

# Effects of structural variations of non-ionic surfactants on micellar properties and solubilization: surfactants containing very long hydrocarbon chains

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Polyoxyethylene mono-ethers of dotriacontanol ( $C_{32}E_{41}$ ) and 4,9-dimethyltritiacontanol ( $C_{35}E_{40}$ ) have been synthesized. The micellar weights in water at 298K were  $4.82 \times 10^5$  and  $5.90 \times 10^5$ , the aggregation numbers 212 and 260, and the levels of hydration 290 and 283 mol water  $\text{mol}^{-1}$  surfactant, respectively. The solubilization of azobenzene, cortisone acetate, griseofulvin, sulphadiazine, phenylbutazone, betamethasone, tolbutamide, and menaphthone was studied in 2% solutions of the above surfactants. The presence of large micelles did not result in increased solubilization;  $C_{32}E_{41}$  and  $C_{35}E_{40}$  had a lower solubilizing capacity than that of cetomacrogol.

Arnarson & Elworthy (1980) have previously shown that increasing the hydrocarbon chain length in non-ionic surfactants from  $C_{16}$  to  $C_{22}$  gave bigger micelles, but not the expected increase in solubilizing capacity obtained in the ionic series of surfactants by this variation. The micelle size of polyoxyethylene behenyl ether ( $BE_{21}$ ) was 2.5 times as large as that of  $C_{16}E_{20}$ , a surfactant similar to cetomacrogol (Cmg), but five of the eight test substances were solubilized to a greater extent in  $C_{16}E_{20}$  than in  $BE_{21}$ . Solubilization of the other three substances was only slightly better in  $BE_{21}$  than in  $C_{16}E_{20}$ . The purpose of this paper is to confirm this effect by using non-ionic surfactants containing 32 and 35 carbon atoms in their hydrocarbon chains.

At the start of the work, for the reasons given in the discussion section in Arnarson & Elworthy (1980), there was the possibility that polyoxyethylene dotriacontanol ether  $\text{CH}_3[\text{CH}_2]_{31}[\text{OCH}_2\text{CH}_2]_{41}\text{OH}$  ( $C_{32}E_{41}$ ), might be insoluble in water at 298K. A parallel synthesis of polyoxyethylene 4,9-dimethyltritiacontanol ether,  $\text{CH}_3[\text{CH}_2]_{29}\text{CH}(\text{CH}_3)[\text{CH}_2]_4\text{CH}(\text{CH}_3)[\text{CH}_2]_{10}[\text{OCH}_2\text{CH}_2]_{40}\text{OH}$ , ( $C_{35}E_{40}$ ), was undertaken, as the introduction of methyl branches makes the chain more liquid (Markley 1964), and there was a better chance of obtaining a water-soluble compound. This approach also permits the study of effects of chain branching on micellization and solubilization, the compounds differing by only one carbon atom in the straight chain, and by one ethylene oxide unit.

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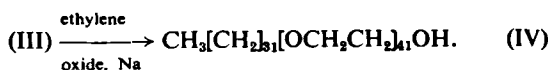
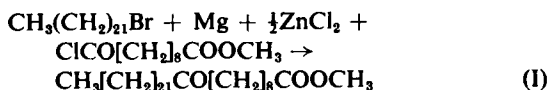
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## MATERIALS AND METHODS

The solubilizates used and the measurements of light scattering, density, viscosity, solubilization and critical micelle concentration (cmc) were as described by Arnarson & Elworthy (1980) at 298K. The synthetic work is reported in an abbreviated manner: further details are obtainable from the authors.

### Polyoxyethylene dotriacontan-1-ol ether

Reaction scheme:



Methyl-10-oxodotriacontanoate (I) was prepared by the method of Reinhard & Dixon (1965), but using toluene instead of benzene, distilling off low boiling materials, and crystallizing from light petroleum. M.p. 340-341K, yield 65%. Analysis: Calc. C, 77.9%; H, 12.7%. Found: C, 77.8%, H, 12.7%.

1-Bromodocosane was prepared from the behenyl alcohol previously used (Arnarson & Elworthy 1980) by treatment with bromine and red phosphorus (Vogel 1978a). Analysis: Calc. C, 69.2%; H, 11.9%, Found: C, 68.8%; H, 11.6%. Methyl hydrogen sebacate was prepared according to Vogel

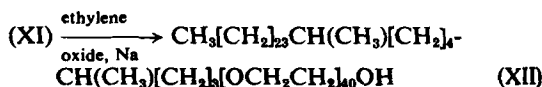
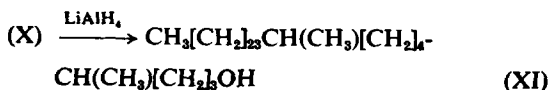
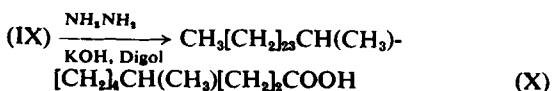
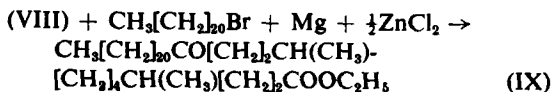
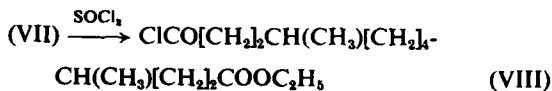
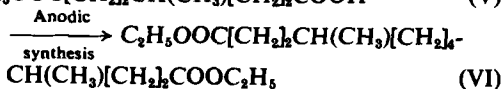
(1978b) (equivalent weight 216, found 216), and the methyl-9-chloroformylnonanoate obtained from it by treatment with thionyl chloride, followed by distillation. Strong peaks at 1785 and 1740  $\text{cm}^{-1}$  were assigned to acid chloride and ester functions.

*Dotriacontanoic acid* (II), from (I) by the method of Huang-Minlon (1946) except that the reaction mixture was finally heated to 513K. Yield 64%, M.p. 368K after recrystallization from toluene (Pollock & Stevens 1965, give 369K). Analysis: Calc. C, 79.9%; H, 13.4%. Found: C, 80.0%; H, 13.5%.

*Dotriacontan-1-ol* (III) from (II) by reduction with lithium aluminium hydride in tetrahydrofuran. After treatment with alkali and drying the reaction mixture, 7 days continuous extraction with ether gave 54% of (III). M.p. 359–360K. Analysis: Calc. C, 82.4%, H, 14.2%. Found: C, 82.4%; H, 14.1%. No carbonyl peaks were present in the i.r. spectrum.

*Polyoxyethylene dotriacontanol ether* (IV).  $9 \times 10^{-4}$  M potassium was dissolved in 0.01 M (III), and 0.44 M ethylene oxide added. The mixture was heated in a sealed steel bomb at 150 °C for 20 h. The product was purified, and its polyoxyethylene content determined as previously described (Arnarson & Elworthy 1980). 41 ethylene oxide units were present, and this compound is abbreviated as  $\text{C}_{32}\text{E}_{41}$ .

*Polyoxyethylene-4,9-dimethyltrtriacontan-1-ol ether*  
Reaction scheme:



*Monoethyl 4-methylpimelate* (V). 1,5-Dihydroxy-3-methylpentane (Flucka) was brominated, the product reacted with sodium cyanide, and hydrolysed to the diethyl ester using standard reactions (Vogel 1978a, c). After hydrolysis, the half ester was prepared using a method similar to that for methyl hydrogen sebacate (Vogel 1978b). Analyses: Calc. C, 59.4%; H, 9.0%. Found: C, 59.7%; H, 9.7%.

*Diethyl 4,9-dimethyldodecanediote* (VI). Prepared by anodic synthesis of (V), using the general method of Greaves et al (1950), followed by distillation. Yield, 69%. B.p. 413K/4 Pa. Analysis: Calc. C, 68.8% H, 10.9%. Found: C, 68.6%; H, 10.8%.

*Monoethyl 4,9-dimethyldodecanoate* (VII). After hydrolysis of (VI), the half ester was prepared as before (Vogel 1978b). Fractional distillation did not give an efficient separation of half ester and diacid. The mixture was dissolved in ether, and extracted with four portions of 1 M NaOH solution, so that the total amount of alkali used was just sufficient to neutralize the entire mixture. The last two fractions were combined, made acid, extracted and fractionally distilled. Yield 29% based on the diacid, b.p. 403/2 Pa equivalent weight 282 (theoretical 286). Analysis: Calc. C, 67.1%; H, 10.5%. Found: C, 67.2%; H, 10.6%.

*Ethyl 4,9-dimethyl-12-oxotriactanoate* (IX). The acid chloride of (VII) was prepared as for methyl-9-chloroformylnonanoate. Heneicosyl bromide was prepared from recrystallized behenic acid by the method of Cason & Walba (1972) m.p. 311K. Analysis: Calc. C, 67.2%; H, 11.5%. Found: C, 67.2%; H, 11.8%. (IX) was prepared by the method of Reinhard & Dixon (1965), as modified for methyl-10-oxodotriacontanoate; yield 69% before recrystallization. Recrystallization of a small portion from chloroform gave material with m.p. 315K. Analysis: Calc. C, 78.7%; H, 12.8%. Found: C, 78.6%; H, 12.7%.

*4,9-Dimethyltrtriacontanoic acid* (X). Prepared as described for dotriacontanoic acid. Yield 93%. After recrystallization from acetone, the product had m.p. 317K, and equivalent weight 524 (theoretical 522). Analysis: Calc. C, 80.5%; H, 13.4%. Found: C, 80.1%; H, 13.3%.

*4,9-Dimethyltrtriacontan- $\alpha$ -ol* (XI). Prepared as described for dotriacontan-1-ol, but using anhydrous

ether instead of tetrahydrofuran. Yield 63%, m.p. 309K. Analysis: Calc. C, 82.7%; H, 14.2%. Found: C, 82.7%; H, 14.5%. No carbonyl peaks were present in the i.r. spectrum.

*Polyoxyethylene 4,9-dimethyltrtriacontanol ether.* The method described for polyoxyethylene dotriacontanol ether was used. The product contained 40 ethylene oxide units, and is abbreviated to  $C_{35}E_{40}$ .

## RESULTS AND DISCUSSION

### Synthetic work

The Huang-Minlon reduction of the ketoesters gave difficulties until the temperature was raised from the normal 453 to 513K. Presumably, when the esters are hydrolysed, the potassium salts of the acids form micelles in diethylene glycol. The ketone function would be deep within the micellar structure, and access of reagent to it would be hindered at low temperatures. The separation of monoethyl 4,9-dimethyldodecanoate from its parent acid gave considerable difficulty, and the method of staged extraction finally adopted works because the dibasic acid is twice as likely to be converted to its sodium salt as the half ester. The last point is that the saturated unbranched dotriacontanoic acid and dotriacontan-1-ol are extremely difficult to handle because of their insolubility in all normal solvents. This is the reason for the very long ether extraction required in the preparation of dotriacontan-1-ol.

### Micellar structure

Light scattering results are given in Fig. 1(b) as plots of  $c/S_{90}$  against  $c$ , where  $S_{90}$  is the scatter at  $90^\circ$  to the incident beam from a solution of concentration,  $c$ . Dissymmetry values ( $Z_{45}$ ) were in the range 1.02–1.06. Micellar weights were calculated

from the Rayleigh equation. The cmc's of  $C_{32}E_{41}$  and  $C_{35}E_{40}$  were found to be 8 and  $9 \times 10^{-6}$  mol  $kg^{-1}$  respectively. Since the lowest concentrations used in the experimental work exceeded the cmc's by a large factor, no corrections were made, apart from the normal subtraction of solvent scattering from solution scattering.

Micellar hydration,  $w$ , was calculated on the assumption that the micelles were spherical, using the equation (Tanford 1961) for the intrinsic viscosity:

$$(\eta) = v(\bar{v} + wv_1^\circ)$$

where  $v$  is the shape factor,  $\bar{v}$  the partial specific volume of solute, and  $v_1^\circ$  the specific volume of solvent. The results of the viscosity measurements are given in Fig. 1(a).

The expected increase in micelle size occurs, with increasing hydrocarbon chain length; the  $C_{32}E_{41}$  and  $C_{35}E_{40}$  micelles are 5–6 times larger than those of cetomacrogol, which contains a hexadecyl chain.

Table 1. Micellar properties of  $C_{32}E_{41}$  and  $C_{35}E_{40}$ .

Surfactant	$M \times 10^{-3}$	$n$	$dn/dm$ ( $kg\ mol^{-1}$ )	$\rho$ ( $kg\ m^{-3}$ )	$(\eta)$ $kg\ mol^{-1}$	$w$
$C_{32}E_{41}$	482	212	0.303	1142	18.1	290
$C_{35}E_{40}$	590	260	0.304	1122	17.8	283

$m$  = micellar mass.  $n$  = aggregation number.  $dn/dm$  = specific refractive index increment.  $\rho$  = density.  $w$  = hydration (mol water/mol micellar surfactant).

The results for the long chain compounds are consistent with other aggregation numbers found in this series of surfactants.

The aggregation number is linearly related to the number of carbon atoms in the hydrocarbon chain. The numbers in brackets in Fig. 2 represent the ratio (number of ethylene oxide units)/(number of carbon atoms in hydrocarbon chain). They vary from 1.0 to 1.5, but no more closely matching results are available in the literature. The two methyl branches present in the  $C_{35}E_{40}$  surfactant do not seem to significantly effect the aggregation number compared to the straight chain structures (Fig. 2), but the effect of such short branches on this quantity may not be significant in so large a hydrocarbon structure.

### Solubilization

A reasonably linear relationship between  $(\log P)/V_m$  and mol solubilized/mol surfactant was found, where  $P$  is the octanol–water partition coefficient and  $V_m$  is the molar volume of solubilize. For

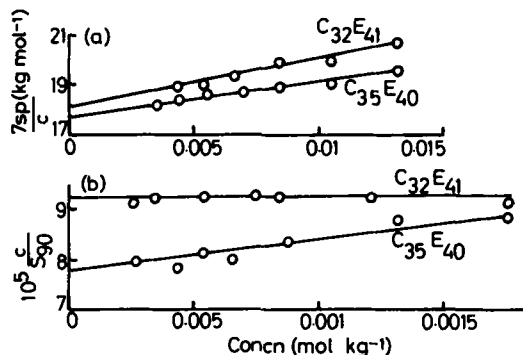


FIG. 1. (a) Reduced viscosity against concentration for  $C_{32}E_{41}$  and  $C_{35}E_{40}$ . (b) Concentration/scattering ratio against concentration for  $C_{32}E_{41}$  and  $C_{35}E_{40}$ .

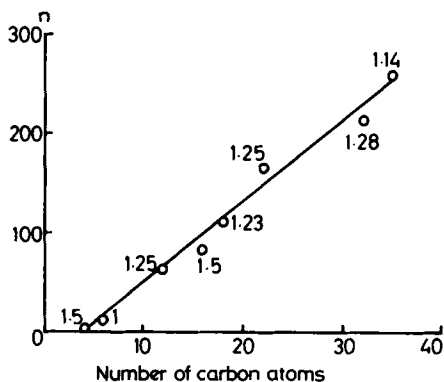


FIG. 2. Micellar aggregation number,  $n$ , against the number of carbon atoms in the hydrocarbon chain. The numbers are the ratio number of ethylene oxide units: number of carbon atoms in the hydrocarbon chain.  $C_{22}$ , interpolated from Arnarson & Elworthy, unpublished data.  $C_{18}$ , Elworthy & Patel, unpublished.  $C_{16}$ , Elworthy (1960).  $C_{12}$ , interpolated from Becher (1961).  $C_4$  and  $C_6$ , Elworthy & Florence (1965).

reasons given by Arnarson & Elworthy (1980) sulphadiazine was excluded. For  $C_{32}E_{41}$ : mol solubilized/mol surfactant =  $-0.0472 + 8.32 (\log P)/V_m$ ,  $r^2 = 0.981$ . For  $C_{35}E_{40}$  mol solubilized/mol surfactant =  $-0.0975 + 16.15 (\log P)/V_m$ ,  $r^2 = 0.980$ .

Comparison of the results in Table 2 with those reported for  $C_{16}E_{20}$  (Arnarson & Elworthy 1980)

Table 2. Solubilization results.

Solubilizate	Amounts solubilized in			
	$10^3 \text{ g g}^{-1}$	$C_{22}E_{11}$ $10^4 \text{ mol mol}^{-1}$	$10^3 \text{ g g}^{-1}$	$C_{34}E_{40}$ $10^5 \text{ mol mol}^{-1}$
Azobenzene	1.34	16.7	2.53	31.6
Cortisone acetate	0.29	1.7	0.35	2.0
Griseofulvin	0.29	1.9	0.45	2.9
Sulphadiazine	0.07	0.6	0.26	2.3
Phenylbutazone	0.94	6.9	1.39	10.2
Betamethasone	0.26	1.5	0.23	1.3
Tolbutamide	0.43	3.6	1.06	8.9
Menaphthone	0.68	9.0	1.32	17.4

shows that, on a mol solubilize/mol surfactant basis,  $C_{32}E_{47}$  has about half the solubilizing capacity of  $C_{16}E_{20}$ , and  $C_{35}E_{40}$  is slightly worse. On a g solubilize/g surfactant basis,  $C_{32}E_{41}$  has about one fifth and  $C_{35}E_{40}$  about one half the capacity of  $C_{16}E_{20}$ . The micellar masses are 5 times and 6 times greater (respectively) than those of  $C_{16}E_{20}$ . Taking these results in conjunction with those on  $BE_{21}$  (Arnarson & Elworthy 1980), shows that solubilizing ability decreases as the saturated alkyl chain length is increased above  $C_{16}$ . These results are contrary to those found for the ionic surfactants, where

increase in hydrocarbon chain length increases the amount solubilized. It is difficult to propose reasons for the decrease in solubilization with increased hydrocarbon chain length in the non-ionic series, unless the intrusion of part of the polyoxyethylene chain into the hydrocarbon core of the micelles may be responsible. It may be significant that hexadecane is the highest member of the alkyl series to be liquid below  $25^\circ\text{C}$ , and it is possible that intrusion of polyoxyethylene occurs to maintain the longer hydrocarbon chains in a liquid state. The two methyl branches present in  $C_{35}E_{40}$  should maintain part at least of the chain in a liquid condition, and the amount solubilized is higher in  $C_{35}E_{40}$  than in  $C_{32}E_{41}$ . It is clear that attempts to increase solubilization in non-ionic surfactants cannot be achieved by simply lengthening the hydrocarbon chain, and that other variations of the surfactant structure must be used.

#### Acknowledgements

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