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Markus A. Schafheutle[a]; Heino Finkelmann[a]
[a] Institut für Makromolekulare Chemie, Universität Freiburg, Freiburg, F.R. Germany

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Shapes of micelles and molecular geometry

Synthesis and studies on the phase behaviour, surface tension and rheology of rigid rod-like surfactants in aqueous solutions

by MARKUS A. SCHAFHEUTLE and HEINO FINKELMANN
Institut für Makromolekulare Chemie, Universität Freiburg,
Hermann Staudinger Haus, Stefan-Meier-Strasse 31, D-7800 Freiburg,
F.R. Germany

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Amphiphiles with rigid rod-like hydrophobic moieties have been synthesized in order to investigate the effect of the packing restraints of such moieties on the micellar association behaviour of amphiphiles in aqueous solution. Investigations of the phase behaviour of amphiphile/water mixtures reveal that liquid-crystalline phases exist in defined temperature and concentration regimes and that they are all lamellar, regardless of the hydrophilic-hydrophobic balance of the amphiphile. For these lyotropic liquid-crystalline phases a polymorphism is observed which is similar to the polymorphism of thermotropic smectic liquid crystals. Surface tension measurements indicate critical micelle concentrations of the amphiphiles in dilute solutions which are similar to those of conventional surfactants. From rheological measurements it can be assumed that the variation of temperature and/or concentration of the solution does not influence the micellar shape. This is in contrast to the behaviour of non-ionic surfactants having a flexible hydrophobic group.

1. Introduction

Conventional surfactants having a flexible hydrophobic moiety, e.g. an alkyl or perfluorinated alkyl chain, associate in aqueous solution to form micelles of different shapes. Spherical, cylindrical, ellipsoidal or discoidal micelles are known [1–4]. The micellar geometry which exists at a particular temperature and concentration of a binary aqueous surfactant solution depends on the hydrophilic–lipophilic balance of the amphiphilic molecule and for polysurfactants on the degree of polymerization [5]. Complex phase behaviour is shown by binary mixtures of non-ionic oligomeric ethylene glycol surfactants in water. Different micellar geometries appear when temperature and concentration are varied, which often implies the existence of polymorphic lyotropic liquid-crystalline phases. Complex rheological behaviour indicates that the size of the micelles and their geometry change within the isotropic phase regime of these binary mixtures [6].

Appropriate modification of the chemical constitution of the surfactant molecule can result in a simplification of the association and aggregation behaviour of the aqueous amphiphilic solution and eliminate the effect of concentration and temperature on the micellar geometry. Replacing the flexible hydrophobic part of an amphiphile with a rigid hydrophobic moiety causes packing restraints which should only permit the formation of micelles having a specific geometry [7–12]. A rigid rod-like hydrophobic moiety should cause the formation of disc-like micelles, while a disc-like hydrophobic moiety surrounded by the hydrophilic groups should cause the for-

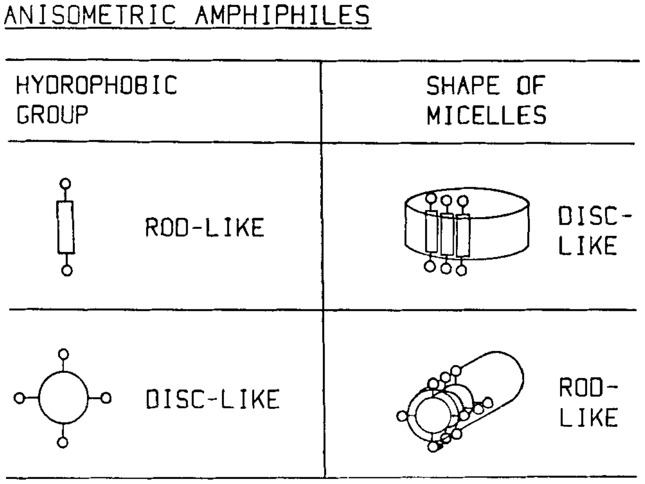


Figure 1. Geometrical packing of anisometric surfactant molecules into anisometric micelles.

mation of rod-like micelles (see figure 1). Disc-like surfactants have been synthesized by Boden *et al.* and shown to form rod-like micelles in the liquid-crystalline phases [7–10]. Measurements on surfactants having a semi-flexible, rod-like hydrophobic moiety indicate the tendency towards the formation of disc-like micelles with decreasing flexibility of the hydrophobic part of the surfactants [5]. For these rigid amphiphiles, packing restraints strongly influence the micellar geometry in aqueous solution. Their behaviour diverges from that displayed by conventional surfactants.

In this paper we describe the synthesis, phase behaviour, surface tension and rheological properties of aqueous solutions of new surfactants having a rigid rod-like hydrophobic moiety terminally substituted at both ends of the rod with monodisperse oligo(ethylene glycol) units. Variation of the length of the hydrophilic group should show whether the micellar geometry in aqueous solution is influenced by variation of the hydrophilic-lipophilic balance of the surfactant and whether packing constraints affect the shape of the micelle.

2. Synthesis

In order to determine whether the hydrophilic-lipophilic balance and/or packing restraints influence the micellar shape, the hydrophilicity of the surfactant was varied while the hydrophobic group was kept unchanged. This can be achieved by using non-ionic, monodisperse oligo(ethylene glycol) groups of different length.

The route for the synthesis of the new amphiphiles is presented schematically in figure 2. Chlorination of tri- (**1**) or tetra(ethylene glycol) (**2**) and subsequent reaction with di- or tetra(ethylene glycol)monomethylether yields the monodisperse hydrophilic chains (**3**–**5**). The products **3**–**5** were purified by repeated short path destillation. With this procedure monodisperse oligo(ethylene glycols) were obtained, which was determined for **4** by gas chromatography. Reaction with methyl-4-hydroxybenzoate yields compounds **6**–**x**, where **x** denotes the number of glycol units in the hydrophilic chain. Esterification of **6**–**x** with hydroquinone yields the desired amphiphiles **7**–**x**. The hydrophilicity of **7**–**x** is determined by the length of the glycol chains with $x = 5$ to 7. All amphiphiles were purified by flash chromatography and recrystallization, they were analysed by N.M.R. and I.R. spectroscopies as well as H.P.L.C.

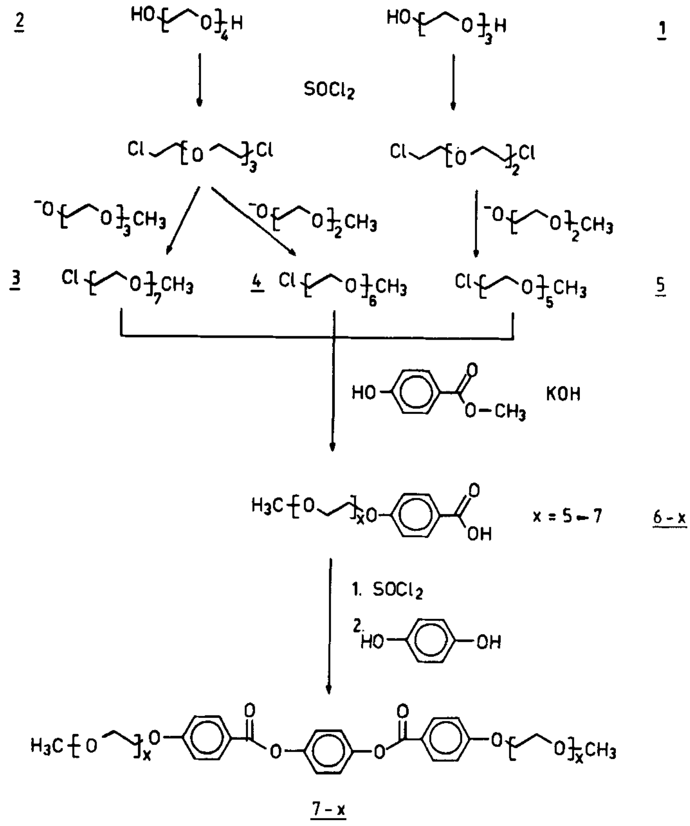


Figure 2. Synthesis scheme of the rod-like amphiphiles **7–x**.

3. Phase behaviour

The phase behaviour of the binary amphiphile/water solutions was studied by polarizing microscopy combined with differential thermal analysis. X-ray measurements were also performed in order to determine the structure of the liquid-crystalline phases.

Phase diagrams of the binary mixtures of amphiphiles **7–x** with water are shown in figures 3 to 5. All three amphiphiles exhibit qualitatively the same phase behaviour with water at low temperatures whether in the homogeneous or heterogeneous crystalline state. A melting line with one dystectic (*D*) and two eutectics is observed. The dystectic suggests the formation of a compound having hydrated glycol chains. The number of water molecules per amphiphile can easily be obtained from the maximum of the dystectic–isotropic coexistence line. **7–5**, **7–6** and **7–7** exist as octahydrate, undecahydrate and tetradecahydrate respectively. These results are summarized in table 1 together with the average number of water molecules per glycol

Table 1. The number of water molecules per surfactant molecule (*T*) and per ethyleneglycol unit (EO) at the maximum of the dystectic (*D*) and of the S_C phase.

Substance	H_2O/T (D)	H_2O/EO (D)	H_2O/T (S_C)	H_2O/EO (SC)
7–5	8	0, 8	47	4, 7
7–6	11	0, 9	24	2
7–7	14	1	19, 6	1, 4

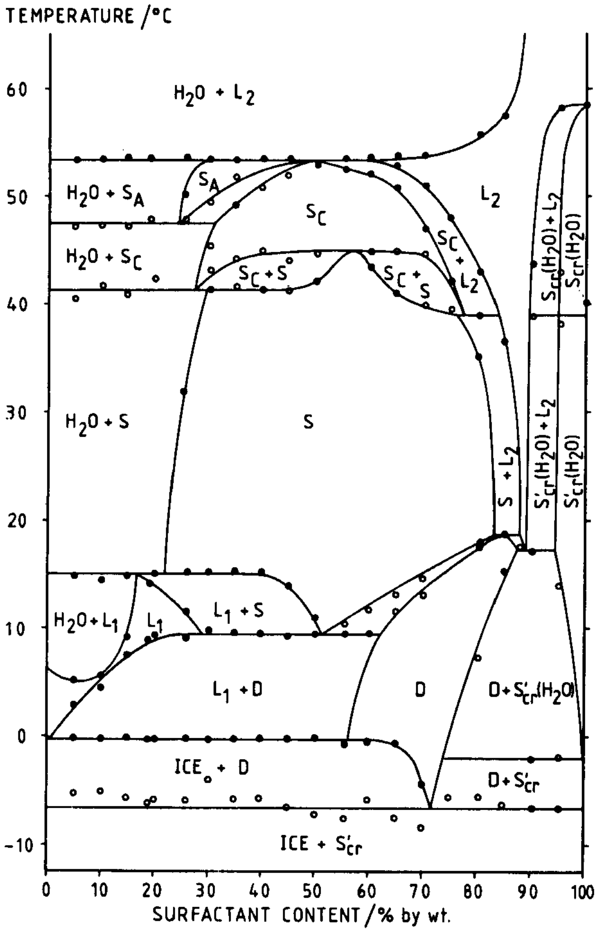


Figure 3. Phase diagram of the **7–5** water mixture. Concentration in wt %. $L_{1,2}$ = isotropic solution, S = smectic phase. *D* = Dystectic, S_{cr} = crystalline surfactant. (open circles = detected by DTA, closed circles = detected by optical microscopy with and without polarizers).

unit. It seems unlikely that hydration of the glycol units would vary with the length of the oligo(ethyleneglycol) chain. This behaviour can be explained by assuming that (i) the water molecules have to be symmetrically distributed along the two oligo-(ethyleneglycol) chains of the amphiphile and (ii), beyond a particular distance from the hydrophobic rod-like unit, the degree of hydration of the glycol units has to be independent of the length of the glycol chain. These considerations lead to the scheme proposed in figure 6, in which the experimental results are considered. The first two glycol units neighbouring the hydrophobic unit are not hydrated. This type of distribution could also obtain for amphiphiles **7–4** and **7–8** (with two times 4 or 8 ethyleneglycol units, respectively). With respect to compound formation with water, these new amphiphiles behave similarly to semiflexible surfactants previously investigated [5].

At temperatures above the crystalline phase regime, the liquid phase regimes change dramatically with the hydrophilicity of the amphiphiles. The most hydrophilic amphiphile in this series, **7–7** which has 7 glycol units at each end of the rod-like moiety (see figure 5), exhibits a broad isotropic phase regime. At higher temperatures

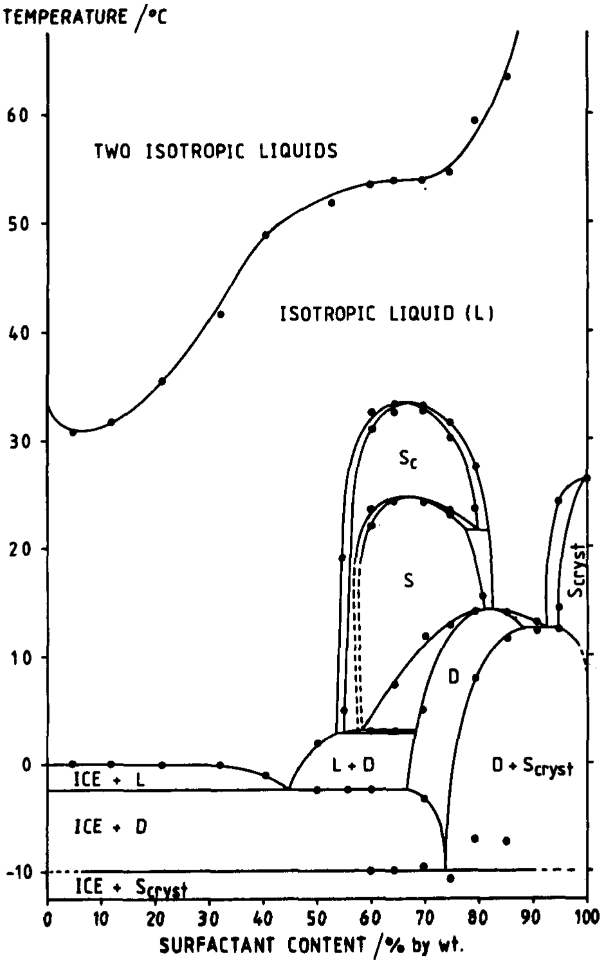


Figure 4. Phase diagram of the **7–6** water mixture.

a miscibility gap with a lower critical consolute point at 46·6°C exists. The lower critical consolute point shifts to lower temperatures with increasing hydrophobicity (for **7–6**, T_{cr} = 31°C and for **7–5**, T_{cr} = 5·2°C). This is similar to the well-established solution behaviour of conventional non-ionic surfactants. Interestingly the phase boundary line of the miscibility gap is highly deformed. This deformation becomes more pronounced with increasing hydrophobicity of the amphiphile. Strong interactions between the water and surfactant molecules are probably responsible for this behaviour [13]. Similar deformation of the cloud curve have been observed for polymeric solutions or mixtures [14–16]. This behaviour of these solutions is attributed to the polydispersity of the molecular weight of the polymers. In the **7–x** systems, however, only a binary mixture of a monodisperse surfactant, and water exists and polydispersity cannot be invoked.

With respect to the question whether the rod-like hydrophobic moiety of the amphiphile influences micellar association behaviour, the structure of the anisotropic liquid-crystalline phase regimes in the three phase diagrams proves to be quite interesting. The three amphiphiles exhibit only lamellar liquid-crystalline phases with

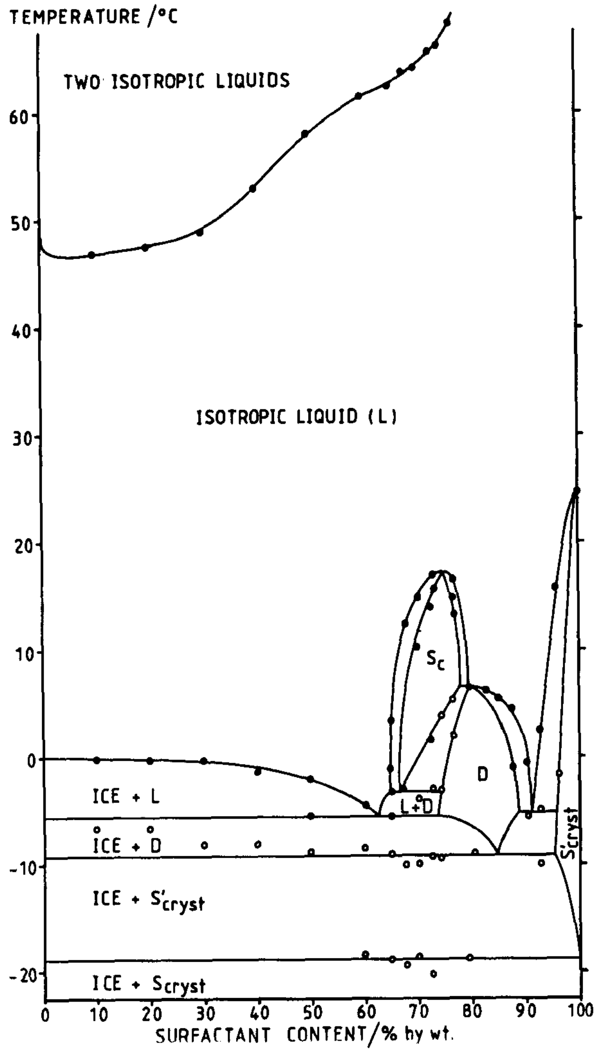
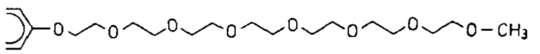


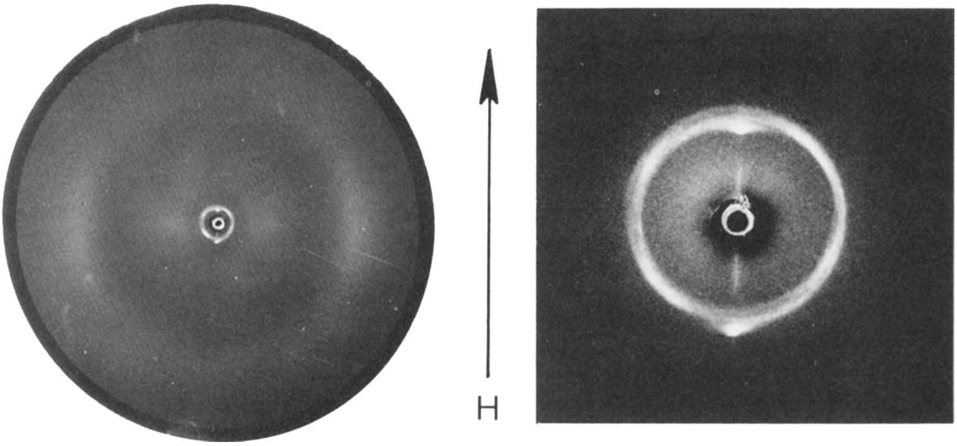
Figure 5. Phase diagram of the 7–7 water mixture.



								Σ
7-5	0	0	1	1,5	1,5			4
7-6	0	0	1	1,5	1,5	1,5		5,5
7-7	0	0	1	1,5	1,5	1,5	1,5	7

Figure 6. Assumed distribution of the water molecules about the ethyleneglycol units of different 7–x at their dystectics.

water. No hexagonal or cubic phases appear which might indicate a non-disc-like micellar aggregation. This observation supports the idea that rigid rod-like constitution of an amphiphile results in the formation of only lamellar micelles. This is true in the liquid-crystalline phase regime. The micellar shape in the isotropic solution region is discussed in §5.



(*a*) (*b*)

Figure 7. X-ray diffraction pattern of 70 per cent by weight of **7–6** at 26°C. (*a*) wide angle reflections at 4·3 Å and small angle reflections at 36·5 Å. (*b*) The direction of the magnetic field is shown by an arrow.

Although the lamellar structure of the liquid-crystalline phases does not change when the hydrophilic–lipophilic balance of the amphiphile is varied, the concentration and temperature range of the lamellar phases do broaden with decreasing hydrophilicity of the amphiphiles. This behaviour is also observed with conventional surfactants. An unexpected polymorphism of the lamellar phase has been observed. Detailed polarizing microscope and X-ray investigations (see figure 7) reveal that the lamellar phase of **7–7** (see figure 5) is isomorphic with the structure of thermotropic smectic C phases. In the hydrophobic part of the lamellar structure, the rigid rod-like moieties are tilted with respect to the layer normal. Although the tilted hydrophobic layers are separated by the long oligo(ethyleneglycol) chains and water, a surprisingly strong layer-to-layer correlation with the tilt direction exists. This causes the smectic C structure.

Additional unusual phase behaviour is observed for **7–6** (figure 4) in which the hydrophilic chain is just one glycol unit less than **7–7**. While **7–7** exhibits only the smectic C phase, a first order phase transition is observed for **7–6** which indicates the existence of an additional smectic phase. The exact structure has not yet been determined, but preliminary results indicate a higher ordered tilted smectic structure.

Reduction of the amphiphile hydrophilicity in going from **7–6** to **7–5** (see figure 3) causes an increase in the number of polymorphic variants of the smectic phase. At high temperatures a smectic A phase also appears which is isomorphic to the conventional L_α phase. This amphiphile (**7–5**) shows, with increasing temperature, the phase sequence crystalline–high ordered smectic–smectic C–smectic A–(biphasic) isotropic in the concentration regime from 22 to 49 per cent by weight in water. Similar results were found for di(ethyleneglycol) hexasubstituted triphenylene [10], for which a polymorphism of disordered hexagonal–hexagonal–nematic was observed in aqueous solution.

Phase diagrams of these new amphiphiles reveal that the introduction of the rigid rod-like hydrophobic moiety not only determines the micellar aggregation behaviour but also causes a polymorphism of the liquid-crystalline state which had only previously been observed for thermotropic liquid crystals. These new amphiphiles bridge the gap between conventional lyotropic liquid crystals and thermotropic liquid crystals.

Interestingly anisotropic phases have also been found for aqueous solutions of rigid rod-like derivatives substituted with ionic groups. These phases are called chromonic phases, after sodium chromoglucate, one of the first substances investigated to display such phases [17, 18]. The first chromonic system was the sodium salt of bromophenanthrene sulphonic acid [24]. For these chromonic phases, polarizing microscope investigations revealed textures which were often similar to textures of thermotropic smectic and nematic liquid crystals. We expect that these substances with chromonic phases might be the ionic counterparts to the non-ionic amphiphiles described in this paper.

4. Surface tension measurements

The formation of lyotropic liquid-crystalline phases of the new compounds suggests that these amphiphiles associate in aqueous solution in a manner similar to that of conventional surfactants. However, because of the rigid hydrophobic moiety and the two hydrophilic groups at the ends of the rods, the association as well as the packing of the molecules at the air-water interface have to be consistent with the molecular geometry of the amphiphiles. Surface tension measurements provide a useful method to obtain further information about the association and surface adsorption behaviour of dilute solutions.

In figures 8, 9 and 10 the surface tension is shown as a function of the concentration of **7–x** (x = 5 to 7), respectively, in aqueous solutions for different temperatures. With increasing amphiphile concentration in water, the surface tension is reduced to about 50–60 mN/m and remains constant above a critical concentration. This reduction in the surface tension is less than that observed with conventional non-ionic surfactants. The point of intersection of the two straight $\sigma(\lg c)$ lines indicates the critical micelle concentration (c.m.c.) [20–22]. For **7–7** (see figure 10) a slight increase in the c.m.c. is found with increasing temperature. This is usually not observed with oligo(ethylene glycol) surfactants [4, 20, 21]. This result, however, is within experimental error. The c.m.c. yields the concentration when it is assumed that the entire solution-air surface is occupied by amphiphilic molecules. With the Gibbs equation,

$$\Gamma_2 = -(\delta\sigma/\delta c_2)(c_2/RT),$$

the surface concentration (Γ_2) of the surfactants as a monolayer can be calculated from the slope of the surface tension versus concentration curve for c_2 smaller than the c.m.c. This also yields the area occupied per molecule at the surface. The data and calculated results for the three amphiphiles are summarized in table 2.

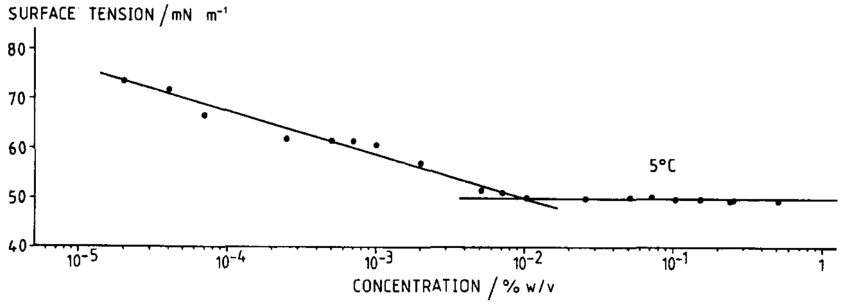


Figure 8. Surface tension behaviour of **7–5** water mixtures at different concentrations. The point of intersection is the c.m.c.

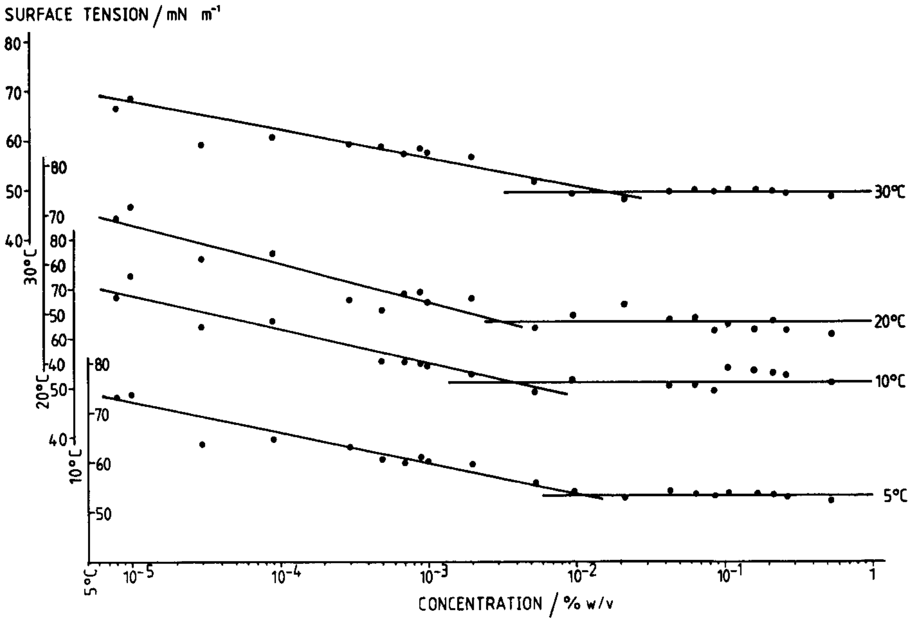


Figure 9. Surface tension behaviour of **7–6** water mixtures at different concentrations.

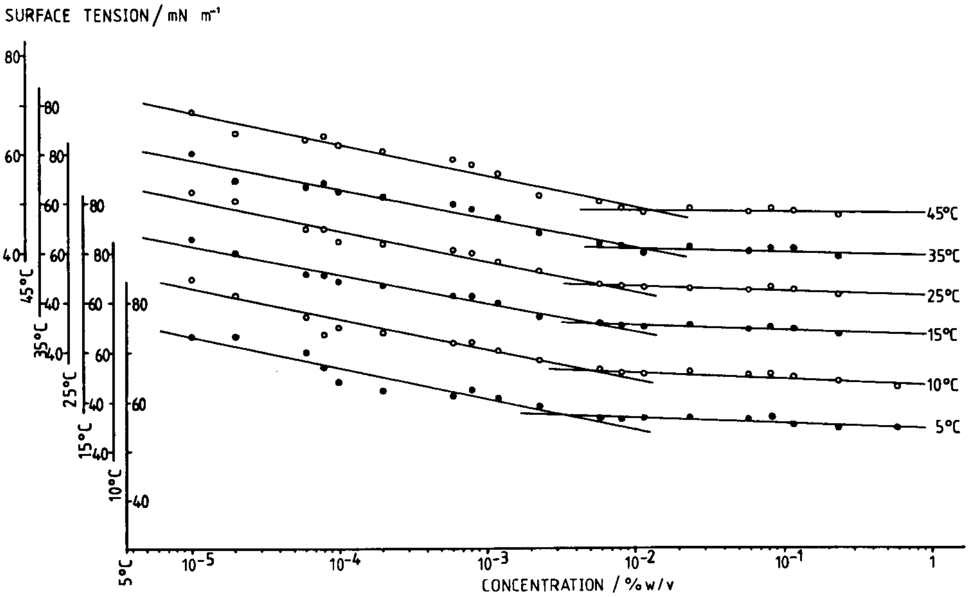
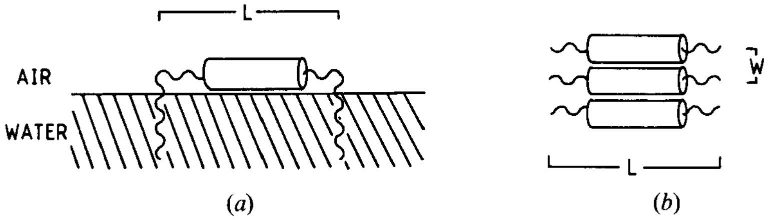


Figure 10. Surface tension behaviour of **7–7** water mixtures at different concentrations.

In proposing a model for the alignment of the amphiphiles at the surface we assume that the rigid hydrophobic moieties lie parallel to the surface and that the hydrophilic chains dip into the water (see figure 11 (*a*)). This assumption seems to be consistent with the experimental data. From X-ray measurements of a 70 per cent by weight solution of **7–6** in water in the S_C-phase (see figure 7 (*a*)), the wide angle reflection yields a lateral distance of the parallel-aligned molecules of 4.3 Å, which has



(a) (b)

Figure 11. Arrangement of the rod-like surfactants at the water surface. (*a*) looking parallel to the surface, and (*b*) looking perpendicular on the surface (L = length and W = width of the surfactant molecules).

Table 2. c.m.c. and the area per surfactant molecule on the water surface as a function of the temperature.

	T/°C	c.m.c./10^{-5} mol l^{-1}	Area per molecule at the c.m.c./Å^2
7–5	5	12 ± 7	104 ± 16
7–6	5	11 ± 2·7	161 ± 52
	10	4 ± 4	119 ± 33
	20	1 ± 1	119 ± 44
	30	44 ± 40	185 ± 5
7–7	5	3 ± 3	143 ± 57
	10	4 ± 4	147 ± 24
	15	5 ± 4	161 ± 21
	25	6 ± 5·7	152 ± 28
	35	10 ± 10	166 ± 25
	45	10 ± 10	158 ± 26

been assigned to the width of the molecules (see figure 11 (*b*)). Dividing the surface area per molecule at the c.m.c. (see table 2) by the width, the calculated length of the surfactants at the water surface is of the order of 35 ± 5 Å at 20°C (see figure 12). This length is consistent with a parallel alignment of the long molecular axes of the amphiphiles on the surface as we have proposed and excludes an arrangement of the long molecular axes perpendicular to the surface. Interestingly, the calculated length of the amphiphiles on the surface at the c.m.c. clearly correlates with the interlamellar distance of the S_C-phase of **7–6** from X-ray measurements. This indicates that the two-dimensional arrangement of the amphiphiles on the water surface at the c.m.c.

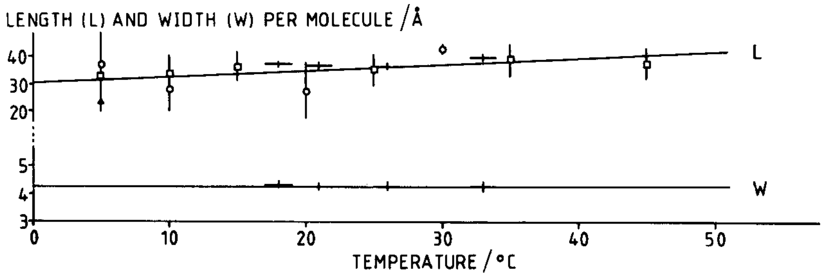


Figure 12. Length and width per surfactant molecule on the surface from surface tension measurements and at 70 per cent **7–6** in the S_C-phase from X-ray diffraction. △, **7–5** surface tension; ○, **7–6** surface tension; □, **7–7** surface tension; +, **7–6** X-ray.

is very similar to the packing in the smectic phase, when viewing the cross section of the smectic layers.

5. Viscosity of the isotropic amphiphile solutions

The viscosities of the isotropic solutions are very sensitive to the dimension, shape and intermolecular interactions of the solute particles. Attempts to interpret the viscosity data of semi-dilute and concentrated solutions quantitatively and theoretically have failed because of the complex variation of the micellar shape, size, association and intermicellar interaction with temperature and concentration. Nevertheless this method indicates qualitatively that changes occur in micellar solutions with varying temperature and concentration, as exemplified by non-ionic surfactants [6, 19]. For amphiphiles of the **7–x** type rheological measurements should provide information on whether the rigid hydrophobic moiety prevents complex viscosity/temperature behaviour of the isotropic surfactant solutions due to a constant micellar shape.

Figures 13 and 14 show the viscosity as function of temperature for different concentrations of **7–6** and **7–7**, respectively, in water; measurements for pure water

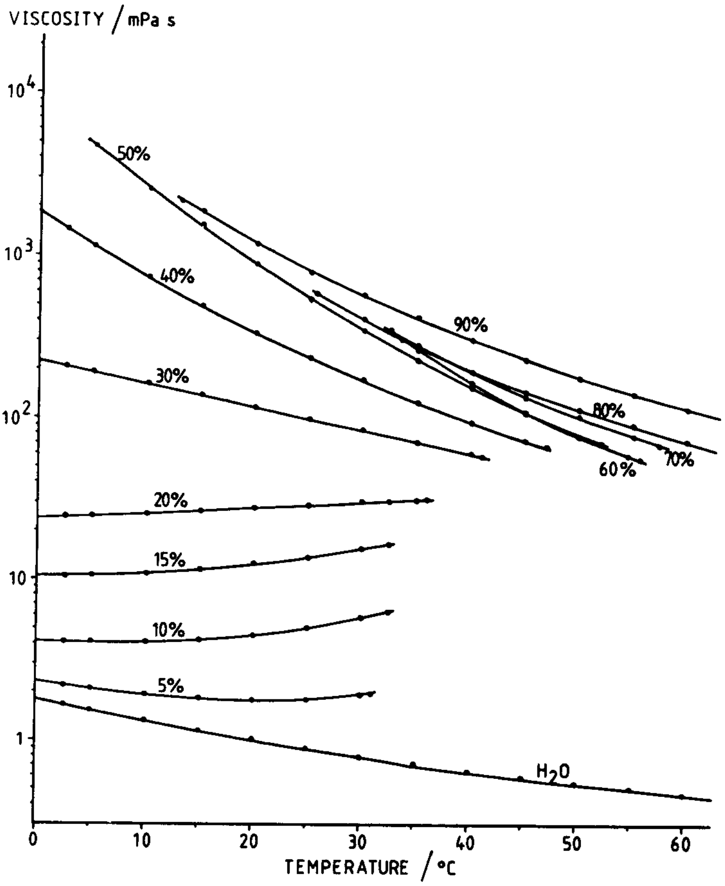


Figure 13. Temperature dependence of the viscosity of **7–6** water mixtures. The curve indexed H_2O is the viscosity curve of pure water.

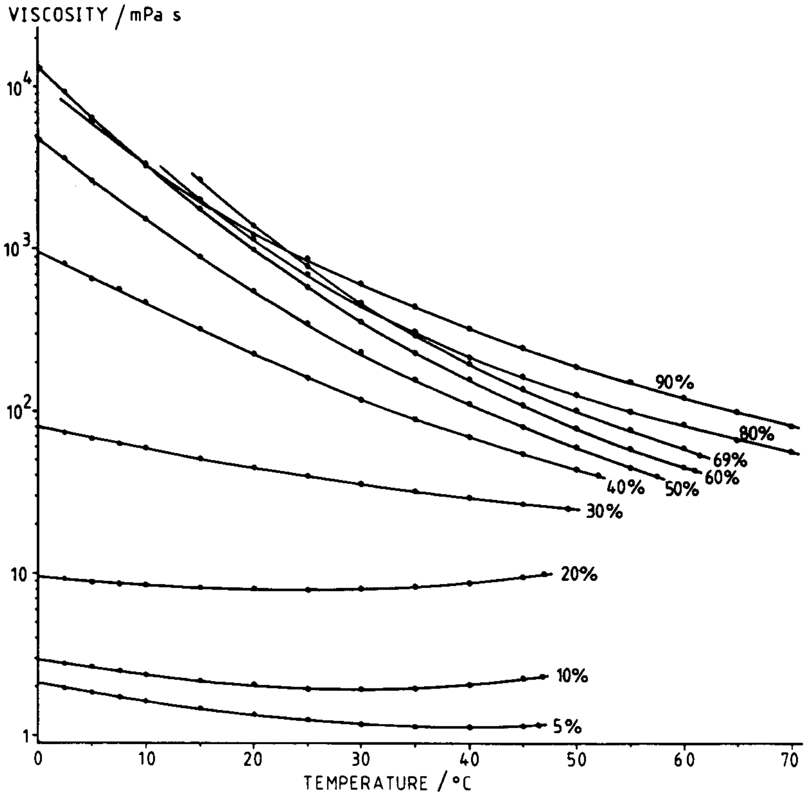


Figure 14. Temperature dependence of the viscosity of 7–7 water mixtures.

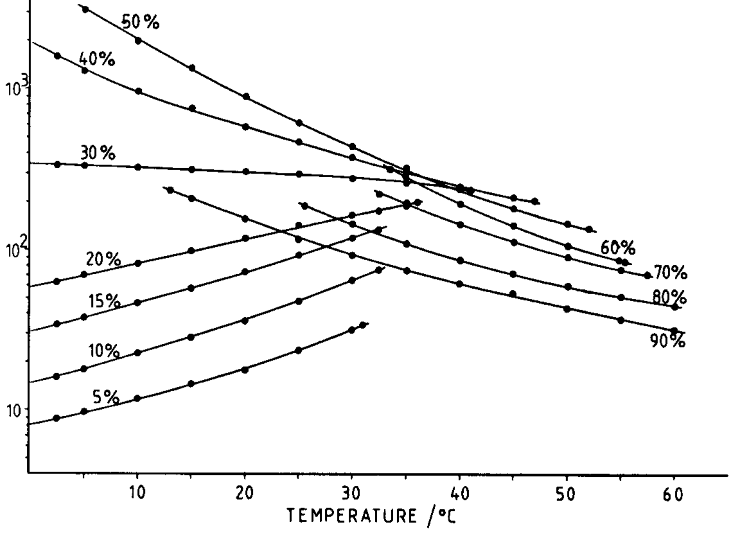


Figure 15. Temperature dependence of the reduced viscosity of aqueous solutions of **7–6** at different concentrations.

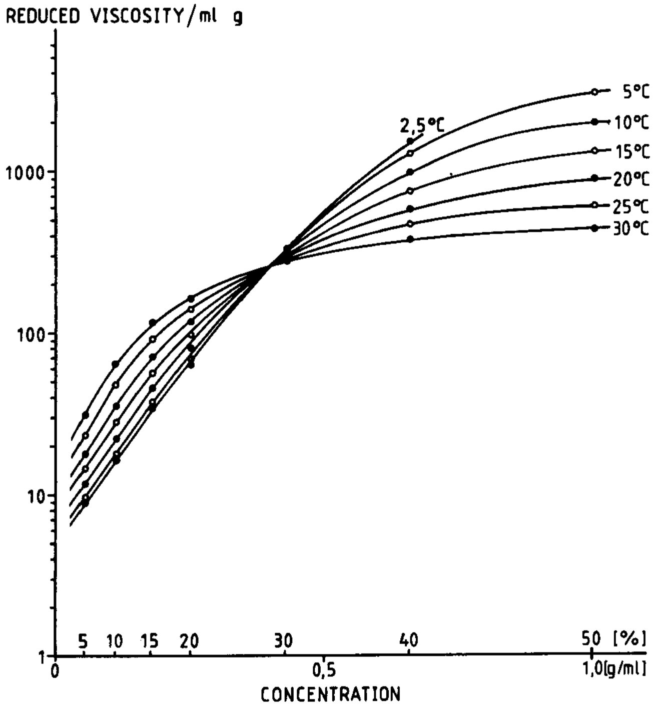


Figure 16. Concentration dependence of the reduced viscosity of aqueous solutions of **7–6** at various temperatures.

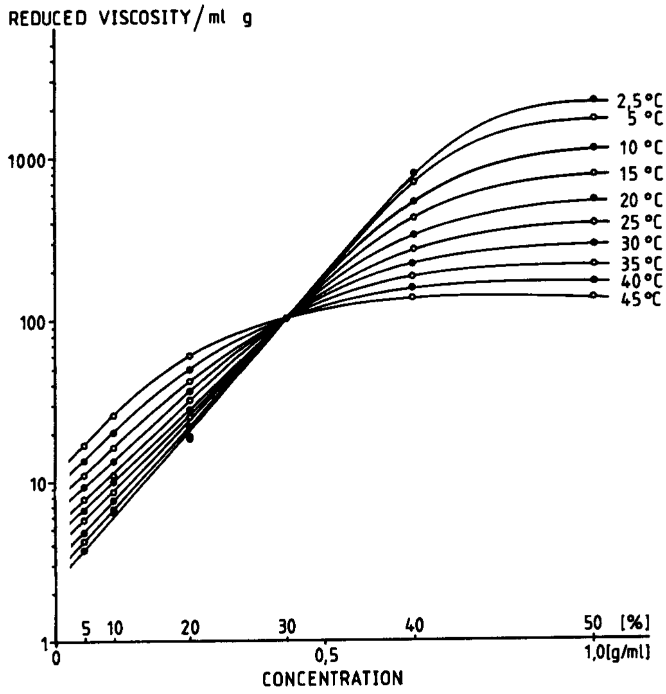


Figure 17. Concentration dependence of the reduced viscosity of aqueous solutions of **7–7** at various temperatures.

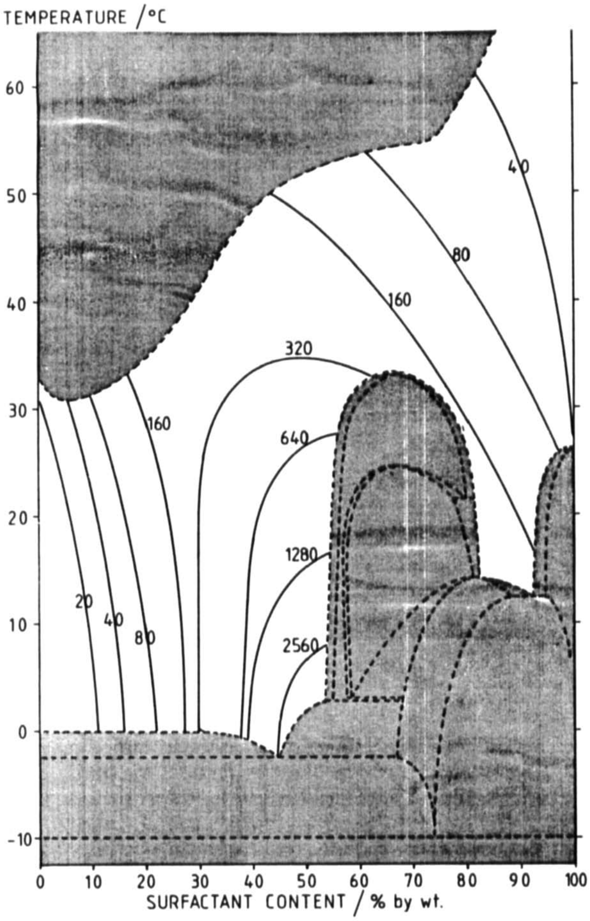


Figure 18. Lines of equal reduced viscosity drawn into the phase diagram of **7–6**. The numbers on these contour lines have the unit (ml/g).

are included in figure 13. For all amphiphile solutions, only slightly curved $\lg \eta$ (T) plots are observed over the entire concentration regime. This clearly differs from the results obtained for conventional non-ionic surfactants having flexible hydrophobic alkyl chains [6, 16]. This is a qualitative indication that the micellar association of the rigid rod-like amphiphiles remains basically unchanged upon varying the temperature and verifies the consideration that a rigid anisometric molecular geometry of the amphiphiles simplifies the association and aggregation behaviour in aqueous solutions. With increasing concentration, up to 20 per cent by weight for **7–6** and 30 per cent by weight for **7–7**, the slope of the $\lg \eta$ (T) curves at higher temperatures is positive and becomes negative for more concentrated solutions. For shear rates between 0 to 60 s^{-1}, at all temperatures and concentrations, newtonian flow behaviour is observed.

To eliminate the contribution of the solvent viscosity, the reduced viscosity of **7–6** solutions is shown, as an example, in figure 15. The curves display essentially the same relation as we have discussed. An interesting aspect becomes evident when the reduced viscosity for different temperatures is plotted against the concentration of **7–6** (see figure 16) and **7–7** (see figure 17) in water. Points of intersection at 28·4 per cent

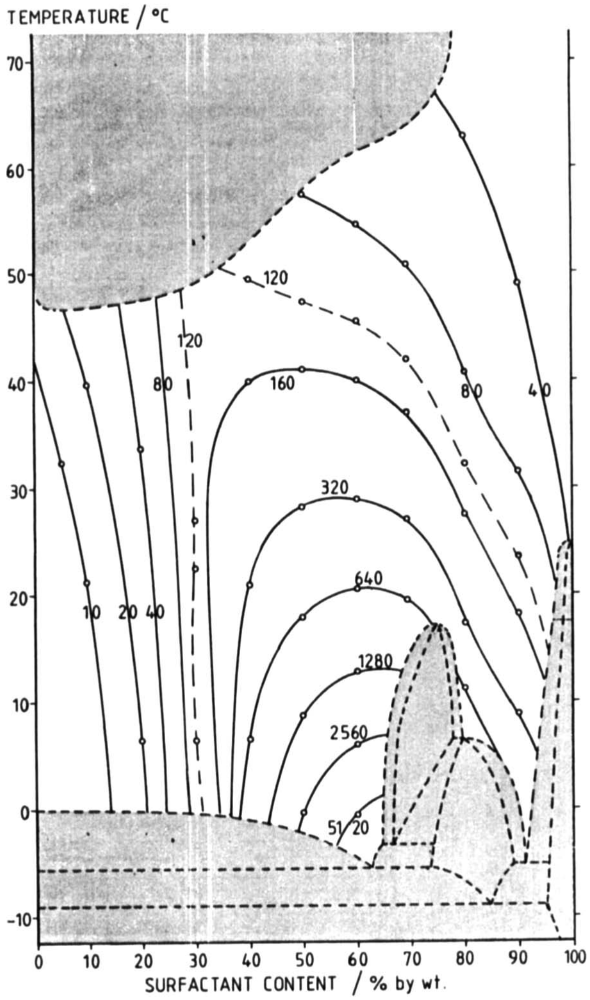


Figure 19. Lines of equal reduced viscosity drawn into the phase diagram of 7–7. The numbers at these contour lines have the unit (ml/g).

7–6 and 30 per cent by weight **7–7** reveal that at these concentrations the reduced viscosity of the solutions does not change with temperature. Extrapolation of these $\lg \eta_{\mathrm{red}}(c)$ curves to zero amphiphile concentration should yield the intrinsic viscosity, which gives information about the aggregation number of the micelles in dilute solutions. This will be discussed in a forthcoming paper.

The relationship between the rheological results of the isotropic solutions and the liquid-crystalline phase regime is shown in figure 18 for **7–6** and figure 19 for **7–7**, where contour lines of equal reduced viscosity are plotted in the phase diagrams. The highest reduced viscosity is found at lowest temperatures in front of the low concentration isotropic-to-liquid-crystalline phase boundary. The liquid-crystalline phase boundaries are, however, not related to a single defined reduced viscosity. This would be expected if the reduced viscosity depends only on the micellar dimensions. These results motivate us to look for further information about micellar interactions and/or micellar size.

6. Conclusions

With the synthesis of amphiphiles having a rigid rod-like hydrophobic moiety, an interesting new class of amphiphiles has been described in which only lamellar association of the micellar solutions occurs, due to the molecular geometry of the amphiphile. These model systems may lead to a better understanding of the physico-chemical properties of micellar solutions by eliminating the variations of the micellar shape with temperature and/or concentration. Furthermore, these systems bridge the gap between thermotropic and lyotropic liquid crystals.

7. Experimental part

7.1. *Synthesis*

7.1.1. *Chlorination of the ethyleneglycols*

1 mol **1** or **2** was dissolved in 300 ml dry tetrahydrofuran (THF) and 2·2 mol dry pyridine, 2·2 mol thionyl chloride was added dropwise under stirring and nitrogen atmosphere. The mixture was heated to reflux. After all the $SOCl_2$ was added, the mixture was refluxed overnight. The cooled mixture was added to ice and extracted with methylethylketone (MEK). The collected organic phases were neutralized with sodium bicarbonate ($NaHCO_3$), dried over sodium sulphate, and gravity filtered. The solvent was removed under reduced pressure. The brown oily residue was distilled *in vacuo* using a 20 cm Vigreux column to yield a colourless clear liquid.

$2Cl_2$ 63°C (10 μbar),

$1Cl_2$ 60°C (40–50 bar),

Yield: 1 mol ($\approx$ 100 per cent) dichloride.

7.1.2. *Etherification of the ethyleneglycols*

1·04 mol of di- or triethylene glycol was dissolved in 100 ml of dry toluene and 1 mol of sodium was added under N_2-atmosphere. The mixture was refluxed until all of the sodium had reacted. The cooled mixture was slowly added, dropwise, to the dichloride at 120°C. A small amount of KI was added as a catalyst. After all of the sodium salt solution was added, the mixture was stirred for 36 h at 160°C. After cooling, the mixture was filtered and distilled on a short path distillation apparatus.

5Cl 135°C (100 μbar),

4Cl 125°C (6 μbar),

3Cl 136°C (5 μbar),

Yield: 0·7 mol (70 percent) monochloride.

7.1.3. *Etherification of the monochlorides with methyl-4-hydroxybenzoate*

1 mol of **3**, **4** or **5** and 1·03 mol of methyl-4-hydroxybenzoate were dissolved in 350 ml of diglyme. KI was added as a catalyst and 1 mol of KOH was then added to the mixture. The mixture was stirred overnight at 120°C. A second 1·1 mol of KOH was added and the mixture was stirred again at 120°C overnight. The mixture

was cooled, acidified with concentrated HCl to pH 1, filtered and concentrated to dryness. The residue was recrystallized several times in a diethylether/methanol mixture (10 : 1).

Yield: 650 mmol (65 per cent) **6–x** (x = 5 to 7)

I.R. (film): 3170 cm^{-1} (broad O–H), 1705 cm^{-1} (C=O), 1600 cm^{-1} (Φ).

^{1}H-NMR (CDCl$_3$/TMS): 9·9 ppm (1 H, s, -COOH),

8·03 ~ 6·95 ppm (4 H, 2d, -OOC-**Φ**-O-), 4·18 ppm (2H, t, **Φ**-O-CH$_2$-),

3·98 ~ 3·55 ppm ((4*x*–2)H, *m*, -O-CH$_2$-CH$_2$-O-), 3·35 ppm (3H, *s*, -O-CH$_3$).

7.1.4. *Chlorination of* **6–x**

1 mol of **6–x** was dissolved in 300 ml of SOCl$_2$ and some drops of dimethylformamide (DMF) were added. The solution was stirred overnight at room temperature. Excess SOCl$_2$ was removed in vacuo and the residue was used in the next reaction without further purification.

I.R. (film): 1760 cm^{-1} (C=O), 640 cm^{-1} (C–Cl).

7.1.5. *Esterification of* **6–x** *with hydroquinone*

2·5 mol of the chloride of **6–x** and 2·5 mol triethylamine were dissolved in dry THF. The mixture was cooled to – 10°C and a solution of 1 mol hydroquinone in 500 ml dry THF was added dropwise to the cooled mixture. Following addition of the hydroquinone solution, the mixture was stirred overnight at room temperature. The solvent was removed and the residue was purified by flash chromatography [23] (Kieselgel 60, 40–63 μm, Merck, diethyl ether: acetone 1 : 2). Recrystallization in ethanol at – 16°C yielded a waxy white solid.

Yield: 0·3–0·4 mol (30–40 per cent) **7–x** (x = 5 to 7),

mp: **7–5** 58·6°C,

7–6 26·3°C,

7–7 24·6°C.

^{1}H-N.M.R. (CDCl$_3$/TMS): 8·2 – 7·0 ppm (8 H, 2*d*, -OOC-**Φ**-O-),

7·2 ppm (4H, *s*, -O-**Φ**-O-), 4·3–3·6 ppm (4 × H, *m*, -O-CH$_2$-CH$_2$-O-),

3·3 ppm (6H, *s*, -O-CH$_3$).

I.R. (Film): 2900 cm^{-1} (C–H), 1730 cm^{-1} (C=O), 1600 cm^{-1} (Φ).

7.2. *Measurements*

The *phase behaviour* was studied by polarizing microscopy (Leitz Ortholux Pol BK II) using a hot stage and a hot stage coupled with a differential thermal analysis instrument (Mettler Hot Stage FP 80/82 and FP 80/84). Samples of different concentrations were prepared using an analytical balance (accuracy ± 10^{-3} g) and mixing in Teflon® capsules on a vibration mill.

X-ray diffraction patterns were obtained using a Kiesig camera with a thermostated interior and a 1 T magnetic field.

Surface tension measurements were made with a Krüss Tensiometer K10 (Hamburg) by the plate method thermostated by a Haake F3C thermostat. The surface tension as function of time was recorded by a plotter connected to the tensiometer and the equilibrium value was taken. Different concentrations were obtained by taking a series of dilutions.

Rheological measurements were performed with a Haake Rotovisco RV 100 and CV 100 with a cone–cone (Couette) unit (ME 30, ME 15). The temperature was regulated by a Haake F3C thermostat. All samples were weighed on an analytical balance, prepared with twice distilled water and mixed for at least 1 h on a Staudiner wheel. The solutions were filtered three times with a Millipore membrane filter (22–45 μm). The measured viscosity was taken only after the viscosity remained constant for at least 15 min. The measurements were performed with shear rate increasing from 0 to 60 s^{-1}. Within this shear rate range and at all temperatures all investigated solutions exhibited a newtonian flow behaviour in the isotropic phase regime.

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