Molecular design of thermotropic liquid crystalline polyhydroxy amphiphiles exhibiting columnar and cubic mesophases of the normal type

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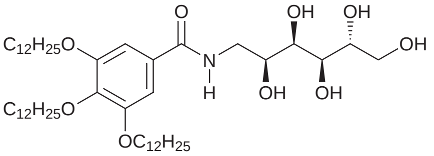
The phase sequence Col_{h1}–Cub_{V1}–S_A–Col_{h2}–Cub_{I2}, which represents a major part of the theoretical lyotropic phase diagram of detergent solvent systems, was realized for the first time in a binary mixture of two thermotropic amphiphilic liquid crystals without any solvent.

The molecular self-organization of amphiphilic molecules in aqueous systems with formation of micelles and lyotropic mesophases is a well known phenomenon.[1] Different types of lyomesophases can be detected depending on the amphiphile structure,[2] the concentration and the temperature. Beside the layer-like lamellar phase (L_α, smectic A: S_A) other mesophases consisting of curved aggregates occur. Cylindrical aggregates organize into hexagonal columnar phases (H, Col_h) and globular or non-globular spheroids can build cubic mesophases (discontinuous cubic phases, Cub_I). Another type of cubic mesophase consisting of two mutually interwoven networks of branched cylinders (bicontinuous cubic mesophases, Cub_V) occurs at the transitions between smectic and columnar phases. For each of the non-lamellar mesophases two different types are possible. Normal phases (type 1) have the stronger cohesive forces located in the continuum surrounding the aggregates. In the reversed (or inverse) phases (type 2) they are located inside the aggregates.

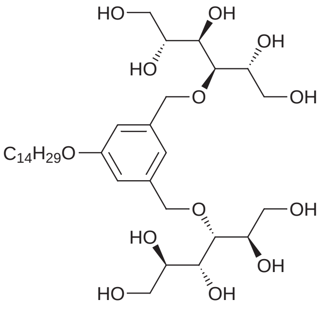
Many amphiphilic molecules can form not only lyotropic phases in aqueous systems, but also thermotropic mesophases as pure materials.[3] In particular, amphiphilic polyhydroxy compounds[3] and carbohydrate derivatives can have a wide variety of different thermotropic mesophases.[4] The formation of large dynamic hydrogen bonding networks between the hydroxy groups and the micro-segregation of the hydrophilic and the lipophilic parts of the individual molecules into separate regions are important driving forces for their self-organization. The kind of mesophase formed depends on the temperature and the chemical structure of the amphiphiles. Double chain compounds usually form columnar mesophases (Col_{h2}) or bicontinuous cubic mesophases (Cub_{V2}). Amphiphiles with three long aliphatic chains, such as **1** (see Fig. 1), can form micellar cubic mesophases built up from spheroidic closed micelles (Cub_{I2}).[5,6] Because the stronger cohesive forces (hydrogen bonding) are located inside the aggregates surrounded by the flexible alkyl chains the thermomesophases of these molecules are similar to the reversed lyotropic mesophases of detergent solvent systems. Interestingly, most non-lamellar thermomesophases of pure amphiphiles belong to the reversed type.† In particular, the concept of taper-shaped molecules[7] is based on this type of molecular organization.

Therefore we set out to design novel amphiphilic polyhydroxy compounds which can organize to thermotropic mesophases which represent analogues of normal lyotropic systems. Their aggregates should consist of micro-segregated lipophilic cores surrounded by polar shell regions providing cohesive forces *via* dynamic hydrogen bonding. To achieve this, we have synthesized the amphiphilic molecule **2**‡ consisting of two large hydrophilic polyhydroxy units and a single lipophilic chain connected *via* an aromatic linking unit (**2**, Fig. 1).



1

Cr 94 °C Cub_{I2} 227 °C Iso



2

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, "78\ ^\circ\mathrm{C}"] & \mathrm{Col_{h1}} \arrow[rrr, bend left, "212\ ^\circ\mathrm{C}"] & \mathrm{Cub_{V1}} \arrow[l, "202\ ^\circ\mathrm{C}"'] & \mathrm{Col_{h1}} \arrow[l, "211\text{–}212\ ^\circ\mathrm{C}"'] & \mathrm{Iso} \arrow[l, "212\ ^\circ\mathrm{C}"']
\end{tikzcd}$$

Fig. 1 Thermotropic phase transitions of **1** and **2**. The transition temperatures of **2** from the Col_{h1} phase to the Cub_{V1} phase depend on the cooling rate. Abbreviations: Cr = crystalline solid; Col_{h1} = normal hexagonal columnar phase,; Cub_{V1} = normal bicontinuous cubic phase; Cub_{I2} = reversed discontinuous cubic mesophase; Iso = isotropic liquid state.

Compound **2** was studied by polarizing microscopy and X-ray diffraction. On heating, the material melts at 78 °C into a birefringend mesophase with a non-specific texture. This mesophase turns into the isotropic liquid state at 212 °C. On cooling from the isotropic melt the formation of a spherulitic texture can be observed at the same temperature. Immediately after its occurrence optically isotropic domains appear and rapidly coalesce to a highly viscous optically isotropic phase. On further cooling a mosaic-like texture occurs at 202 °C. On re-heating this texture remains without changes up to the isotropization temperature at 212 °C. The X-ray diffraction pattern of this birefringent phase is characterized by three sharp reflexes in the small angle region and a diffuse scattering in the wide angle region. The ratio of the positions of the small angle reflections is $1:3^{1/2}:2$, proving a hexagonal two-dimensional lattice with a hexagonal lattice parameter of $a_{\mathrm{hex}} = 4.66$ nm at $T = 80$ °C and $a_{\mathrm{hex}} = 4.49$ nm at $T = 180$ °C (hexagonal columnar mesophase). The diameter of the columns (*ca.* 4.5 nm) is in good agreement with a radial arrangement of the molecules ($L = 3.0$ nm in their most extended conformation) in cylinders with the fluid alkyl chains assembled in their centers. The number of molecules which should be arranged on average in the cross-section of a 0.45 nm thick slice of the columns is about 8.§

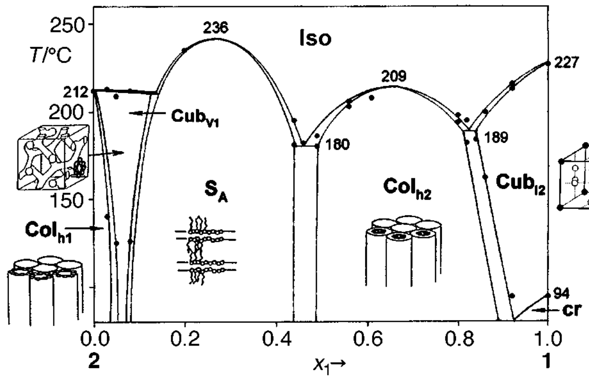


Fig. 2 Phase diagram of the binary system **1**/**2**. The transition temperatures observed in the heating scans (polarizing microscopy) are shown. In the cooling scans a Cub$_{V1}$/Col$_{h1}$ dimorphism is found for the pure compound **2** (Fig. 1) and the Cub$_{V1}$–Col$_{h1}$ transition is shifted to lower temperatures and lower concentrations of **1**. A *Ia3d* cubic lattice is shown as an example for the bicontinuous Cub$_{V1}$ phase (the cylinders are filled with the alkyl chains). The Cub$_{I2}$ phase is described in ref. 5(*c*),(*d*). Abbreviations: S$_A$ = smectic A phase, Col$_{h2}$ = reversed hexagonal columnar phase. Other abbreviations, see Fig 1.

The optically isotropic mesophase should be a cubic mesophase as indicated by the optical isotropy, the high viscosity and the cornered phase boundaries which occurring during its growth. Proof of this using X-ray scattering was not possible because of the high temperatures required. Remarkably the cubic mesophase is only formed on cooling the sample from the isotropic liquid state after passing the small range of a columnar mesophase. It seems that the cubic phase is the thermodynamical stable phase in the temperature range between 202 and 212 °C, however the formation of this three-dimensionally ordered mesophase is hindered for kinetic reasons, and its formation from the columnar phase is more strongly hindered in the heating cycles.¶

The normal type of the mesophases of **2** was proven by means of miscibility experiments.[5b,d] The phase diagram of **2** with the triple chain amphiphile **1**[5b] is shown in Fig. 2. In the contact regions of the hexagonal columnar mesophase of **2** with the reversed micellar cubic phase (Cub$_{I2}$) of **1**, the columnar phase of **2** is lost and is completely replaced by the cubic mesophase. In a concentration range between X_1 = 0.1 and 0.4 a broad region of a smectic A layer structure is found. The stability of this mesophase is significantly higher than those of the mesophases of the pure compounds. Upon a further increase of the content of **1** a second columnar mesophase is induced. Because the interface curvature changes continuously from left to right, the induced columnar phase which is intermediate between the S$_A$ and the reversed micellar Cub$_{I2}$ phase should be a reversed columnar phase (Coh$_{h2}$). Thus, in the contact region between **2** and **1**, five different mesophases can be observed:‖ Col$_{h1}$–Cub$_{V1}$–S$_A$–Col$_{h2}$–Cub$_{I2}$. This sequence represents a major part of the theoretical lyotropic phase diagram of detergent solvent systems, which was realized for the first time in a binary system of two different amphiphiles in the absence of any solvent and is a proof of the normal type of the mesophases of **2**. Thus, with exception of normal cubic mesophases consisting of spheroidic closed micelles (Cub$_{I1}$) all the main mesophase types found in lyotropic systems were successfully realized as their thermotropic closed analogues.‖

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Notes and references

† The first amphiphilic compound which could have a normal (probably bicontinuous) cubic mesophase was recently reported (ref. 8), furthermore some polysaccharides with cubic or columnar mesophases have been described (ref. 9); however, no experimental proof of the normal type phase structure was given in these references.

‡ Synthesized by etherification of 3,5-bisbromomethyl-1-tetradecyloxybenzene (obtained by reduction of methyl 3,5-tetradecyloxybenzene-1,3-dicarboxylate with LiAlH$_4$, followed by treatment with PBr$_3$) and 1,2:5,6-di-*O*-isopropylidene-D-mannitol (NaH in DMF) followed by deprotection (10% HCl in MeOH). Expected C, H analyses, mass and ^{1}H and ^{13}C NMR spectra were obtained: δ_H(400 MHz, DMSO-d_6, 27 °C, SiMe$_4$) 0.83 (t, 3 H, *J* 6, CH$_3$), 1.22–1.38 (m, 22 H, CH$_2$), 1.65–1.69 (m, 2 H, CH$_2$), 3.31–3.67 (m, 16 H, C*H*$_2$OH, C*H*OH, CH$_2$OC*H*), 3.91 (t, 2H, *J* 7, OCH$_2$), 4.18 (d, 2H, *J* 7, OH), 4.30 (t, 2H, *J* 6, OH), 4.45 (t, 2H, *J* 6, OH), 4.50–4.59 (m, 8H, OH, C*H*$_2$OCH), 6.81 (s, 3H, aromatic H); δ_C(126 MHz, DMSO-d_6, 30 °C, SiMe$_4$) 13.9 (CH$_3$), 22.0, 25.5, 28.6, 28.7, 28.8, 28.9, 29.0, 31.2 (CH$_2$), 67.3 (OCH$_2$), 64.0, 63.0 (*C*H$_2$OH), 70.4, 71.0, 71.1, 77.9 (*C*HOH, CH$_2$O*C*H), 73.0 (*C*H$_2$OCH) 158.5, 140.5, 118.4, 112.2 (aromatic C); *m*/*z* (ESI-MS) 701 ([M + Na]$^+$, 100%).

§ $n = (a_{hex}{}^2/2)h(N_A/M)\rho$ with ρ = 1 g cm^{-3}, N_A = Avogadro constant, M = molecular mass, h = 0.45 nm (diffuse scattering in the wide angle region of the X-ray pattern).

¶ No prolonged heating is possible at these temperatures due to decomposition.

‖ As in other binary mixtures of amphiphilic polyhydroxy compounds [ref. 5(*b*)] no reversed bicontinuous cubic mesophase (Cub$_{V2}$) could be detected between the S$_A$ phase and the reversed Col$_{h2}$ phase, although the reason for this is not yet clear. However, this phase was realized with other polyhydroxy amphiphiles [ref. 5(*b*),(*d*)].

1 G. J. T. Tiddy, *Phys. Rep.*, 1988, **57**, 1; J. M. Seddon and R. H. Templer, in *Handbook of Biological Physics*, ed R. Lipowsky and E. Sackmann, Elsevier, Amsterdam, 1995, vol. 1, p. 97.
2 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525.
3 C. Tschierske, *Progr. Polym. Sci.*, 1996, **21**, 775.
4 Reviews: J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1984, **110**, 205; G. A. Jeffrey, *Acc. Chem. Res.*, 1986, **12**, 179; G. A. Jeffrey and L. M. Wingert, *Liq. Cryst.*, 1992, **12**, 179; H. Prade, R. Miethchen and V. Vill, *J. Prakt Chem.* 1995, **337**, 427.
5 (*a*) K. Borisch, S. Diele, P. Göring and C. Tschierske, *Chem. Commun.*, 1996, 237; (*b*) K. Borisch, S. Diele, P. Göring, H. Müller and C. Tschierske, *Liq. Cryst.*, 1997, **22**, 427; (*c*) K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *Angew. Chem.*, 1997, **109**, 2188; *Angew. Chem., Int. Ed Engl.*, 1997, **36**, 2087; (*d*) K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529.
6 Columnar and cubic mesophases of dendrimers: V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.*, 1997, **119**, 1539.
7 A. Eckert, B. Kohne and K. Praefcke, *Z. Naturforsch*, 1988, **43b**, 878; G. Lattermann and G. Staufer, *Liq. Cryst.*, 1989, **4**, 347; K. Praefcke, B. Kohne, W. Stephan and P. Marquardt, *Chimia*, 1989, **43**, 380; K. Praefcke, P. Marquardt, B. Kohne and W. Stephan, *J. Carbohydr. Chem.*, 1991, **10**, 539; V. Percec, D. Tomazos, J. Heck, H. Blackwell and G. Ungar, *J. Chem. Soc., Perkin Trans. 2*, 1994, 31.
8 V. Vill, T. Böcker, J. Thiem and F. Fischer, *Liq. Cryst.*, 1989, **6**, 349.
9 V. Vill, *Habilitationsschrift*, Hamburg, 1997, p. 35.

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