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Branched non-ionic oligo-oxyethylene Y-amphiphiles Effect of molecular geometry on the micellar shape 1

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A homologous series of branched, non-ionic surfactants with the general formula $C_nG(E_mM)_2$, where C_n denotes an alkyl chain, G = glycerol and E_mM = oligo-oxyethylene mono-methyl ether, has been prepared from alkyl bromides ($n = 10-16$) and several monodisperse 1,3-di(methoxyoligo-oxyethylene) ethers of glycerol ($m = 3-5$). The branched hydrophilic chain is introduced to modify the interfacial area compared to corresponding linear oligo-oxyethylene surfactants (I-amphiphiles) without essentially changing the hydrophilic-lipophilic balance. The phase behaviour of these Y-surfactants in aqueous solution reveals that according to established packing models the branched hydrophilic group strongly stabilizes the cubic and hexagonal mesophases, while a lamellar phase is not observed.

1. Introduction

Linear oligo-oxyethylene surfactants C_nE_m have been intensively investigated during the past years [1-7]. Their micellar association and aggregation to give lyotropic liquid crystalline (LC) phases in aqueous solution has been carefully analysed depending on the chemical constitution of the surfactants. Due to the linear hydrophilic oligo-oxyethylene group and the hydrophobic alkyl chain, the hydrophilic-lipophilic balance (HLB) of these surfactants can be easily varied simply by changing the numbers m and n of the oxyethylene units, E_m , or the CH_2 units, C_n , of the alkyl chain. This variation systematically affects the micellar shape and polymorphism of lyotropic LC phases in aqueous solution.

A simple model to predict the preferred micellar geometry in the absence of interactions between the aggregates has been given by geometrical arguments with the critical packing parameter F [7-9],

$$F = v_1/A \cdot l_c, \quad (1)$$

where v_1 is the lipophilic chain volume, A the hydrocarbon/water interfacial area per molecule and l_c the average chain length of the liquid alkyl chain. Above the critical micelle concentration (CMC) for $0 < F \leq 1/3$ spherical micelles, $1/3 < F \leq 1/2$ cylindrical micelles and for $1/2 < F \leq 1$ disc-like micelles are predicted. This approach has been very helpful in interpreting the micellar polymorphism. Applying the relation to non-ionic oligo-oxyethylene surfactants by varying the hydrophilic or lipophilic chain length, i.e. changing the HLB, many features of the phase behaviour can be understood.

The basic idea of the model is to relate molecular architecture to the shape of the micelles. Changing the lipophilic chain volume v_1 or the interfacial area A of surfactants is directly reflected in the shape of the aggregates. However, a variation of these

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parameters is normally connected with an entire modification of the chemistry of the surfactants; at least the empirical formula is changed. This variation complicates elucidation of pure packing effects in terms of the shape of the micelles. In an ideal case the molecular architecture should be modifiable without affecting the HLB of the surfactants.

In this paper we present a concept and the synthesis of a homologous series of amphiphiles that comes close to the ideal case where the molecular architecture of the surfactants is modified without affecting the HLB. Besides the synthesis, the phase behaviour of the new amphiphiles will be described with respect to the origins of the polymorphic behaviours of the aqueous lyotropic LC systems.

2. Concept

According to the simple model mentioned above, the critical packing parameter F and therefore the micellar geometry can be altered by

- (i) the ratio v_1/l_c , i.e. of the lipophilic chain volume v_1 to the average chain length of the hydrophobic alkyl chain l_c or
- (ii) the hydrocarbon/water interfacial area A .

If we require a constant HLB, v_1 also has to remain constant. Consequently, the ratio v_1/l_c can only be altered via l_c . This can be achieved if the linear hydrophobic chain of the I-amphiphile becomes branched (see figure 1), for example if the linear alkyl chain becomes split into two chains of $l_c/2$ resulting in a V-amphiphile. Due to the splitting of the alkyl chain into $l_c/2$, the critical packing parameter of the V-amphiphile, F_V , becomes larger compared to F_I for the linear I-amphiphile. Therefore we can assume that if the I-amphiphile forms LC phases in aqueous solution, the LC phases of the corresponding V-amphiphile should be shifted towards a stabilization of the lamellar phase. The same should hold for the interfacial area, if we consider amphiphiles with a

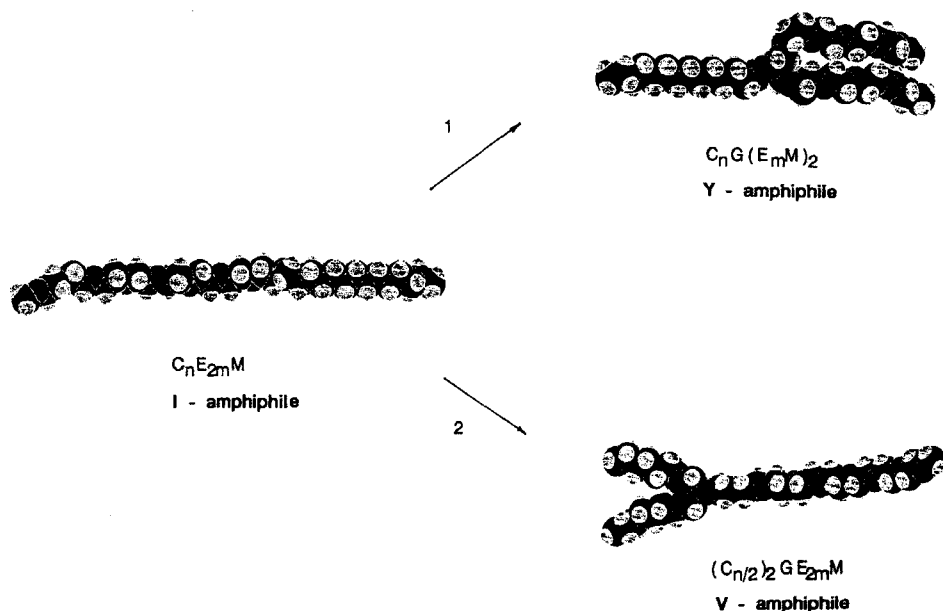


Figure 1. The concept of branching of the hydrophobic (1) or hydrophilic (2) group of a I-amphiphile to give the Y- or V-amphiphiles having the same overall chain length.

4. Phase behaviour

The phase behaviour of the amphiphiles **2a–e** has been determined over the whole concentration range in aqueous solution to identify the lyotropic LC phase behaviour. Except for amphiphile **2a**, which exhibits no mesophases, the phase diagrams for **2b–g** with water are displayed in figure 2. The phase behaviour of these systems is very similar and some characteristic data are additionally summarized in table 1. All amphiphiles are soluble over the whole concentration range, forming the isotropic solution L_1 . At high temperatures the solubility is limited by a broad miscibility gap with a lower critical consolute point at the critical temperature T_c , where two isotropic solutions coexist.

In the concentration range from approximately 35 wt% to 70–80 wt%, lyotropic mesophases exist in a temperature range which is limited at low temperatures by the crystallization of one component. Interestingly, for all systems shown in figure 2, the polymorphism is restricted only to cubic and hexagonal phases. The existence of two cubic phases is confirmed by contact preparations of the surfactants with water. In the concentration gradient between pure surfactant and pure water, the isothermal phase boundary lines can be clearly identified under the microscope by sharp lines. This is illustrated in figure 3 for **2e** with water. While between crossed polarizers only the hexagonal phase is seen due to the birefringence of the fan shaped texture, without the analyser, the phase boundary line between the cubic I_1' and I_1'' phases and the cubic/isotropic phase becomes evident. Preliminary small angle X-ray measurements indicate the existence of a primitive cubic phase at low and a body-centred cubic phase at higher concentrations. The hexagonal phase is identified additionally to the microscopic texture, by X-ray measurements with Bragg reflections having the ratio $1:\sqrt{3}:2:\sqrt{7}$ of the hexagonal lattice distances.

At temperatures below 0°C, the biphasic crystalline phase region exists where at concentrations below the eutectic point pure water crystallizes and coexists with the isotropic phase or mesophase. For the pure surfactants **2a, b, e, f**, no crystallization is observed. Therefore for these systems below 0°C, only water crystallizes and no eutectic point can be located. The pure surfactants **2c, d, g** crystallize and for **2d**, a distecticum D (refer to figure 2) with water exists at approximately 80 wt% surfactant. This distecticum corresponds to a composition of 10 water molecules per surfactant or monohydrated oxyethylene units.

Table 1. Selected physical data for $C_nG(E_mM)_2$ surfactants (T_{max} =maximal transition temperature of the LC phase; T_c =lower critical consolute temperature; F =melting temperature of pure surfactant. Temperature in °C \pm 0.4°C); *data from contact preparation.

Surfactant	LC phases T_{max}			T_c	F
	I_1'	I_1''	H_1		
2a $C_{10}G(E_4M)_2$	—	—	—	54.2	—
2b $C_{12}G(E_4M)_2$	8.1	7.1	2.1	53.4	—
2c $C_{14}G(E_4M)_2$	19.0	17.6	31.6	53.0	–19.9
2d $C_{16}G(E_4M)_2$	22.4	22.0	38.6	52.4	–1.5
2f $C_{12}G(E_3M)_2$	1.0	1.0	14.3	42.2	—*
2e $C_{14}G(E_3M)_2$	6.9	6.6	23.9	38.7	—
2g $C_{14}G(E_3M)_2$	21.4	18.5	18.0	61.8	–1.3

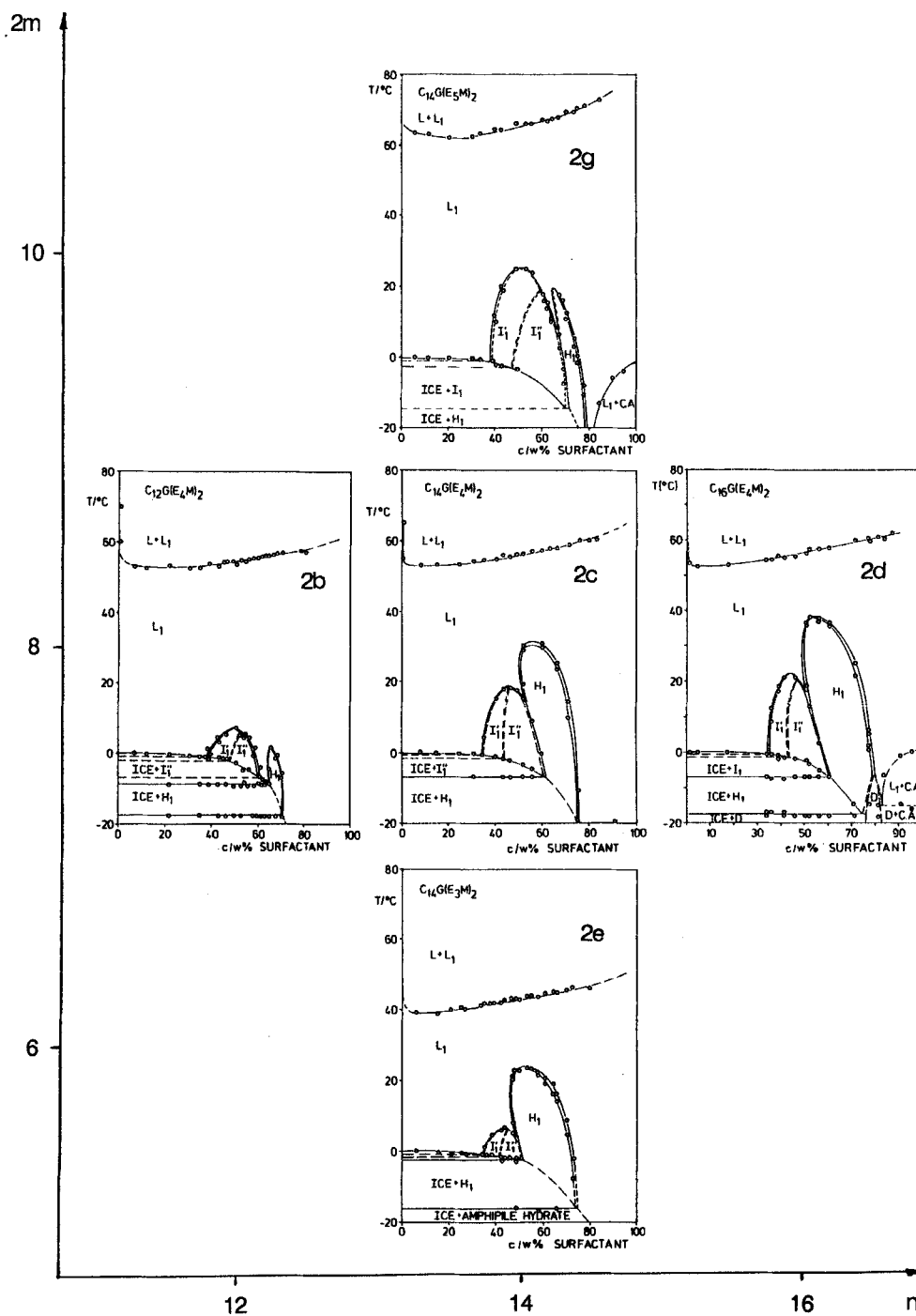


Figure 2. The binary phase diagrams of $C_nG(E_m)_2$ and water. The dependence of phase behaviour on alkyl chain length n and the number of oxyethylene units $2m$ per surfactant.

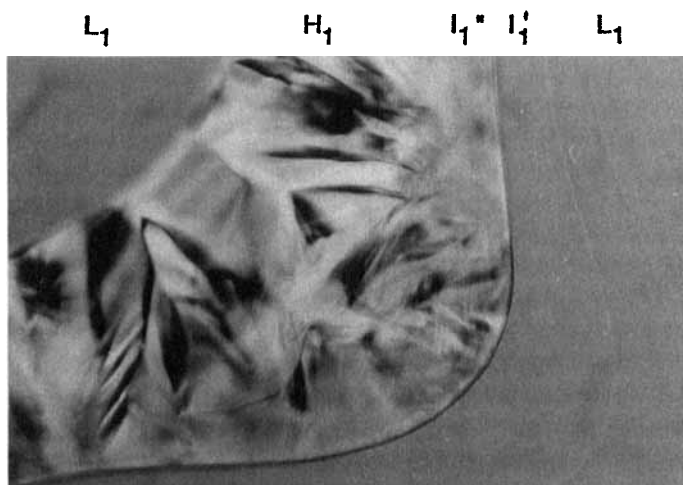


Figure 3. Water penetration into $C_{14}G(E_3M)_2$ showing the cubic I_1' and I_1'' phases and the hexagonal H_1 phase with increasing surfactant concentration from right to left at $T=1^\circ\text{C}$.

5. Discussion

Before examining details of the phase behaviour of these new Y-amphiphiles in aqueous solution as a function of the chain lengths m and n , the liquid crystalline polymorphism has to be compared to the corresponding linear I-amphiphiles with respect to the micellar packing model.

From detailed measurements by Tiddy *et al.* [4] on linear I-amphiphiles $C_nE_m-CH_3$ with $n=12$ and $m=4, 6, 8$ we have learned that for $m < 8$ lamellar phases exist and the cubic I_1 phase only appears for systems with $m > 6$. In other words, simply by varying the hydrophilic chain length by a small amount, the LC polymorphism is strongly affected and especially the cubic phases, composed of spherical micelles, disappear for $m < 8$.

For the Y-amphiphiles under investigation the branching of the hydrophilic chains into two sub-chains increases the interfacial area compared to the corresponding I-amphiphiles. According to the packing model and the concept mentioned above, for the Y-amphiphiles, the cubic phases should become more stable, whilst the appearance of a lamellar phase should be suppressed. Actually this assumption and concept is completely verified with the Y-amphiphiles. Within this series no lamellar phase is obtained, although the hydrophobic chain is lengthened by two CH_2 groups and $m < 8$ for **2e** and **2f**. Additionally it has to be noted that all systems exhibit two cubic phases even for $m=6$ and $m=8$, and when the alkyl chains are lengthened, the cubic phases still exist. Obviously the interfacial area is sufficiently extended by the glycerol unit and the two hydrophilic chains to realize the situation that the critical packing parameter F remains $< 1/3$.

If we analyse the LC phases of these systems in more detail, some systematic variations of the phase regimes are obtained by changing the hydrophobic and hydrophilic chain length n and m that essentially corresponds to conventional linear surfactants, but with the exception of unchanged polymorphism. In the following we will discuss the upper temperature limit T_m and the concentration range d at the reduced temperature $T_{red} = T_m - 8^\circ\text{C}$ for the cubic and hexagonal phases.

It is interesting to note that for the cubic phases, with increasing $(m)_n$ (**2e**, **2c**, **2g**), as well as with increasing $(n)_m$ (**2b**, **2c**, **2d**), the upper temperature limit rises. This is summarized in figures 4 (a) and (b). On the other hand the concentration range d of the cubic phases becomes smaller with increasing $(n)_m$ (see figure 4(a)), but slightly broadens with increasing $(m)_n$ (see figure 4(b)). These effects may be explained by using the following arguments. Lengthening of the alkyl chain with a constant hydrophilic group stabilizes the micelles via hydrophobic interactions, and this is reflected in the shift of the CMC towards lower concentration, an increase in T_m and a broadening of the overall LC phase regime. On the other hand, the lipophilic volume becomes larger and the phase regime of the cubic phase narrows in favour of the hexagonal phase, as expected from equation (1). Lengthening of the ethylene glycol chains with a constant hydrophobic group increases the solubility of the surfactant as well as the interfacial area, and the cubic phase becomes more stable at the expense of the hexagonal phase. The LC phase regime, for example, at a constant temperature of 0°C , remains constant.

For the phase regimes of the hexagonal phase essentially the same arguments hold. With respect to the width d of the phase, the reverse behaviour is observed as for the cubic phase with increasing $(n)_m$ and $(m)_n$ (see figure 5) which is in accordance with the

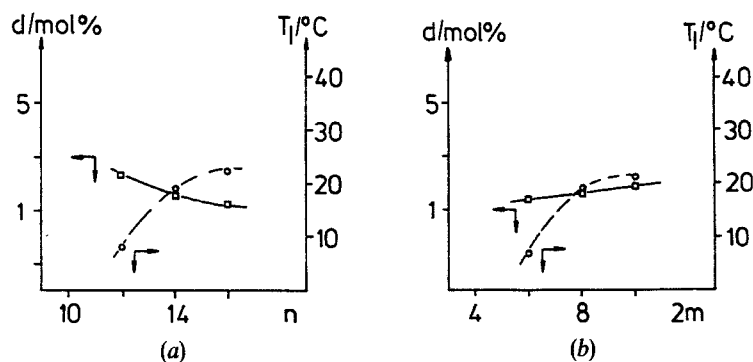


Figure 4. The maximal transition temperature T_I of the I_1 phase and the phase width d at reduced temperature ($T_{\text{red}} = T_I - 8^\circ\text{C}$) depending on (a) alkyl chain length n , and (b) number of oxyethylene units $2m$ per surfactant.

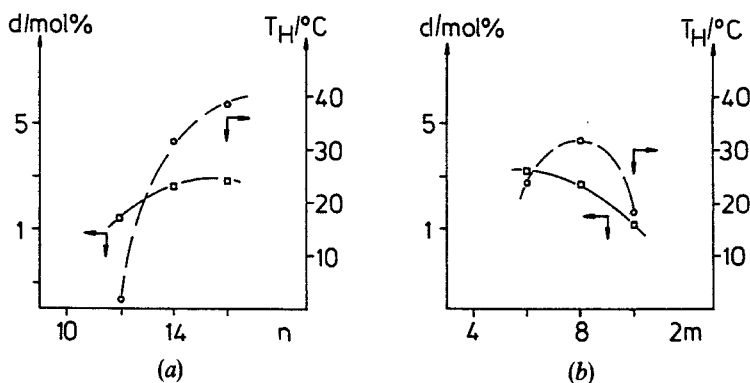


Figure 5. The maximal transition temperature T_H of the H_1 phase and the phase width d at reduced temperature ($T_{\text{red}} = T_H - 8^\circ\text{C}$) depending on (a) alkyl chain length n , and (b) number of oxyethylene units $2m$ per surfactant.

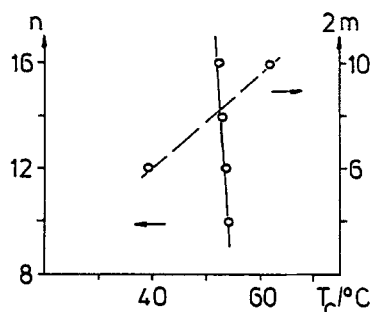


Figure 6. The dependence of the cloud point T_c on alkyl chain length n and number of oxyethylene units $2m$ per surfactant.

model. Increasing n causes a larger hydrophobic volume v_1 and larger F which is a factor that causes stabilization of the hexagonal phase. On the other hand by increasing m , the interfacial area A increases and the hexagonal phase width decreases, and this causes the cubic phase to increase. While T_m behaves as expected with rising n , as a function of m , we find a maximum for $m=8$. Obviously at higher m values the larger interfacial area will avoid the formation of rod-like micelles.

Finally, the lower critical consolute temperatures T_c of the surfactant solution **2** have to be mentioned (see figure 6). Interestingly, a lengthening of the hydrophobic alkyl chain from **2a** to **2d** by 6 CH_2 groups lowers T_c by only 2°C . This is in contrast to the corresponding 1-amphiphiles, where T_c is shifted by 14°C on effecting the same variation of the hydrophobic chain [4, 10]. On the other hand, arising m number causes increasing T_c , and this directly reflects in an increasing solubility to the surfactants.

6. Experimental

6.1. Synthesis

6.1.1. Preparation of 1,3-di(methoxyoligo-oxyethylene) ethers of glycerol of general formula $\text{HG}(\text{E}_m\text{M})_2$, with $m=3-5$ (1)

0.5 mol of sodium was dissolved in 1.5 mol of mono-disperse m -oxyethylene mono-methyl ether under nitrogen. The mixture was stirred at 100°C until all of the sodium had reacted. 0.5 mol of epichlorohydrin was slowly added to the mixture at 80°C . The mixture was stirred for 4 h at 100°C . After cooling to room temperature, the reaction mixture was filtered and short path distilled under reduced pressure at 160°C (5×10^{-3} mbar) for $m=3$ and at 230°C (2×10^{-3} mbar) for $m=4$. For $m=5$ the product was purified by flash chromatography using a diethyl ether/acetone mixture (1/1 v/v) as eluent. The product was obtained in 40–70 per cent yield. IR (film) 3600–3100 (O–H); 2930, 2850 (C–H); 1450, 1340 (C–H); 1320–180 (C–H, C–O); 110 cm^{-1} (C–O–C). $^1\text{H NMR}$ (80 MHz, CDCl_3/TMS): δ 3.4 (s, OCH_3); 3.4–3.8 (m, OCH_2); 3.9 ppm (q, OCHR_2).

6.1.2. Preparation of **2a–g** with the general formula $(\text{C}_n\text{G}(\text{E}_m\text{M}))_2$, $n=10-16$ and $m=3-5$

0.1 mol of sodium hydride in 50 ml of dry diethyl ether was added dropwise to 0.1 mol of **1** under nitrogen. The reaction mixture was stirred for 24 h at room temperature. Thereafter, 0.1 mol of n -alkyl bromide was added to the mixture and stirred at room temperature for 24 h. Sodium bromide was filtered off and the product **2** purified by flash chromatography using a diethyl ether/acetone mixture (5/1 v/v) as

Table 2. Analytical data and yields of $C_nG(E_mM)_2$.

Surfactant	Yield/%	Analysis found (calculated)	
		C/%	H/%
2a $C_{10}G(E_4M)_2$	50	60.63(60.75)	10.53(10.53)
2b $C_{12}G(E_4M)_2$	48	61.43(61.85)	10.63(10.70)
2c $C_{14}G(E_4M)_2$	47	62.66(62.84)	10.74(10.85)
2d $C_{16}G(E_4M)_2$	53	63.49(63.76)	11.13(11.00)
2e $C_{14}G(E_3M)_2$	51	63.85(64.10)	11.02(11.11)
2g $C_{14}G(E_5M)_2$	40	61.34(61.87)	10.57(10.67)

eluent. All products were colourless low viscosity oils. The analytical data for **2a–g** are shown in table 2. IR (film): 2910, 2840, 1450, 1340 (C–H); 1300–1000 cm^{-1} (C–O–C). ^1H NMR(80 MHz; CDCl_3/TMS): δ 3.7 (m, OCHR₂); 3.4–3.6 (m, OCH₂); 3.3 (s, OCH₃); 1.5 (t, CH₂); 1.3 (m, CH₂) 0.9 ppm (t, CH₃).

6.2. Measurements

The phase behaviour was studied by polarizing microscopy (Leitz Ortholux Pol BK II) using a hot stage (Mettler Hot Stage FP 80/82). Samples of different concentrations were prepared using an analytical balance and mixed in Teflon capsules on a vibrating mill. Penetration technique experiments were performed to obtain preliminary information about the phase behaviour. X-ray diffraction patterns were obtained using a Kiesig camera with a thermostatted cell.

7. Conclusion

The branching of the hydrophilic oligo-oxyethylene chains of linear I-amphiphiles into the two sub-chains of the corresponding Y-amphiphiles clearly affects the micellar aggregation. Because the HLB essentially remains constant, a comparison between the phase behaviour of I- and Y-amphiphiles allows us to elucidate pure packing effects on the micellar shape and the formation of LC phases. Forthcoming results on corresponding V-amphiphiles will clarify whether a branching of the hydrophobic chain will cause the same systematic change in the phase behaviour, but biased towards the stabilization of a lamellar structure.

References

- [1] DEGIORGIO, V., 1985, *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*, edited by V. Degiorgio and M. Corti (North Holland).
- [2] MITCHELL, D. J., TIDY, G. J. T., WARING, L., BOSTOCK, T., and McDONALD, M. P., 1983, *J. chem. Soc. Faraday Trans. 1*, **79**, 975.
- [3] HERRINGTON, T. M., and SAHI, S. S., 1988, *J. Colloid Interface Sci.*, **121**, 107.
- [4] CONROY, J. P., HALL, C., LENG, C. A., RENDALL, K., TIDY, G. J. T., WALSH, J., and LINDBLOM, G., 1990, *Prog. Colloid Polym. Sci.*, **82**, 253.
- [5] JAHNS, E., and FINKELMANN, H., 1987, *Colloid Polym. Sci.*, **265**, 304.
- [6] FONTELL, K., 1990, *Colloid Polym. Sci.*, **268**, 264.
- [7] ISRAELACHVILI, J. N., MITCHELL, D. J., and NINHAM, B. W., 1976, *J. chem. Soc. Faraday Trans. 2*, **72**, 1525.
- [8] ISRAELACHVILI, J. N., MARCELJA, S., and HORN, R., 1980, *Q. Rev. Biophys.*, **13**, 121.
- [9] TANFORD, C., 1980, *The Hydrophobic Effect* (Wiley-Interscience), p. 51.
- [10] JEATES, S. G., CRAVEN, J. R., MOBBS, R. H., and DOOTH, C., 1986, *J. chem. Soc. Faraday Trans. 1*, **82**, 1865.