

Effects of structural variations of non-ionic surfactants on micellar properties and solubilization: variation of oxyethylene content on properties of C₂₂ monoethers

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Studies on erucyl alcohol ethoxylated with 40 and 47 units, and on behenyl alcohol ethoxylated with 33 and 43 units, gave values of 106, 101, 271, and 304 (all $\times 10^3$) for the micellar weight, 51, 42, 152, and 137 for the aggregation numbers, and 257, 362, 209, and 311 moles water mol⁻¹ surfactant for the micellar hydration, respectively. Measurements of the solubilization of azobenzene, cortisone acetate, griseofulvin, sulphadiazine, phenylbutazone, betamethasone, tolbutamide, and menaphthone showed that the erucyl derivatives were better solubilizers than the behenyl compounds, and that solubilization increased as the polyoxyethylene chain was shortened; this change was more pronounced with the erucyl compounds.

In general, increase of polyoxyethylene chain length decreases solubilizing power (Elworthy et al 1968). Thakkar & Hall (1967) showed this to be the case for the solubilization of testosterone in polysorbate solutions, and Barry & El Eini (1976) obtained the same results for hydrocortisone, dexamethasone, testosterone, and progesterone in solutions of polyoxyethylated cetyl alcohol.

Lengthening the alkyl chain in polyoxyethylene monoalkyl ether surfactants causes a decrease in solubilizing capacity (Arnarson & Elworthy 1980, 1981). It was found that the solubilizing capacity of CH₃(CH₂)₂₁(OCH₂CH₂)₂₁OH (abbreviated to BE₂₁ where B = behenyl and E_n = ether) was lower than that of C₁₆E₂₀, and that of CH₃(CH₂)₃₁(OCH₂CH₂)₄₁OH(C₃₂E₄₁) was in turn lower than that of BE₂₁, although the micelle size increased with increasing hydrocarbon chain length. When erucyl (E) alcohol (CH₃(CH₂)₇CH = CH(CH₂)₁₂OH) was used as the hydrophobe, the micelle size decreased, and the solubilizing capacity increased compared with the behaviour given by the saturated surfactant BE₂₁. Because of the large differences in behaviour brought about by the introduction of a *cis* double bond, the study has been extended by varying the polyoxyethylene chain length.

MATERIALS AND METHODS

The methods used for measuring light scattering, density, viscosity, and solubilization (at 298 K) were described by Arnarson & Elworthy (1980); the same solubilizates were used. The samples of behenyl and

erucyl alcohols used were described by those authors; the samples were ethoxylated by ICI Organics Division. After purification and analysis for polyoxyethylene chain length four surfactants were used: BE₃₃, BE₄₃, EE₄₀, and EE₄₇.

RESULTS DISCUSSION

Light scattering results as plots of c/S_{90} vs c , where S_{90} is the scatter at 90° to the incident beam from a solution of concentration, c are linear. Dissymmetry values (Z_{45}) were in the range 1.00-1.05. Micellar weights were calculated from the Rayleigh equation. The intrinsic viscosities $[\eta]$, together with micellar weights, are in Table 1.

The compounds previously studied (Arnarson & Elworthy 1980), BE₂₁ and EE₂₄ had micellar weights of 254×10^3 and 102×10^3 , aggregation numbers of 203 and 74, and hydrations of 106 and 134 mole water mol⁻¹ surfactant, respectively. In both the B and E series of surfactants the aggregation number falls with increasing polyoxyethylene chain length, which is normal behaviour with non-ionic surfactants (e.g. Elworthy & Macfarlane 1963).

Table 1. Micellar properties of BE₃₃, BE₄₃, EE₄₀, and EE₄₇. M = micellar mass. n = aggregation number. dn/dm = specific refractive index increment. ρ = density. Micellar hydration, w, in moles water mole⁻¹ micellar surfactant.

Surfactant	M $\times 10^{-3}$	n	dn/dm kg mol ⁻¹	ρ kg m ⁻³	$[\eta]$ kg mol ⁻¹	w
BE ₃₃	271	152	0.246	1138	13.4	209
BE ₄₃	304	137	0.306	1153	18.9	311
EE ₄₀	106	50.8	0.278	1132	16.2	257
EE ₄₇	101	42.3	0.326	1140	21.6	362

* Correspondence.

These authors showed that micellar weight decreased as the hydrophilic chain was lengthened in polyoxyethylene monohexadecyl ethers. In the E series the increase in monomer molecular weight due to the increasing polyoxyethylene content is just balanced by the decrease in aggregation number, and the micellar weight is roughly constant in the EE₂₄ to EE₄₇ range. The B series shows an increase in micellar weight going from BE₂₁ to BE₄₃. Although both hydrocarbon chains have approximately the same molar volume, their packing in the micelle is obviously very different, as is evident from the smaller micelle size found in the E series.

Taken overall, the solubilization results (Table 2) show that the E series surfactants are better solubilizers than the B series, which is consistent with previous results (Arnarson & Elworthy 1980). Similarly, plots of amount solubilized (mol mol⁻¹) against (log P)/V_m, where P is the octanol-water partition coefficient and V_m is the molar volume, were found to be linear, with a correlation coefficient lying between 0.94–0.96 for the four surfactants reported here. Plots of amount solubilized (g g⁻¹), were found to be linear with percentage hydrocarbon in the surfactant over the range of polyoxyethylene contained in the surfactant, and demonstrate the differences between the two series of surfactants (Fig. 1). With the exception of sulphadiazine (which is solubilized in such small amounts that estimation is difficult), and cortisone, the other solubilizates are much more soluble in the E series than the B series. The change in amount solubilized with hydrocarbon content is much greater in the E series than in the B series, although the micelle size of the B surfactants decreases with hydrocarbon content, while that in the E surfactants is roughly constant.

To facilitate comparison, values have been interpolated for EE₂₅ and BE₂₅ (Table 2). These com-

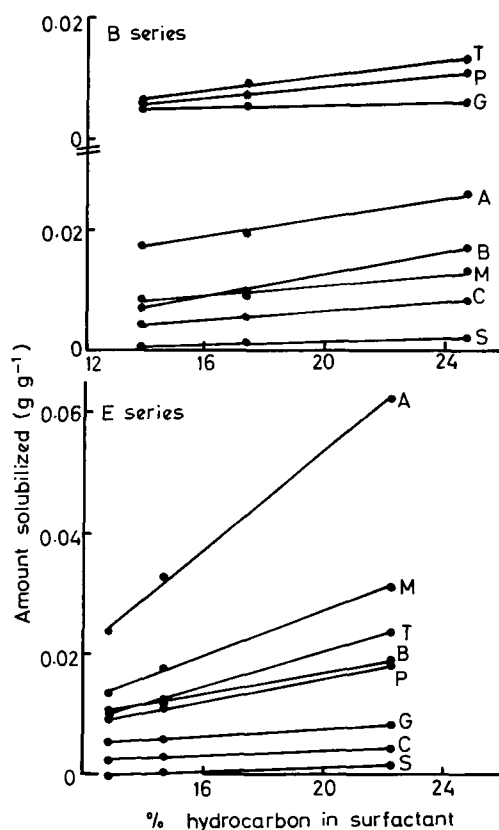


Fig. 1. Amount solubilized (g g⁻¹) against percentage hydrocarbon content of surfactants (w/w). For key to solubilizates, see Table 2.

pounds have almost the same hydrocarbon content (21.6 and 21.7% w/w respectively), the same number of ethylene oxide units, and the same micellar hydration (141 mol water mol⁻¹ surfactant). Azobenzene and phenylbutazone have the highest log P values of the solubilizates studies, and are likely

Table 2. Solubilization results.

	Be ₃₃		BE ₄₃		Surfactants EE ₄₀		EE ₄₇		EE ₂₅ /BE ₂₅ *
	10 ² gg ⁻¹	10 ² mol mol ⁻¹	10 ² gg ⁻¹	10 ² mol mol ⁻¹	Amount solubilized		10 ² gg ⁻¹	10 ² mol mol ⁻¹	
Azobenzene (A)	1.94	19.0	1.75	21.3	3.64	41.7	2.35	30.9	2.57
Cortisone acetate (C)	0.54	2.4	0.41	2.3	0.25	1.5	0.22	1.3	0.60
Griseofulvin (G)	0.58	2.9	0.50	3.1	0.60	3.5	0.52	3.5	1.40
Sulphadiazine (S)	0.14	1.0	0.09	0.8	0.05	0.4	-0.04	-0.4	0.89
Phenylbutazone (P)	0.72	4.1	0.65	4.7	1.14	7.7	0.91	7.1	1.83
Betamethasone (B)	0.93	4.2	0.70	3.9	1.13	6.0	1.05	6.4	1.28
Tolbutamide (T)	0.92	6.0	0.63	5.2	1.21	9.4	0.97	8.6	1.97
Menaphthone (M)	0.98	10.2	0.83	10.8	1.76	21.3	1.32	18.3	2.51

* ratio of g solubilize/g surfactant, interpolated for EE₂₅ and BE₂₅.

to have the highest solubility in hydrocarbons, but are solubilized unequally in EE₂₅ and BE₂₅. Unfortunately very few data are available on the solubility of these solubilizates in pure liquids. Elworthy & Lipscomb (1968a) give the solubility of griseofulvin in heptane as 1.49×10^{-5} mol kg⁻¹ heptane. On the assumption that the solubility in docosane is approximately the same as that in heptane, then the 0.217 g hydrocarbon present in 1 g surfactant would dissolve 1.1×10^{-6} g griseofulvin. The observed value is ca 6000 times greater than the calculated one. Such a large difference makes it clear that the hydrocarbon core is not the main site of solubilization for griseofulvin. Elworthy & Lipscomb (1968b) showed that concentrated solutions of polyoxyethylene glycol could dissolve reasonable quantities of griseofulvin, and it seems likely that this material is solubilized in a region of the micelle close to the hydrocarbon core, which is rich in polyoxyethylene. The volume of this region is at the moment impossible to estimate. However, the surface area of the hydrocarbon core in EE₂₅ is 3.6×10^2 m² and in BE₂₅ is 2.8×10^2 m². As the polyoxyethylene rich layer is immediately adjacent to the core surface, this layer will have a greater area in the EE₂₅ compared with the BE₂₅, and the amount solubilized is greater in the former surfactant than in the latter.

It has been suggested (Arnarson & Elworthy 1980, 1981) that some intrusion of polyoxyethylene into the outer part of the hydrocarbon core may occur in

the B series. This intrusion would affect the solution properties of the core, and, by moving the intruded core/polyoxyethylene boundary outwards in the micelle, decrease the polyoxyethylene concentration in the layer immediately adjacent to the boundary. This may be another reason for the solubilization in the B surfactants being poorer than in the E series.

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