

RESEARCH PAPERS

THE CRITICAL MICELLE CONCENTRATION OF CETOMACROGOL 1000

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The critical micelle concentration of cetomacrogol has been determined by the iodine and solubilisation methods, and also from surface tension measurements. Results from the three methods were 0.0070, 0.006 to 0.008, and 0.0063 per cent respectively. The presence of sodium chloride in the solutions decreased the critical micelle concentration. From surface tension data, an area per molecule at the air:water interface of approximately 120\AA^2 was calculated.

NON-IONIC surface active agents generally form micelles at low concentrations. This, together with their non-conductance in solution, has led to some difficulty in determining their critical micelle concentrations (CMC), as the solutions are so dilute that only small differences in physical properties are observable in the immediate pre- and post-CMC regions. Recently, a new method has been used by Ross and Olivier¹ and by Becher² for the determination of the CMC of non-ionic detergents. The method is applicable at very low concentrations.

Cetomacrogol 1000 is a non-ionic detergent of general formula $\text{CH}_3[\text{CH}_2]_{15 \text{ or } 17}\text{OCH}_2[\text{CH}_2\text{OCH}_2]_{19-23}\text{CH}_2\text{OH}$. In this work Ross and Olivier's method has been used to determine the CMC of this detergent in water and in sodium chloride solutions of various concentrations. Values of the CMC have also been obtained from solubilisation and surface tension experiments.

EXPERIMENTAL

Materials. The cetomacrogol used was a commercial sample based on cetyl alcohol. The molecular weight calculated from the above formula lies between 1121 and 1297, depending on the number of ethylene oxide residues in the chain. The measured molecular weight, from freezing point depression in benzene was 1210. The sodium chloride, iodine, and dimethyl yellow used were Analar materials.

Iodine method for determining CMC¹. Spectra were measured on a Hilger and Watts' Uvispek spectrophotometer, and certain of the optical densities on a Unicam SP600 spectrophotometer. A stock solution of iodine was made up to contain 30 mg. l^{-1} iodine, and this solution was used to dilute a 0.1 per cent solution of cetomacrogol containing the same concentration of iodine. After a rough experiment to determine the CMC approximately, solutions were prepared to contain detergent concentrations close to the CMC. The optical densities of these solutions were measured in 1 cm. cells at 360 and at 390 μm . By plotting optical density against detergent concentration, two straight lines were obtained

which intersected at the CMC (except for concentrated sodium chloride solutions, see later).

Solubilisation experiments. Dimethyl yellow was shaken with solutions of cetomacrogol of varying concentrations for 14 days at 20°. The solutions were centrifuged, 5 ml. samples withdrawn and diluted to 25 ml. with absolute ethanol, and their optical densities measured at

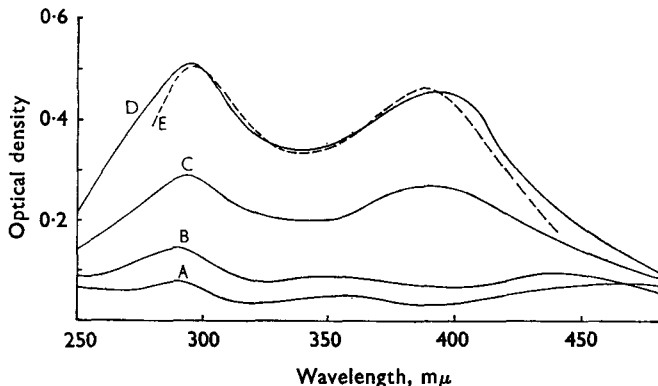


FIG. 1. Spectra of solutions containing iodine 30 mg.l.⁻¹ and varying concentrations of cetomacrogol.

- A. Iodine alone.
- B. Iodine + 0.002 per cent cetomacrogol.
- C. Iodine + 0.01 " " "
- D. Iodine + 0.02 " " "
- E. Iodine + 0.02 " " " + 0.6667N sodium chloride.

413 mμ, according to the directions of Kolthoff and Stricks³. To ensure that equilibrium was attained, the more concentrated solutions were treated in this way after 5, 8, 11 and 14 days. The measured optical density did not increase after the eighth day, showing that the solutions were saturated with dye.

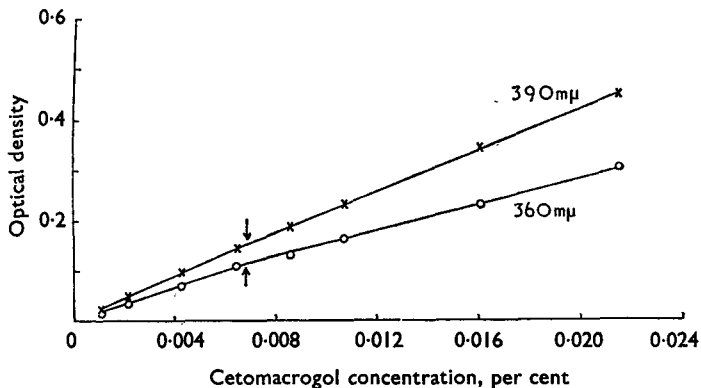


FIG. 2. Optical densities of cetomacrogol solutions in water containing iodine 30 mg.l.⁻¹

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Surface tension measurements were made using the ring pull method, the usual corrections being applied to the results⁴. The surface tension of each solution was determined repeatedly until a constant result was obtained. Adsorption effects on the walls of flasks were avoided by making up the solutions, allowing them to stand for two hours, discarding them, and draining the flasks thoroughly. Fresh solutions were then made up in the same flasks. The dish which held the solution for measurement was treated similarly. Measurements were made at 20°.

RESULTS AND DISCUSSION

In Figure 1 the spectra of solutions containing the same amount of iodine (30 mg.l.⁻¹) and varying concentrations of cetomacrogol are shown. The presence of a small concentration of detergent causes a

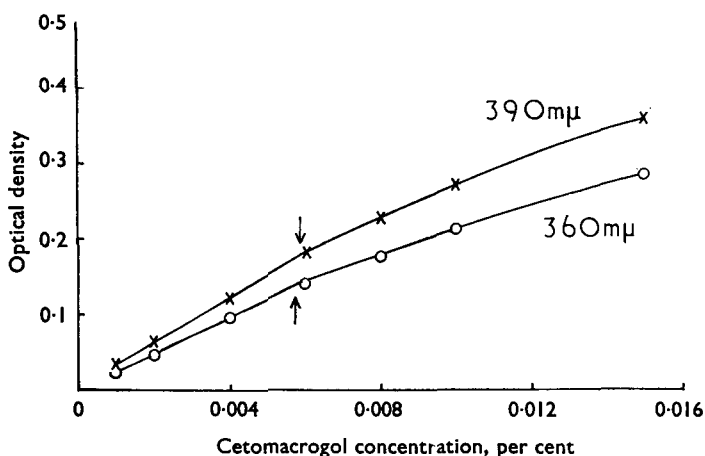


FIG. 3. Optical densities of cetomacrogol in N sodium chloride containing iodine 30 mg.l.⁻¹.

large increase of optical density compared with the solution of iodine in water. The curve run for iodine-0.02 per cent cetomacrogol-0.6667N sodium chloride has the same general shape as the curve for iodine-0.02 per cent cetomacrogol. The curves are generally similar to those recorded by Ross and Olivier¹, who found that the spectra of different detergents in the presence of iodine had a λ_{\max} at 360 m μ ; they chose this wavelength to make measurements for the CMC determination. In the present work the λ_{\max} appeared to be at 390 m μ , so measurements were made at both these wavelengths. The values obtained for the CMC were the same, within experimental error, at both wavelengths, e.g., Figure 2 shows that the CMC in water determined at 360 was 0.0068 per cent, while at 390 m μ it was 0.0069 per cent. A further experiment gave 0.0071 per cent and 0.0070 per cent at the two wavelengths respectively. The iodine method provides a rapid means of determining the CMC.

It has been shown^{2,5} that the CMCs of polyoxyethylene derivatives of alcohols and phenols can be expressed by an equation of the type:

$$lnc_o = A + B.R$$

where c_o is the CMC in units of per cent $\times 10^4$, R is the ratio of the number of moles of ethylene oxide to the number of moles of alcohol or phenol present in the detergent. A and B are constants. A appears to depend on the nature of the alcohol or phenol present, while B depends

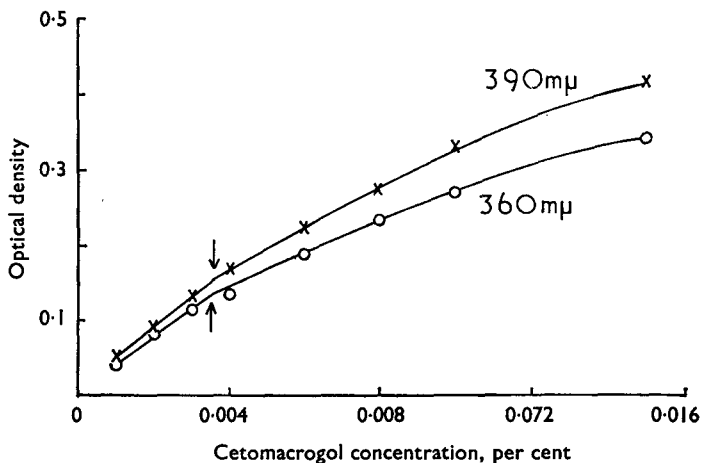


FIG. 4. Optical densities of cetomacrogol solutions in 2N sodium chloride containing iodine 30 mg.l.⁻¹.

on the electrolyte concentration of the solution². For polyoxyethylene derivatives of lauryl alcohol, Becher² gives the equation:

$$lnc_o = 3.72 + 0.038 R$$

while for these derivatives of stearyl alcohol:

$$lnc_o = 3.69 \pm 0.0068 R$$

Lauryl and stearyl alcohols esterified with twenty-two ethylene oxide units gave calculated CMCs from these equations of 0.0095 and 0.0046 per cent respectively. The observed value for cetomacrogol of 0.0070 per cent is of the correct order as it falls between these values.

The curves for the determination of the CMC in N and 2N sodium chloride solutions are shown in Figures 3 and 4. Although a straight line was obtained for the optical density:concentration plot below the CMC, a curve was obtained above it. This makes the determination of the CMC in concentrated salt solutions uncertain, although the curve flattens considerably as the CMC is approached.

As the salt content of the solutions was increased, the CMC decreased. The effect is small compared with that on ionised detergents; the CMC of sodium dodecyl sulphate in water⁶ is 10 mm.l.⁻¹, in 0.2N sodium chloride⁷ it is 0.8 mm.l.⁻¹, a twelve-fold decrease. Cetomacrogol shows a decrease from 0.0070 per cent in water to 0.003 per cent in 2.5N sodium

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chloride (Fig. 5). Non-ionic detergents are believed to possess a weak positive charge in aqueous solution⁵, and presumably the presence of sodium chloride decreases the charge, thus causing a lessening of the intermolecular repulsive forces which will oppose aggregation of monomers

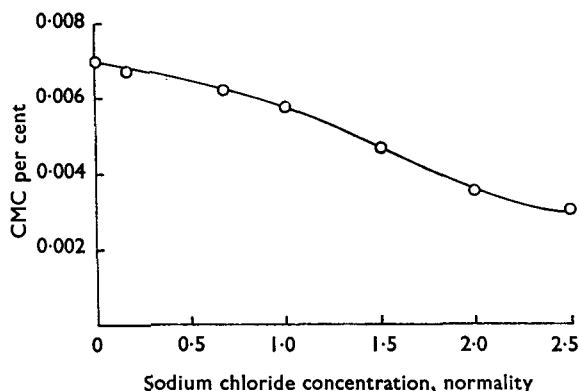


FIG. 5 Variation of CMC with sodium chloride concentration

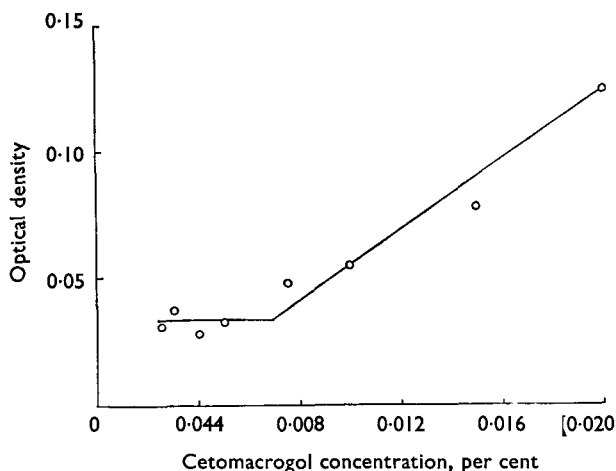


FIG. 6. Solubilisation of dimethyl yellow; optical density versus cetomacrogol concentration per cent. See Text.

to micelles; the CMC will shift to a lower concentration. The effect of salts on cetomacrogol solutions is being investigated further.

A small but roughly constant amount of dimethyl yellow appears to be solubilised in the pre-CMC region (Fig. 6). At concentrations above the CMC, the amount of dye solubilised increases, due to uptake in the micelles. The solubilisation experiments are rather inaccurate, due to the smallness of the optical densities to be measured, and to the difficulty

of removing suspended dye particles from the solutions, even with prolonged centrifugation. From these experiments, the CMC in water can be estimated to be in the region 0.006 to 0.008 per cent, which agrees with the results from the iodine method.

Both these methods involve the addition of a foreign substance to the detergent-water system. In view of this, it was desirable to check the results against a third method where no foreign substance was present. Consequently the surface tensions of a series of solutions were measured. The results are shown in Figure 7 as a surface tension : log concentration

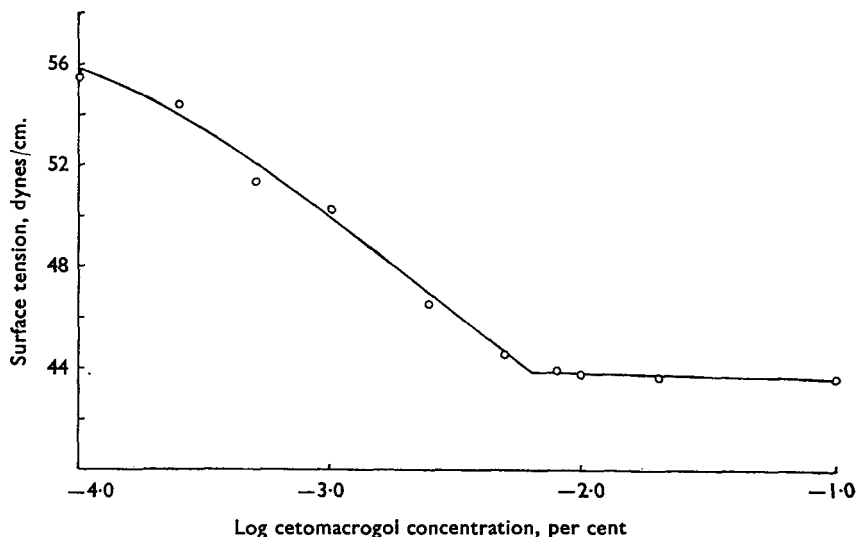


FIG. 7. A plot of surface tension versus log concentration of cetomacrogol (per cent).

plot. As expected the surface tension is almost constant at concentrations greater than the CMC. Below the CMC, the surface tension steadily decreases with increasing concentration, showing that an increasing number of molecules is being adsorbed at the air : water surface. In the region from log concentration of -3 to the CMC, the plot is linear, and the value of the CMC is 0.0063 per cent, in good agreement with the results from the other methods, and indicating that the addition of iodine or dimethyl yellow to the solutions does not affect the CMC appreciably.

From the slope of the surface tension-log concentration graph, the area/molecule can be calculated using the Gibbs equation. In the log concentration -3 to -2.4 region a value of approximately 120 \AA^2 was calculated. The structure of the film at this interface is likely to be one in which the chain of polyoxyethylene units lies in the aqueous phase, while the hydrocarbon part of the molecule is forced up above the surface. The area/molecule is greater than the cross-sectional area of the polyoxyethylene chain (roughly 20 \AA^2 from molecular models), leading to the idea that the chain either lies along the surface, or is

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considerably curled up. A more detailed study would be required to elucidate the complete structure of the surface film.

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REFERENCES

1. Ross and Olivier, *J. phys. Chem.*, 1959, **63**, 1671.
2. Becher, *ibid.*, 1959, **63**, 1675.
3. Kolthoff and Stricks, *ibid.*, 1948, **52**, 915.
4. Harkins and Jordan, *J. Amer. chem. Soc.*, 1930, **52**, 1751.
5. Hsiao, Dunning and Lorenz, *J. phys. Chem.*, 1956, **60**, 657.
6. Brudney and Saunders, *J. Pharm. Pharmacol.*, 1955, **7**, 1012.
7. Matijevic and Pethica, *Trans. Farad. Soc.*, 1958, **54**, 1382.