

## The effect of purity on the surface tension behaviour of a homogeneous non-ionic detergent

The surface tensions of aqueous solutions of both commercial and homogeneous monoalkyl ethers of polyoxyethylene glycols have been described by several authors (Becher, 1967; Lange, 1967). The results have not always been in agreement, and the purity of the compounds studied may be suspect. Homogeneous compounds of this type are not particularly stable in solution (Corkill, Goodman & Ottewill, 1961; Hudson, R. A., personal communication) and although analytical data may suggest that the compound is pure, discrepancies in the surface tension versus log concentration plots can often indicate the presence of impurities which are not detected by other methods.

Most published work indicates a constant value for the surface tension above the critical micellar concentration (CMC), but measurements using highly purified sodium dodecyl sulphate (Elworthy & Mysels, 1966) and a homogeneous monodecyl ether of octaoxyethylene glycol (Hudson & Pethica, 1964) have shown a decrease of surface tension with increasing detergent concentration above the CMC. A few other instances of this behaviour appear in the literature (Brady, 1949; Clayfield & Matthews, 1957; Williams, Woodberry & Dixon, 1957).

As a means of investigating the effect of chemical purity on surface tension, 3,6,9,12,15,18-hexaoxahexacosan-1-ol ( $C_8E_6$ ) was prepared by two routes, both based on the Williamson ether reaction

(A) by two consecutive additions of triethylene glycol to the octyl chain, i.e.  
 $C_8 \rightarrow C_8E_3 \rightarrow C_8E_6$

(B) direct addition of hexaoxyethylene glycol to the octyl chain, i.e.  $C_8 \rightarrow C_8E_6$

In method A the  $C_8E_6$  was obtained from the reaction mixture by extraction and purified by distillation and chromatography; in method B, distillation was avoided. Final purification of both batches was achieved by foam fractionating a 0.35% aqueous solution of the compound (just below the CMC) until the solution was reduced to 60% of its original volume. The foamed solution was then freeze-dried.

Surface tension measurements were determined by the Wilhelmy-plate method at a temperature of  $25^\circ \pm 0.02^\circ$ .

The plot of surface tension versus concentration of  $C_8E_6$  is shown in Fig. 1 (e). Comparison of results from a series of experiments showed that although method A produced what appeared initially to be the best results these were not consistent between batches. This we attributed to breakdown of the compound during the final distillation giving rise to impurities which were not removed by the subsequent purification. Despite the occurrence of minima and decreased slopes above the CMC in samples of B which had not been foamed (see insert to Fig. 1, curve f) this method did produce a final product which gave reproducible values. Increasing the relative amount of solution foamed off beyond 40% did not alter the surface tension curves. It is interesting to note that despite the difference in the shapes of the surface tension curves and the surface tension at the CMC between our results and those of other workers (Corkill, Goodman & Ottewill, 1961; Corkill, Goodman & Harrold, 1963) the CMC values are in reasonable agreement.

Addition of hexaoxyethylene glycol,  $E_6$ ; the mono-octyl ether of tetraoxyethylene glycol,  $C_8E_4$ ; and the disubstituted compound,  $C_8E_6C_8$ , to foamed samples of  $C_8E_6$  prepared by the method B gave curves d, c and a respectively. As expected  $C_8E_6C_8$  gave the most dramatic effect, both lowering the surface tension and producing a large minimum. Comparison of this curve with the unfoamed solution would suggest that the minimum in the latter could be due to a trace of the di-compound.

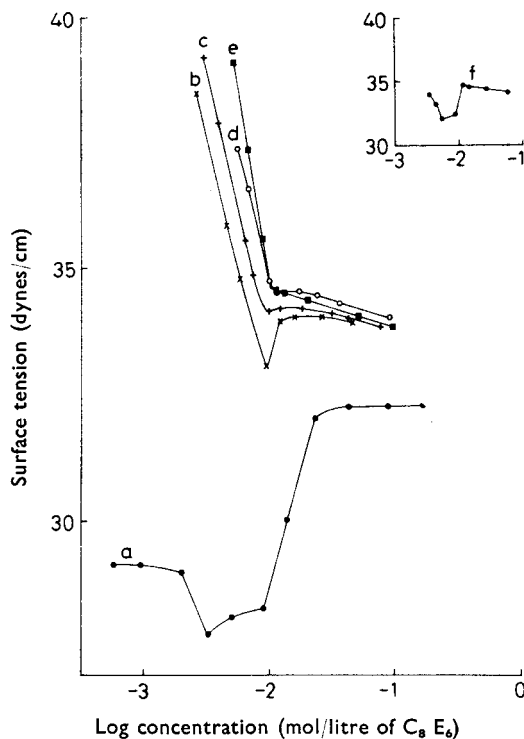


FIG. 1. Variation of surface tension with concentration of  $C_8E_6$  with various additives. (a) a mixture of  $C_8E_6$  and  $C_8E_6C_8$  (98.7:1.3 w/w); (b) the product of the collapsed foam from the  $C_8E_4$  contaminated solution; (c) a mixture of  $C_8E_6$  and  $C_8E_4$  (98.5:1.5 w/w); (d) a mixture of  $C_8E_6$  and  $E_6$  (98.7:1.3 w/w); (e) foamed  $C_8E_6$  prepared by method B; (f) unfoamed  $C_8E_6$  prepared by method B.

$C_8E_4$  and  $E_6$  each produced a small minimum but whereas  $C_8E_4$  reduced the surface tension above the CMC,  $E_6$  slightly increased it. Subsequent foam fractionation and freeze-drying of the contaminated solutions appeared to successfully remove both the  $C_8E_6C_8$  and the  $E_6$  as the residue gave identical surface tension curves to curve e.

With  $C_8E_4$ , although the solution obtained from the collapsed foam had a lower surface tension and an increased minimum (curve b) to that of the originally contaminated solution (curve c), and the minimum disappeared from the surface tension curve of the refoamed solution, the gradient of the slope of this curve below the CMC was slightly less than that of the originally purified compounds.

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