

## The effect of temperature on the micellar properties of a polyoxypropylene-polyoxyethylene polymer in water

Polymers of polyoxyethylene-polyoxypropylene (e.g. Pluronic, Wyandotte Chemical Co.) are known to be surface-active in water, and have been used for many years in pharmaceutical formulations as solubilizers and suspending agents. However, a consideration of the available literature shows that there is some disagreement about whether these materials form micelles in water, as do other non-ionic surface-active agents. For example, several workers have shown the presence of critical micellar concentrations for various Pluronic using surface tension and dye solubilization techniques (Schmolka & Raymond 1965; Sasaki & Shah, 1965; Anderson, 1972). Conversely, attempts to show the presence of micelles by measuring micellar weights have been unsuccessful (Mankowich, 1954; Dwiggin, Bolen & Dunning, 1960; Cowie & Sirianni, 1966). All the above measurements have, with one exception, been carried out at one temperature (25°).

We present below some preliminary results of the solution properties in water of a polyoxyethylene-polyoxypropylene polymer (Pluronic L64), which has a nominal monomer molecular weight of 2900. The micellar properties of the surfactant polymer were investigated over a range of temperatures by surface tension and light-scattering techniques.

Surface tension measurements were made by the drop-volume technique. Plots of surface tension versus concentration showed breaks at 68.00 kg m<sup>-3</sup> (25°), 28.00 kg m<sup>-3</sup> (30°) and 10.00 kg m<sup>-3</sup> (35°). At 25° Sasaki & Shah (1965) found a break of 22.0 kg m<sup>-3</sup> for L64. Such breaks in surface tension/concentration plots are normally indicative of micelle formation (i.e. critical micelle concentration, cmc). The discrepancy between the value of Sasaki & Shah and our value is large and cannot at present be explained. However, the break in the surface tension-concentration curve is not indicative of micelle formation at 25°.

Micellar weights were determined using a Fica 42000 photogoniometer (ARL Ltd), at a wavelength of 546 nm. Fig. 1 shows plots of the ratio of concentration (C)

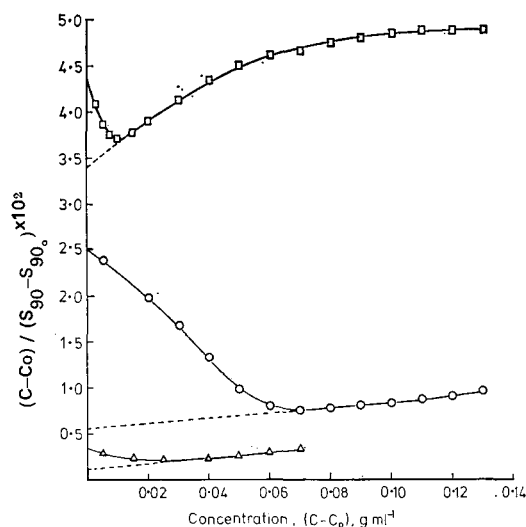


FIG. 1. Plots of  $\frac{C - C_0}{S_{90} - S_{90_0}} \times 10^2$  against  $C - C_0$  at 25°, 30° and 35°. □ 25°. ○ 30°. △ 35°.

to light scattered at  $90^\circ$  ( $S_{90}$ ), against concentration. The limit of  $C/S_{90}$  at infinite dilution, when combined with specific refractive index increments, and an instrumental constant gives micellar weight. For micellar solutions  $C/S_{90}$  ratios are normally corrected by substituting the amount of light scattered ( $S_{900}$ ) at the critical micelle concentration ( $C_c$ ). The plots at  $30^\circ$  and  $35^\circ$  are so corrected. Attempts to correct the light-scattering data at  $25^\circ$ , using the value of apparent cmc from the surface tension results gave a micellar weight which was much less than the nominal monomer value. Consequently, the plot in Fig. 1, for  $25^\circ$  is not corrected for  $C_c$ . The calculated micellar weight at  $25^\circ$  is 2656 which is close to the monomer value. This is in agreement with the findings of Dwiggins & others (1960). At concentrations of L64 up to  $200 \text{ kg m}^{-3}$  there was no indication of aggregation. The plot of  $C/S_{90}$  at  $25^\circ$  is unusual and cannot be explained at present.

Values for micellar weights at  $30^\circ$  and  $35^\circ$  are obtained by extrapolation of the descending portions of the curves to zero concentration giving values of 17 240, aggregation number = 5.9, and 86 896, aggregation number = 29.9, respectively, where aggregation numbers are calculated using the nominal molecular weight of 2900. The initial negative slopes of the curves at  $30^\circ$  and  $35^\circ$  have been observed for other types of non-ionic surfactants (Elworthy & Macfarlane, 1963), and have been taken to indicate an increase in micellar weight with concentration. It is reasonable to assume similar behaviour for the polyoxyethylene-polypropylene polymer. At  $30^\circ$  a stable micellar size is not achieved until a concentration far in excess of the apparent cmc as measured by surface tension.

The above results suggest that Pluronic surfactants may behave differently from other non-ionic surfactants. Firstly, whereas for other non-ionic surfactants micellar size increases with temperature, for the Pluronics there may be temperature ranges within which no micelles form at all. Secondly, the growth of aggregates to a stable size takes place over a much wider concentration range than for other non-ionic surfactants. Thirdly, normal methods for determining cmc values of Pluronics may be inaccurate.

We should like to thank UGINE Kuhlmann Chemicals Ltd. for the gift of Pluronic L64.

*Department of Pharmacy,  
The University,  
Manchester M13 9PL, U.K.*

C. McDONALD  
C. K. WONG

November 28, 1973

#### REFERENCES

- ANDERSON, R. A. (1972). *Pharm. Acta Helv.*, **47**, 304-308.  
COWIE, J. M. G. & SIRIANNI, A. F. (1966). *J. Am. Oil. Chem. Soc.*, **43**, 572-575.  
DWIGGINS, C. W., BOLEN, R. J. & DUNNING, H. W. (1960). *J. Phys. chem.*, **64**, 1175-1178.  
ELWORTHY, P. H. & MACFARLANE, C. B. (1963). *J. chem. Soc.*, 907-914.  
MANKOWICH, A. (1954). *J. Phys. chem.*, **58**, 1027-1030.  
SASKI, W. & SHAH, S. G. (1965). *J. pharm. Sci.*, **54**, 71-74.  
SCHMOLKA, I. R. & RAYMOND, A. J. (1965). *J. Am. Oil. Chem. Soc.*, **42**, 1088-1091.