

Thermodynamics of micellization of some non-ionic surfactants in mixed solvents

C. McDONALD

Department of Pharmacy, The University, Manchester, U.K.

The thermodynamics of micellization of three non-ionic surfactants in mixed solvents are reported. The contribution of the alkyl chains of the surfactant molecules to micellization is estimated from solubility data.

The thermodynamics of micellization are widely used in the examination of properties of surfactant solutions, and herein are presented such, approximate, parameters of three non-ionic surfactants in mixtures of water and formamide, water and *N*-methylformamide (NMF), water and dimethylformamide (DMF) and in water alone, where applicable. The surfactants used in the measurements were dodecyl tetraoxyethylene glycol monoether (C₁₂E₄), dodecyl hexaoxyethylene glycol monoether (C₁₂E₆) and dodecyl octaoxyethylene glycol monoether (C₁₂E₈). The synthesis and purification of these materials have been reported previously (McDonald, 1969).

RESULTS AND DISCUSSION

Thermodynamic parameters are calculated from the critical micelle concentrations (CMC) of the surfactants, in the various solvents, which have been reported previously (McDonald, 1967, 1969, 1970a). The hypothetical state for the monomers is chosen as unit mol fraction, with individual molecules behaving as at infinite dilution, and the final state is considered to be that of the micelle itself. It can be shown (Corkill, Goodman & Harrold, 1964; Molyneux, Rhodes & Swarbrick, 1965) that, provided the concentration of free surfactant molecules, i.e. the CMC, is low, the standard free energy, ΔG_m^0 , for the transfer of 1 mol of the surfactant from solvent to micelle can be represented by equation 1.

$$\Delta G_m^0 = RT \ln \text{CMC (mol fraction)} \quad \dots \quad (1)$$

It is assumed that the CMC values are small enough for equation 1 to be valid, although this may be only true, approximately, in solvents where the concentrations of amides are high. The partial enthalpy of micellization, ΔH_m^0 , may be calculated from the variation of CMC with temperature, equation 2. From the usual relation between free energy, enthalpy and entropy, the entropy of micellization, ΔS_m^0 , may be obtained. The thermodynamic parameters, at 25°, are shown in Table 1.

$$\Delta H_m^0 = -RT^2 \frac{d \ln \text{CMC}}{dT} \quad \dots \quad (2)$$

It should be noted from Table 1 that no thermodynamic parameters are available for C₁₂E₄ in water, since the cloud point of this material is 9° (McDonald, 1969). Table 1 shows that, on a mol fraction basis, formamide is least effective in decreasing the spontaneity of micelle formation, NMF and DMF have approximately equivalent effects at lower concentrations, and DMF may be most effective at higher concentrations. For all, but two, of the mixed systems studied, the negative free energy

values are accompanied by favourable enthalpy and entropy changes. From the available data, ΔH_m° values appear to tend towards zero as the concentrations of water increase. Indeed, for $C_{12}E_6$ and $C_{12}E_8$ in 0.33 mol fraction formamide, and, of course, in water, endothermic heat changes are observed for such compounds.

Table 1. *Thermodynamics of micellization at 25°C*

	Solvent	mol	ΔG_m°	ΔH_m°	ΔS_m°
$C_{12}E_4$	% w/w	fraction	kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{ deg}^{-1}$
Formamide ..	100	1.0	-17.0	-2.3	+49
	90.0	0.78	-19.8	-1.3	+62
	*55.0	0.33	-26.1	—	—
NMF ..	50.0	0.24	-20.5	-10.7	+33
	40.0	0.17	-23.4	-9.0	+48
DMF ..	60.0	0.27	-19.5	-11.5	+27
$C_{12}E_6$					
Formamide ..	100	1.0	-16.6	-3.6	+43
	90.0	0.78	-19.7	-1.0	+63
	55.0	0.33	-25.2	+1.5	+90
	42.0	0.22	-26.3	—	—
	25.0	0.12	-28.3	—	—
NMF ..	76.0	0.49	-15.7	—	—
	50.0	0.24	-20.8	-13.2	+25
DMF ..	25.0	0.09	-27.0	-7.4	+66
	75.0	0.42	-15.1	—	—
	65.0	0.31	-18.0	—	—
	60.0	0.26	-19.7	-11.5	+27
	44.0	0.16	-22.8	—	—
	30.0	0.10	-26.1	-9.2	+56
†H ₂ O ..			-33.0	+16.3	+155
$C_{12}E_8$					
Formamide ..	100	1	-16.2	-3.1	+44
	90.0	0.78	-19.5	-1.2	+61
	55.0	0.33	-24.3	+2.1	+89
NMF ..	49.0	0.23	-20.5	-13.5	+23.4
DMF ..	60.0	0.27	-19.6	-13.0	+19.2
	45.0	0.17	-22.7	—	—
	32.0	0.10	-25.1	—	—
H ₂ O ..			-32.0	+18.6	+170

For aqueous solutions of non-ionic surfactants large positive enthalpies and entropies of micellization have been attributed to partial desolvation of the monomers, on transfer to the micelle (Corkill, Goodman & Tait, 1964). If this is assumed to be so, the addition of amides to water in some way decreases or modifies the solvation of surfactant monomers by water. The observed enthalpies may represent a balance between desolvation of the monomers on one hand and possible hydrogen bond effects due to solvent-solvent, solvent-solute and solute-solute interactions. Presumably, in water the desolvation effects predominate whereas, in most systems studied here, one or other of the latter possibilities predominates.

Similarly, the overall entropy effects may be composed of two opposing entities; a desolvating effect and an aggregation effect. In the present systems the former effect appears to predominate, although the numerical entropy values are all much lower than corresponding values in water. This suggests a decrease in importance of the desolvating effect. Another factor which could affect the thermodynamic parameters is the variation of aggregation numbers as the solvent constituents change, but nothing is known of this for the present systems.

It is possible to divide the free energy of micellization into two components, one being due to the hydrocarbon part of the surfactant molecule which favours micellization, ΔG_h , and the second being due to the glycol chain, ΔG_e , which might be expected to oppose micellization. An individual knowledge of ΔG_h and ΔG_e would enable a comparison to be made with ΔG_m^o . Although solubility measurements of the hydrocarbon component, in the relevant solvents, may give approximate values for ΔG_h , it is not usually possible to measure directly ΔG_e , which may only be calculated from the difference between ΔG_m^o and ΔG_h . The values for ΔG_h used here have been obtained from solubility measurements of dodecane in H_2O -amide mixtures (McDonald, 1970b). Since the transfer of hydrocarbon from solvent to the hydrocarbon interior in the micelle is being considered, the values of free energies of solution of dodecane in the various solvents are used with the signs changed. Since the processes involved are not exactly analogous the limitations involved in using such data must be remembered. Values of ΔG_h and ΔG_e are shown in Table 2.

Table 2. *Solvophobic and solvophilic contributions to thermodynamics of micellization at 25°C*

$C_{12}E_n$		Solvent % w/w	mol fraction	ΔG_h kJ mol ⁻¹	ΔG_e kJ mol ⁻¹
Formamide	..	100	1.0	-26.1	+9.1
		90.0	0.78	-28.0	+8.2
		*55.0	0.33	-33.9	+7.8
NMF	50.0	0.24	-29.7	+9.2
DMF	60.0	0.27	-27.9	+8.4
$C_{12}E_6$					
Formamide	..	100	1.0	-26.1	+9.5
		90.0	0.78	-28.0	+8.3
		55.0	0.33	-33.9	+8.7
NMF	50.0	0.24	-29.7	+8.9
DMF	25.0	0.12	-31.5	+4.5
		60.0	0.26	-27.9	+8.2
		30.0	0.10	-31.0	+4.9
$C_{12}E_8$					
Formamide	..	100	1.0	-26.1	+9.9
		90.0	0.78	-28.0	+8.5
		55.0	0.33	-33.9	+9.6
NMF	50.0	0.24	-29.7	+9.2
DMF	60.0	0.26	-27.9	+8.4
		30.0	0.10	-31.0	+5.9

* 21°. † Taken from Corkill, Goodman & Harrold, 1964.

In all systems it may be seen that the hydrocarbon chain is the driving force for micellization. Free energies of micellization decrease or increase as do the free energies of transfer of hydrocarbon from solvent to micelle interior. In the H_2O -formamide systems it can be seen that for any concentration of formamide ΔG_e increases as does the length of the ethylene oxide chain, i.e. micellization is less spontaneous. An individual ethylene oxide unit has only a small effect in opposing micelle formation (about +0.2 kJ mol⁻¹). This is not surprising since each ethylene oxide unit consists of one oxygen atom which presumably opposes micellization and two methylene groups which would favour micellization. For the surfactants

considered here the hydroxyl group of the glycol chain appears to be the dominant factor in opposing micelle formation (about $+8 \text{ kJ mol}^{-1}$).

The direct effects of the solvents on both the hydrocarbon and glycol chains of the surfactant molecules must also be considered in the micellization process. The equation of the negative value of the free energy of solution with the transfer of a hydrocarbon chain of a surfactant from solvent to micelle may be true, in water, where a complete desolvation of the hydrocarbon in passing to the micelle is envisaged. It may not be so in other solvents, where it is possible that the hydrocarbon chain may "carry" some of the solvent into the hydrophobic centre of the micelle (see later). Hence the calculation of ΔG_e from ΔG_h and ΔG_m^o may also be in doubt.

The exact nature of the effects of additives on micellization in water cannot be explained solely from thermodynamic parameters. However, comparison of such parameters can give information on the effects of additives on the micellization process.

For the present systems NMF and DMF are more effective than formamide in altering the thermodynamics of micellization, although the changes in the parameters are quantitative rather than qualitative. In a study of the effects of additives on the micellization of ionic surfactants Emmerson & Holtzer (1967), divide the additives into those which penetrate the micelle and those which do not. Low concentrations of penetrating additives were less effective in increasing CMC's than similar concentrations of non-penetrating additives. At high additive concentrations, when micelles may be still expected in solutions containing non-penetrating additives, no micelles were present in solutions containing the penetrative type. Penetrative additives might be expected to be molecules which contain a certain hydrophobic content, although they may be miscible, or partially miscible with water. Confirmation of this may be shown from the effects of aliphatic alcohols on the micellization of a non-ionic surfactant (Hermann & Benjamin, 1967). As the hydrocarbon chain length of the alcohols increased, changes in thermodynamics of micellization were attributed to complex formation between the longer chain length alcohols and the micelles.

For the amide systems considered here CMC's increased regularly with increasing concentrations of amides (McDonald, 1969) and there were no obvious manifestations of complex formation between the amides and the micelles. It is unlikely however that micelles form in pure DMF. For example the CMC of $C_{12}E_6$ in such a solvent would be about $0.81 \text{ mol litre}^{-1}$, i.e. 36% w/v. The amides used would appear to be non-penetrative in character.

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