of approximately 10 ml capacity was used. Measurements were made at $30^{\circ} \pm 0.01^{\circ}$ according to the procedure of Bauer & Lewin (1960). Each density represents the mean of two measurements. The precision of repeat measurements was ± 0.00001 g ml⁻¹.

RESULTS

Treatment of osmotic pressure results. Attainment of an osmotic pressure which remains constant for at least 2 h is indicative of complete retention of the micellar species by the osmometer membrane (Attwood, Elworthy & Kayne, 1969, 1970). This was shown to apply to all the solubilized systems investigated here. For such systems, the measured osmotic pressure, π , between a sample solution of concentration c g litre⁻¹ and a 'solvent' of concentration c' g litre⁻¹ is given by

$$\pi = RT(c - c')/M_n + RBT[(c - c')^2 + 2(c - c')(c' - cmc)] \quad \dots \quad (1)$$

where B is the second virial coefficient and RT has the usual meaning (Coll, 1970). Hence the osmotic pressure data were plotted as $\pi/(c - c')$ against $(c - c')$ (Fig. 1)

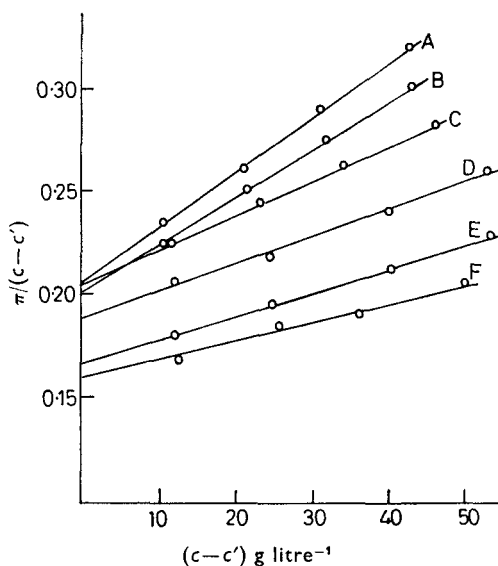


FIG. 1. Variation of reduced osmotic pressure with concentration for cetomacrogol micelles containing A 20%, B 30%, C 60%, D 80%, E 90% and F 100% of the saturation limit of *p*-hydroxybenzoic acid.

and extrapolated to $c = c'$. M_n was calculated from the intercept which is given by

$$\pi/(c - c')_{c=c'} = RT/M_n + 2RTB(c' - cmc) \quad \dots \quad (2)$$

In all the systems studied the correction term $2RTB(c' - cmc)$ had a negligible effect on the value of M_n and hence accurate values of the cmc's and the second virial coefficients are not essential.

Variation of M_n with the degree of saturation of the micelles with each of the solubilizates is shown in Fig. 2. The numbers of molecules of solubilizate and of cetomacrogol per micelle were calculated as a function of the degree of saturation, assuming that all of the micelles contained the same amount of solubilizate. The results are shown in Figs 3 and 4.

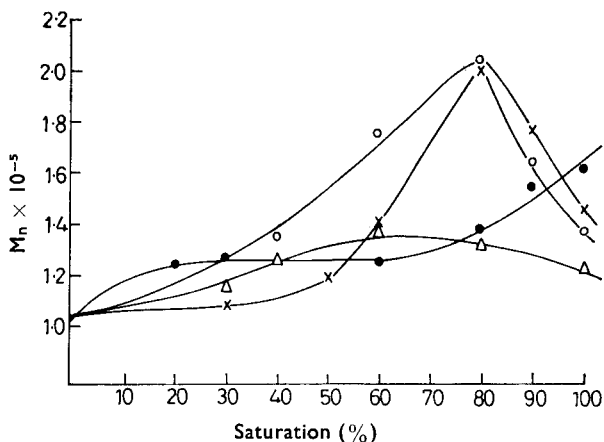


FIG. 2. Variation of micellar weight with the degree of saturation of cetomacrogol micelles with O decane; \times methyl anisate; \bullet *p*-hydroxybenzoic acid and Δ ethyl *p*-hydroxybenzoate.

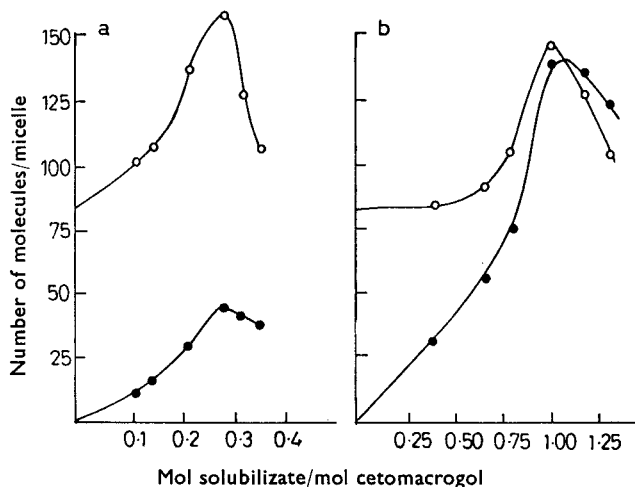


FIG. 3. The number of molecules per micelle of \circ cetomacrogol and \bullet solubilize as a function of the molar ratio of solubilize in the mixture, for the solubilization of decane (a) and methyl anisate (b).

Viscosity results

Figure 5 shows the variation of reduced viscosity with total solute concentration for cetomacrogol micelles saturated to varying extents with decane. Values of the limiting viscosity numbers, $[\eta]$, calculated by regression analysis are given in Table 1. The value of $[\eta]$ obtained for cetomacrogol alone is in reasonable agreement with that quoted by Corby (1969). However, the value for cetomacrogol micelles saturated with decane at 30° is higher than that found by Corby at 20° (5.30). This is unexpected since increase in temperature usually causes micellar dehydration and a consequent decrease in $[\eta]$. The extent of hydration of the micelles was estimated assuming micellar sphericity as w g of H_2O/g of total micellar solids using

$$[\eta] = 2.5 (\bar{V} + wV^o) \dots \dots \dots (3)$$

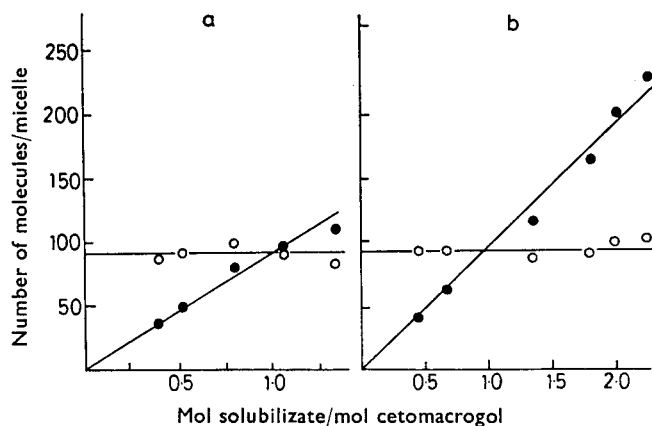


FIG. 4. The number of molecules per micelle of \circ cetomacrogol and \bullet solubilize as a function of the molar ratio of solubilize in the mixture, for the solubilization of ethyl *p*-hydroxybenzoate (a) and *p*-hydroxybenzoic acid (b).

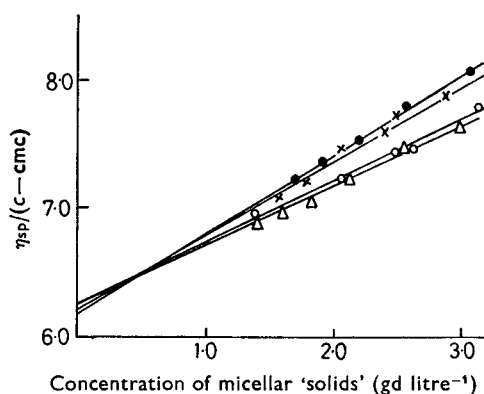


FIG. 5. Variation of reduced viscosity with concentration for cetomacrogol micelles containing \bullet 0%; \times 20%; \circ 80% and \triangle 100% of the saturation limit of decane.

Table 1. *Viscosity, partial specific volume and hydration data for cetomacrogol micelles containing solubilized decane.*

Saturation %	Limiting viscosity number $[\eta]$	Partial specific Volume \bar{V} ml g ⁻¹ of the micellar species	Hydration w g of H ₂ O/g of total micellar solids
0	7.14	0.9205	1.94
20	7.16	0.9240	1.94
40	—	0.9271	—
60	—	0.9309	—
80	7.19	0.9345	1.94
100	7.20	0.9370	1.94

where V^c is the specific volume of the solvent. The partial specific volume of the micellar species, \bar{V} , was calculated from the slope of plots of density, ρ , as a function of the total solute concentration, c , using

$$\rho = \rho_0 + (1 - \bar{V}\rho_0)c \quad \dots \quad (4)$$

where ρ_0 is the density of the solvent, i.e. water saturated with decane. Values of w and \bar{V} are given in Table 1. \bar{V} was a linear function of the percentage saturation of the micelles with decane. Identical values of w were obtained using an equation proposed by Corby (1969).

DISCUSSION

Because of its almost complete insolubility in water, decane is believed to be solubilized exclusively in the hydrocarbon core of the micelle. Fig. 3 shows that the observed increase in M_n up to a maximum value at 80% saturation of the micelles (Fig. 2) is caused by an increase in both the decane content of the micelles and the number of molecules of cetomacrogol per micelle. This increase in aggregation number is similar to increases reported from previous investigations and is probably a result of the need for more monomers to effectively cover the hydrophobic core, which has been expanded by the incorporation of decane. The subsequent decrease in M_n is similar to that reported by Smith & Alexander (1957) for the solubilization of trichlorobenzene and toluene by cetylpyridinium chloride. However, the viscosity data for the decane-cetomacrogol-water system indicate that if there is any increase in $[\eta]$ caused by a decrease in micellar symmetry, as was found by these authors, it is exactly cancelled out by a corresponding decrease in hydration. A more probable interpretation of the viscosity data is that no change occurs in the symmetry and this indicates a constant micellar hydration as shown in Table 1. The maximum value of M_n for both the decane and the methyl anisate systems is approximately 2.0×10^6 and this may represent the maximum size the micelle can attain while still retaining its symmetry. Addition of more solubilizate, to produce a saturation level in excess of 80%, results in the production of more micelles of a smaller size rather than the expansion of the existing ones.

Macfarlane (1970) has shown that if the micelles of cetomacrogol are asymmetric it is unlikely that their axial ratio exceeds a value of 2. To determine whether a spheroidal model was consistent with the experimental data, calculations were made of the micellar dimensions, assuming the micelles to be perfectly spherical, for all degrees of saturation with decane. The volume of the micellar core, V_c , and hence the core radius, r_c , was calculated assuming that the decane and hexadecane composing the core had densities equal to those of these liquids in the pure state. The total hydrated radius, r_h , was calculated from the hydrated volume, V_h , using

$$V_h = \frac{M_n}{N} (\bar{V} + wV^c) = \frac{4}{3} \pi r_h^3 \quad \dots \quad (5)$$

Thus the radius of the oxyethylene region, r_e , of the micelle could be estimated. If the hydration of the micelle is to remain constant during the micellar expansion, as indicated by the viscosity data, the extension of the oxyethylene chain should not vary to any significant extent, otherwise the amount of water mechanically trapped by these chains will also vary. Table 2 shows that r_e is reasonably constant, differing by a maximum of only 0.6 nm from its value in the pure cetomacrogol micelles. This

Table 2. *Micellar dimensions for cetomacrogol micelles containing solubilized decane, calculated assuming the micelles to be spherical.*

Saturation (%)	$V_h \times 10^{-2}$ (nm ³)	r_h (nm)	$V_c \times 10^{-1}$ (nm ³)	r_c (nm)	r_e (nm)
0	4.98	4.92	4.06	2.13	2.79
30	6.08	5.26	5.21	2.32	2.91
40	6.46	5.36	5.63	2.38	2.97
60	8.37	5.85	7.60	2.63	3.22
80	9.79	6.16	9.12	2.79	3.37
90	7.87	5.73	7.47	2.61	3.12
100	6.58	5.40	6.34	2.47	2.92

is not a significant difference in comparison with the total extended length of approximately 8 nm for a chain of 21 units, and hence a spherical model for the micelles is not an unreasonable one for this system.

The partial specific volume of a multicomponent micelle is given by the general equation (Kraemer 1940)

$$\bar{V} = \bar{V}_1 + \sum r_i \bar{V}_i / (1 + \sum r_i) \quad \dots \quad \dots \quad \dots \quad (6)$$

where \bar{V}_1 is the partial specific volume of the pure surfactant micelle and r_i is the number of g of the i^{th} component with partial specific volume \bar{V}_i combining with 1 g of the surfactant. Application of equation 6 in the calculation of \bar{V} for the cetomacrogol micelle saturated with decane, using the specific volume of decane (calculated from an experimental density of 0.722 g ml⁻¹ at 30°) rather than the partial specific volume, gives a value of 0.9381 ml g⁻¹ for \bar{V} . This agrees well with the experimental value, and supports the assumption that the decane is solubilized exclusively in the micellar core. Masterton (1954) has shown that the exposure of aliphatic hydrocarbons to an aqueous environment, as would be the case if the decane was incorporated within the oxyethylene region of the micelle, results in a significant decrease in the molar volume. Such an agreement between theoretical and experimental values of \bar{V} might not then be expected.

Fig. 2 shows a similar increase in M_n following the solubilization of methyl anisate, a maximum M_n of 2.0×10^5 being attained at approximately 80% saturation. As seen from Fig. 3 this is a consequence of an increase in both the number of solubilize and cetomacrogol molecules per micelle, but unlike the decane system the increase in the latter is not apparent until the micelles are approximately 40% saturated. Nmr studies (Corby 1969) of the solubilization process have shown considerable disruption of the micellar core after an initial lack of effect. It was suggested that initial solubilization occurred in the oxyethylene region and then, as the concentration of the ester increased, the core took over as the main site of solubilization. A similar interpretation may be applied to the results reported here. Significant expansion of the micellar core, and therefore an increase in aggregation number, occurs only after 40% saturation, indicating a lack of involvement of this region in the initial stages of solubilization.

As seen from Fig. 4 the solubilization of *p*-hydroxybenzoic acid does not result in any increase in the number of cetomacrogol molecules per micelle, the increase in M_n observed in Fig. 2, being due solely to the inclusion of solubilize into the micelle. Corby considers that *p*-hydroxybenzoic acid is solubilized deep within the

oxyethylene layer of the cetomacrogol micelle. Since the micellar core is not therefore expanded by the solubilization process, additional surfactant molecules are not required to shield the hydrophobic region and hence a lack of any increase in aggregation number might be expected.

A similar effect is produced by the solubilization of ethyl *p*-hydroxybenzoate. Fig. 4 indicates an almost linear increase in the number of solubilizate molecules per micelle which is the main cause of the increase in M_n shown in Fig. 2. Because of the solubility of ethyl *p*-hydroxybenzoate in hexadecane, it is thought possible that some molecules penetrate into the core, although the lack of any significant increase in the number of surfactant molecules per micelle indicates that any expansion of the micellar core caused by such penetration is not likely to be pronounced.

It is evident from this investigation that the site of solubilization within the micelle is an important factor in determining the effect a solubilizate has on the micellar weight of this non-ionic surfactant. Incorporation into the micellar core results in an increase in the number of surfactant molecules per micelle, whereas incorporation into the oxyethylene region of the micelle merely causes an increase in M_n which is due only to the presence of the solubilizate: the number of surfactant molecules per micelle being unaffected by the solubilization process.

Acknowledgement

The authors wish to thank the Science Research Council for the award of a Research Studentship to S.B.K.

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