

**The micellar properties of some non-ionic surface-active agents in polar solvents**

SIR,—Reported here are some preliminary results for the apparent critical micellar concentrations (CMC) of three non-ionic surface-active agents in water where applicable, in mixtures of water and formamide and in formamide. The surface-active agents were dodecyl tetraoxyethylene glycol ( $C_{12}E_4$ ), dodecyl hexaoxyethylene glycol ( $C_{12}E_6$ ) and dodecyl octaoxyethylene glycol ( $C_{12}E_8$ ). Details of their syntheses and purification will be published elsewhere.

Critical micellar concentrations obtained from measurements made at  $21^\circ \pm 0.5^\circ$  by the drop-volume surface tension method and applying the required correction factors, are given in Table 1. No value could be obtained for the CMC of  $C_{12}E_4$  in water as this compound is insoluble at temperatures higher than about  $15^\circ$ .

TABLE 1. THE CRITICAL MICELLE CONCENTRATIONS (MOLES/LITRE) OF  $C_{12}E_4$ ,  $C_{12}E_6$ ,  $C_{12}E_8$  IN VARIOUS SOLVENTS

Compound	Solvent Systems expressed as % w/w formamide			
	0%	55%	90%	100%
$C_{12}E_4$	—	$1.06 \times 10^{-3}$	$9.33 \times 10^{-3}$	$2.53 \times 10^{-2}$
$C_{12}E_6$	$0.90 \times 10^{-4}$	$1.53 \times 10^{-3}$	$9.70 \times 10^{-3}$	$3.06 \times 10^{-2}$
$C_{12}E_8$	$1.41 \times 10^{-4}$	$2.04 \times 10^{-3}$	$10.60 \times 10^{-3}$	$3.50 \times 10^{-2}$

The apparent CMC's increase with increasing concentrations of formamide. Schick (1964) found a similar increase in the CMC's of nonionic surfactants in aqueous solution in the presence of large quantities of urea. He attributed this increase to the ability of urea to disrupt the structure of water thus making more water molecules available for the hydration of the polyglycol side-chains of the surface-active agents. This, he said, brought about an increased surfactant solubility and an increase in CMC. As formamide is chemically similar to urea, and as both these materials raise the dielectric constant of water, a similar effect may be occurring in the mixed water-formamide solvents. However, the much greater solubility of the monodispersed surfactants in formamide alone, as shown by the very high CMC's relative to water, may also be important in determining CMC's in the mixed solvents. More recently it has been reported (Corkill, Goodman & others, 1967) that the presence of urea in aqueous solutions of surfactants brings about a decrease in the apparent heats of micellization,  $\Delta H_m$ . Similar results have been found with the systems described here, and as the concentration of formamide increases,  $\Delta H_m$ , as measured by the change of CMC with temperature, changes from positive to negative in sign. Full details of these results will be published elsewhere.

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#### References

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Schick, M. J. (1964). *J. phys. Chem., Ithaca*, **68**, 3585-3592.