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Penetration by water of polyhydroxy amphiphiles in the crystalline versus the liquid crystalline states

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The penetration of water in contact preparations with polyhydroxy amphiphiles in different aggregation states is compared. The onset of penetration is found at much higher temperatures when the samples are in the solid state than when they are in a super-cooled liquid-crystalline state in the case of the smectic A_d and smectic B_2 phases, but not the columnar hexagonal (D_{hd}) mesophase. The enhanced accessibility of the bilayer smectic phases can be explained by assuming that the molecular arrangement in the layers is similar to that found in the lamellar lyotropic phase, where the polar groups are on the outside and the (partially intercalated) alkyl chains are in the core of the layers.

1. Introduction

The formation of lyotropic liquid crystals in binary systems of amphiphiles and water has been the subject of many studies, predominantly in the 1960s and 1970s. Several comprehensive reviews have appeared [1-3]. Carbohydrate (or more generally, polyhydroxy) amphiphiles have received considerable attention in the past decade [4-6]. Most research on this swiftly growing class of compounds has focused on their thermotropic liquid-crystalline properties. Several carbohydrate amphiphiles are excellent non-ionic surfactants [7-10] and therefore interest in the lyotropic liquid-crystalline behaviour of these compounds is increasing [11-13].

The most straightforward method for a qualitative screening of lyotropic liquid-crystalline behaviour consists of making contact preparations of amphiphiles and water on microscope slides (water was added with a syringe at the edge of the cover-slip) and observing them through a polarizing microscope equipped with a heating/cooling stage. In order to obtain a smooth penetration surface, a sample is heated to the isotropic liquid state and allowed to cool to room temperature before water is added. If the sample exhibits a liquid-crystalline phase on cooling, considerable super-cooling of this mesophase may occur. In some instances the metastable mesophase of a compound persists long enough to permit comparison of the penetration of samples of the same compound in different aggregation states.

2. Results

When crystals of heptyl 1-thio-α-D-glucopyranoside [14, 15] are heated (5 K/min) in the presence of excess water, no visible changes occur up to 46°C. Upon further heating, the crystals dissolve and an isotropic solution is formed. However, when water

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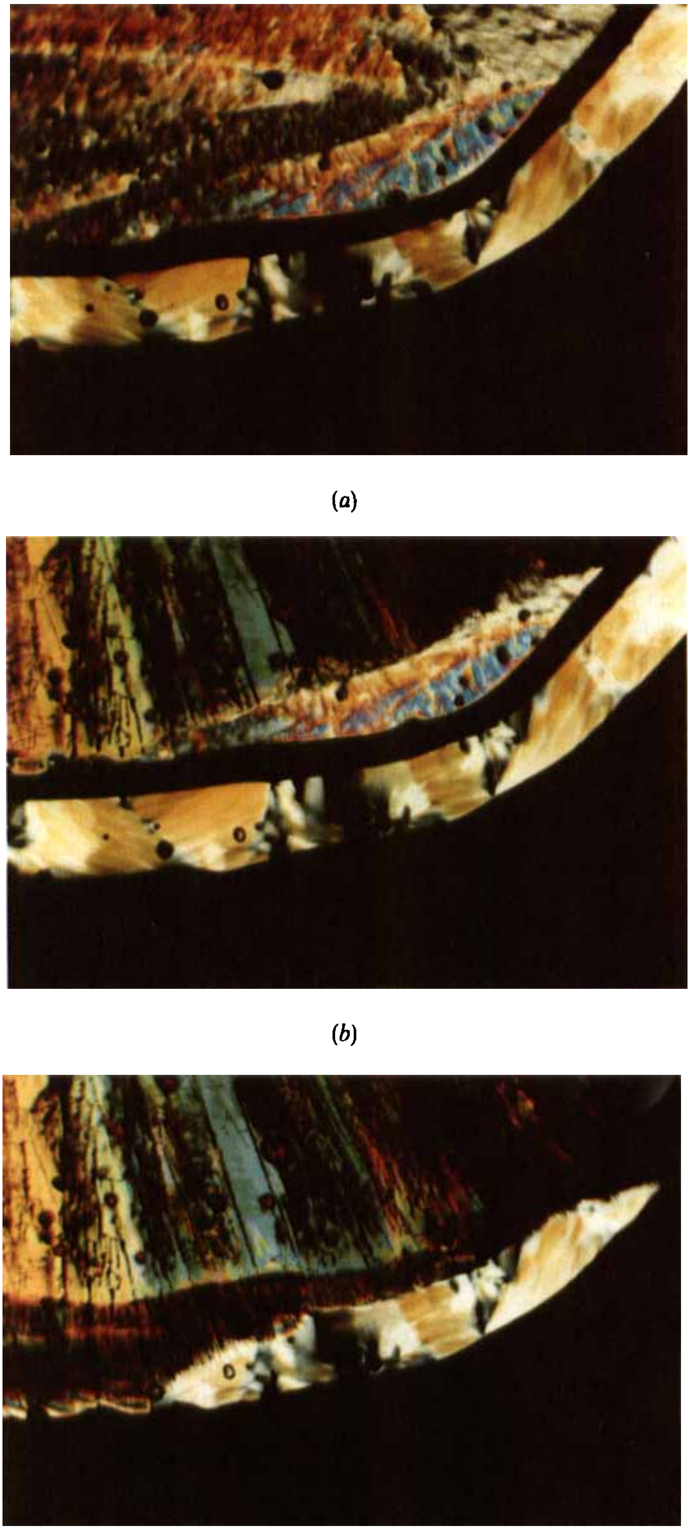

(*a*)

(*b*)

(*c*)

Phase changes in a contact preparation of the smectic A_d phase of heptyl 1-thio-α-D-glucopyranoside (bottom) and water (top), observed at 20°C with crossed polarizers. (*a*) Water has penetrated the anhydrous sample to form bands of hexagonal and optically isotropic (probably cubic [13]) lyotropic mesophases (~200 s after the addition of water). (*b*) Crystallization has started in the smectic A_d phase and is spreading across the sample (~230 s after the addition of water). (*c*) Crystallization is nearly complete (~240 s after the addition of water), demonstrating that all three observed mesophases are metastable at room temperature.

is added to the super-cooled smectic A_d phase of heptyl 1-thio-α-D-glucopyranoside, penetration is observed at room temperature and distinct bands of hexagonal and optically isotropic (probably cubic, compare [13]) lyomesophases are formed. These lyophases are metastable at room temperature; crystallization of the sample takes place within a few minutes. The figure (*a*)–(*c*) shows three different stages of the experiment.

In another experiment, myelin figures protruded from crystals of 4,6-*O*-octylidene-D-glucopyranose [16] at 64°C, whereas transient formation of myelins was observed at room temperature from the super-cooled smectic A_d phase. Water continued to penetrate slowly into the smectic sample. At the interface with water a crystalline hydrate was formed; heating the sample to 56°C resulted in renewed protrusion of myelins.

Most polyhydroxy mesogens described so far exhibit a smectic A_d phase, but two other thermotropic mesophase types (smectic B_2 and columnar hexagonal) have recently been reported. The (±)1,2-alkanediols [17, 18] and (±)3-alkylthio-1,2-propanediols [18, 19] with sufficiently long alkyl chains exhibit a smectic B_2 phase. In a contact preparation with water, crystals of 3-undecylthio-1,2-propanediol are penetrated at 29°C, when myelin figures and a fluid lamellar (L_α) phase are formed, whereas myelin figures protrude from the smectic B_2 phase at 22°C. The columnar hexagonal (D_{hd}) mesophase can form from peg-like molecules consisting of one carbohydrate moiety and two alkyl chains [20]. Dr. David Mannock (University of Alberta at Edmonton, Canada) has kindly provided us with several samples of dialkylglucosylglycerols [21] and dialkylgalactosyl-glycerols [22], which form columnar hexagonal mesophases when heated [23]. In a typical experiment, the penetration temperature of

The onset of water penetration of several polyhydroxy amphiphiles in the solid and the liquid crystalline states.

Compound	Phase without H_2O†	$T_{penetration}$ °C‡	Phase(s) formed†
Heptyl 1-thio-α-D-glucopyranoside	SA_d	<17	cub., hex.
	cryst.	46	iso.
4,6-O-octylidene-D-glucopyranose	SA_d	<17	Myelins, cr. hydr.
	cr. hydr.	56	Myelins
	cryst.	64	Myelins
3-Undecylthio-1,2-propanediol	SB_2	22	Myelins, L_α
	cryst.	29	Myelins, L_α
3-Decylthio-1,2-propanediol	SB_2	<17	Myelins, L_α
	cryst.	28	Myelins
2,3-di-*O*-tetradecyl-1-*O*-β-D-glucopyranosyl-*rac*-glycerol	D_{hd}	52	Myelins§
	cryst.	52	Myelins§
2,3-di-*O*-dodecyl-1-*O*-β-D-glucopyranosyl-*sn*-glycerol	D_{hd}	32	Myelins
	cryst.	32	Myelins

† Abbreviations used: cub. = (optically isotropic) cubic; hex. = hexagonal I; iso. = isotropic liquid; cr. hydr. = crystalline hydrate; cryst. = crystalline, S = smectic; D_{hd} = disordered hexagonal columnar.

‡ Transition temperatures uncorrected.

§ On further penetration by water several hitherto unidentified lyotropic phases are formed.

1,2-*O*-tetradecyl-3-*O*-*β*-D-glucopyranosyl-(±)-glycerol was found to be the same for the solid and the columnar hexagonal phases. The experimental data for a number of compounds are given in the table.

3. Discussion

The results of these experiments can be explained in terms of the accessibilities of the hydrogen-bonded networks in the different aggregation states. Most carbohydrate amphiphiles form bilayer structures in the solid state, with alternating layers of strongly hydrogen-bonded, head-to-head polar moieties and intercalated alkyl chains. In the widely used model for the smectic A_d phase of carbohydrate derivatives with one alkyl chain [24], it is assumed that intercalated sugar-moieties form the core of each bilayer sandwiched between disordered alkyl chains. A similar structure with non-intercalating polar groups in the middle of the bilayers is proposed for the smectic B_2 phase [18]. The columnar hexagonal mesophase of the dialkylglucosylglycerols is believed to consist of disc-like aggregates of 4–5 molecules (compare [18, 20]), with the polar head-groups at the core of each disc and the disordered alkyl chains at the periphery.

In all these models the polar headgroups are surrounded by apolar regions and it is therefore not clear why the smectic phases are more easily penetrated. However, it was recently suggested [25] that the model for the smectic A_d phase is incorrect. It is proposed that the molecular arrangement in the smectic bilayer is very similar to that of the fluid lamellar (L_α) phase, which has the polar head-groups on the outside and the (partially intercalated) alkyl chains inside. Our findings are readily explained by this model and we therefore propose that the observed differences in penetration temperatures provide evidence for a molecular arrangement in the interdigitated bilayers of the smectic A_d phase of polyhydroxy mesogens that is very similar to that found in the L_α phase [26]. Our results indicate that in the smectic B_2 phase, where there is no interdigitization, the polar head-groups should also be on the outside of the layers.

4. Experimental

Microscopic studies were carried out on a Leitz instrument equipped with a heating/cooling stage and a West programmable temperature controller. The photographs in the figure were recorded on Kodacolor Gold 400 film with a Wild MPS 51 camera.

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