

Thermodynamics of Micelle Formation of Non-Ionic Detergents

SIR,—In view of recent interest in the thermodynamics of micellisation of non-ionic detergents (Corkill, Goodman, and Ottewill, 1961; Schick, 1963) we present some results for the molar heats and entropies of micellisation, ΔH_m and ΔS_m respectively, obtained as part of a study of synthetic detergents, in which some compounds containing branched hydrocarbon chains have been synthesised. The thermodynamic properties were obtained from the temperature dependence of the critical micelle concentration, using the conventional equations (e.g. Schick, 1963).

The results show that increasing the length of the hydrophobic group for a constant polyoxyethylene chain length gives an increase of both ΔH_m and ΔS_m . The branched chain compounds yield slightly smaller values than their straight chain isomers. Calculations of ΔH_m and ΔS_m from Schick's (1962) results on ethylene oxide dodecanol, nonyl phenol, octyl phenol, and tridecanol condensates, show that *in general*, these thermodynamic properties become less positive as the polyoxyethylene chain is lengthened, the hydrocarbon moiety being held constant.

The factors controlling ΔH_m and ΔS_m are complex. The structure of water (iceberg effect of Frank and Evans, 1945) about the hydrocarbon chain of the

TABLE I
THERMODYNAMIC PROPERTIES

Compound	ΔH_m k.cal. mole ⁻¹	ΔS_m cal. mole ⁻¹ deg ⁻¹
Me(CH ₂) ₈ n ₆ ..	0.8	2.7
Me(CH ₂) ₈ n ₆ ..	2.2	7.4
Me(CH ₂) ₁₁ n ₆ *	3.5	11.7
(Me) ₂ CHCH ₂ n ₆ ..	0.6	2.2
(Et) ₂ CH-CH ₂ n ₆ ..	1.2	4.0
(Pr) ₂ CH-CH ₂ n ₆ ..	2.0	6.7
(Bu) ₂ CH-CH ₂ n ₆ ..	2.9	9.7
(Bu) ₂ CH-CH ₂ n ₆ ..	2.3	7.7

* Data of Corkill, Goodman, and Ottewill, 1961.
n represents number of ethylene oxide units in molecule.

monomer will be lost when it enters the micelle, giving a positive entropy change. Configurational entropy changes on micelle formation provide an opposite effect. Soap monomers are considerably contracted in aqueous solution (e.g. Elworthy, 1963) while in the micelle they will be more extended. The configuration of the polyoxyethylene chains in the monomer is unknown, but in the micellar form it has been shown (Schick, Atlas, and Eirich, 1962; Elworthy and Macfarlane, 1963) that they are contracted to the extent of about 50 per cent of their extended length. Lack of knowledge of the hydration of polyoxyethylene chains in the monomer compared with their state in the micelle prevents definite assignment of the entropy change for this transference. However, it seems likely that the mesh of polyoxyethylene chains present in the micelle can trap more solvent than the single chain of the monomer, especially as the latter is fairly short (by polymer standards) and cannot be expected to form a true coil in the polymer sense. Also Elworthy and Macfarlane (1963) and Elworthy and McDonald (1963) have shown that extension of this chain increases with temperature, leading to greater micellar solvation at higher than at lower temperatures, due to the trapping effect.

Considering the above factors it seems likely that the increasing positive value for ΔS_m with increasing hydrocarbon chain length (n constant) is due to the entropy change on desolvating the hydrocarbon part of the monomers on

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entering the micelle, and that this is the predominant effect. The general trend apparent in Schick's (1962) results and for our branched chain $C_{10}\Omega_6$ and $C_{10}\Omega_9$ compounds, of ΔS_m decreasing with increasing polyoxyethylene chain length, may be due to the increased solvation shown to occur when the polyoxyethylene chain is lengthened. Due to the trapping effect, there is likely to be more ordering of the water molecules in the polyoxyethylene region of the micelles, compared with this region in the monomers, and in general this difference should increase with chain length.

Acknowledgement. We thank the Medical Research Council for the award of a Scholarship to A.T.F.

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October 25, 1963

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