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Liquid Crystals

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Lyotropic liquid crystal phase formation in 1-(alkanoylmethyl amino) 1-deoxy-D-glucitols

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The lyotropic and thermotropic liquid crystals of a series of 1-(alkanoylmethyl amino) 1-deoxy-D-glucitols (C_8–C_{12}, $C_{18=}$) oleoyl derivative) have been investigated by polarizing optical microscopy and differential scanning calorimetry. For chain lengths longer than the octanoyl derivative, the pure compounds form a lamellar (smectic A) phase before melting to the isotropic liquid. Both the liquid crystal and isotropic phases of the neat surfactant and aqueous mixtures supercool to form metastable states. In water the octanoyl derivative forms hexagonal (H_I) phase, while the C_8–C_{12} compounds give H_1, cubic (V_1) and L_α mesophases. Only the L_α phase is observed with the oleoyl derivative.

1. Introduction

Carbohydrate surfactants comprise a hydrophilic sugar headgroup linked to a hydrophobic alkyl chain (C_n, where $n > 6$). The carbohydrate moiety may be cyclic or acyclic, a sugar monomer, e.g. glucose, xylose, galactose, or an oligomer such as maltose. This group can be joined to an alkyl chain via –O–, –C–, –N–, –S–, ester, amide or acyl linkages. For many years the compounds have been known to form thermotropic smectic A (lamellar, L_α) phases [1, 2], but their lyotropic phases have been neglected. In particular, the sensitivity of phase structure to alkyl chain length is scarcely known. We report here the liquid crystal behaviour of a series of polyhydroxy surfactants, the 1-(alkanoylmethyl amino) 1-deoxy-D-glucitols. These compounds have a linear headgroup derived from D-glucitol which is bonded via an amide linkage to an alkyl chain. In this study, the *n*-octanoyl to *n*-dodecanoyl and the *n*-oleoyl derivatives have been examined. The thermotropic and lyotropic liquid-crystalline properties of each compound were investigated using polarizing optical microscopy and differential scanning calorimetry. Before describing the results we give a brief summary of the factors that determine lyotropic mesophase structures and previous work on polyhydroxy surfactants which prompted the further study of these compounds.

Theory suggests that the type of liquid-crystalline phase formed by a surfactant is determined by the shape of its micelles in the solution (L_1) in equilibrium with this phase. The factors controlling micelle shape are: the average area per chain at the

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micelle surface (a), the micelle radius (taken as the length of the all-trans alkyl chain, (1_t) and the volume of the alkyl chain (v). If these three parameters are known then packing constraint relationships can be used to predict micelle shapes [3–5]. Considering the simple shapes spheres, circular rods and discs (bilayers), then the phases expected can be assessed according to the size of the head group (a).

$$a > \frac{3v}{1_t}\text{: spherical micelle}\rightarrow\text{cubic mesophase } (I_1),$$

$$\frac{3v}{1_t} > a > \frac{2v}{1_t}\text{: rod micelle}\rightarrow\text{hexagonal mesophase } (H_1),$$

$$\frac{2v}{1_t} > a > \frac{v}{1_t}\text{: bilayer micelle}\rightarrow\text{lamellar mesophase } (L_\alpha).$$

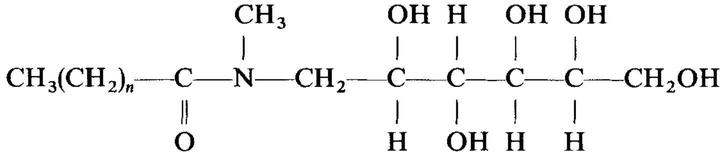
The values of a can be derived from low angle X-ray diffraction measurements on mesophases, whilst 1_t and v are calculated by summing the various bond lengths and molecular volumes, respectively. Typical values are, spherical micelles $a > 70\,\text{Å}^2$; rod micelles $70\,\text{Å}^2 > a > 47\,\text{Å}^2$; disc micelles $a < 47\,\text{Å}^2$. In practice disc micelles appear only for surfactants where $a > c.\ 44\,\text{Å}^2$. Otherwise a lamellar dispersion or inverse (alkyl chain-continuous) mesophases occur. An important assumption in this description is that alkyl chains can pack equally well into any shape. While this works well for polyethyleneoxide surfactants [4], it remains to be tested for other types. From previous work on hydroxyl amphiphiles it is well known that a single OH group is insufficiently polar for lyotropic liquid crystals to occur [6]. However, with two OH groups (1,2 diols, α-hydroxy-carboxylic acids and monoglycerides) lamellar and reversed phases do occur in water [6–8]. Here a is generally less than $40\,\text{Å}^2$, and alkyl chain length has a strong influence on the phase structure. The packing constraints referred to here do not apply to inverse phases where a complex interplay of surface curvature, chain conformation, steric effects and hydration determines the structures. (For a recent review see [9]).

The addition of more OH moieties into the headgroup increases both its size and polarity leading to the occurrence of thermotropic mesophases [1, 2, 10–22]. The monoalkylated derivatives of β and α-D-glucopyranoside with sufficiently long alkyl chains form a smectic A phase [10–12] which, from X-ray data [12], appears to be indistinguishable from the L_α phase of anhydrous soaps. Indeed, monoalkyl monosaccharides and monoalkyl disaccharides generally appear to form thermotropic lamellar phases, whilst with dialkyl derivatives the reversed phases are very common [10–20]. The only report of an anhydrous H_1 phase is with tetraglycerol dodecyl ether [23].

Studies of the lyotropic behaviour of these poly-OH derivatives are rather scarce. Mono-alkyl glycosides do appear to form L_α phases only [21, 25] while disaccharides [20] (sucrose esters) give the sequence L_1, H_1, V_1, L_α. A single report of L_α alone for dodecylmaltoside and dodecylcellobiocide (disaccharides) appears anomalous [21]. A later reference reports the expected $H_1 \rightarrow L_\alpha$ transition with increasing surfactant concentration [22]. In a more recent paper Sagitani *et al.* have demonstrated [23] that increasing head group size for polyglycerol dodecyl ethers does mirror the behaviour of polyoxyethylene surfactants [4], with one glycerol unit ($OCH_2.CH(OH).CH_2$–) being equivalent to *c.* 2–3 EO units. At the initiation of this study we were unaware of any systematic investigation of the influence of chain lengths on mesophase type. We decided to examine the lyotropic phase behaviour of the 1-(alkanoylmethyl amino)-1-deoxy-D-glucitols (alkyl chain length C_7–C_{17}), both because a series of compounds characterized in previous studies [16, 17, 26] was available, and to compare the data with that reported for other poly-OH surfactants [20–25]. This allows an estimation of the effect of the poly-OH ring structure (open or closed) on mesophase type. At the end of this study the influence of chain length on mesophases formed by *n*-alkyl 1-*O*-*β*-D-glucopyranosides (C_7–C_{10}) at room temperature was reported [24].

2. Experimental

Each 1-(alkanoylmethyl amino)-1-deoxy-D-glucitol was synthesized by the reaction of *N*-methyl-D-(−) glucamine (Merck) with a fatty acid [26]. Following the procedure of Hildreth [27], coupling was performed in the presence of ethyl chloroformate by the mixed anhydride method. The products derived from octanoic to dodecanoic acid were recrystallized from ethanol. 1-(Oleoylmethyl amino)-1-deoxy-D-glucitol was recrystallized from a 1 : 9 methanol : ether mixture at −16°C and its purity was confirmed by NMR analysis.



$$\begin{array}{ccccccccccccccccc} & & CH_3 & & & & OH & & H & & OH & & OH & & \\ & & | & & & & | & & | & & | & & | & & \\ CH_3(CH_2)_n & - & C & - & N & - CH_2 - & C & - & C & - & C & - & C & - & CH_2OH \\ & & \| & & & & | & & | & & | & & | & & \\ & & O & & & & H & & OH & & H & & H & & \end{array}$$

1-(Alkanoylmethyl amino)-1-deoxy-D-glucitol; also named 1-deoxyl-1-(*N*-methyl alkanamido)-D-glucitols [17].

The phase behaviour of each compound was determined by polarizing optical microscopy using a Reichert Neopan polarizing microscope with hot stage. Transition temperatures were measured by a Comark digital thermometer (±0·5°C). Each anhydrous compound was heated from room temperature until it melted to the isotropic liquid. Any thermotropic mesophase formation was noted. Each solid was then studied by differential scanning calorimetry using the Mettler TA 3000 Thermal Analysis System with associated control unit, the TC 10 TA processor. The lyotropic phase behaviour was determined by the penetration scan technique. A detailed description of the technique is given in [4]. This allows the study of phase behaviour as a function of both concentration and temperature. The mesophases formed were identified by their characteristic textures [28] and viscosities [5].

3. Results

3.1. *Thermotropic phases*

The compounds employed were mostly those from previous studies where the thermotropic behaviour was examined to check that the behaviour was the same. Our results are in good agreement with those of Goodby *et al.* [17]. The solid *n*-octanoyl derivative (C_8G) softens about 74°C before melting to an isotropic liquid (L) at 80°C. At first a number of crystals (*c.* 1 per cent) coexist with the liquid but these disappear at 83°C. This coexistence of liquid and crystal was still observed after the sample had been dried over P_2O_5 and even after several heating/cooling cycles. The surfactant recrystallizes slowly from the supercooled liquid at room temperature. 1-(Nonanoylmethyl amino)-1-deoxy-D-glucitol (C_9G) melts at 88°C following the same pattern as the octanoyl derivative, with the coexistence of L + crystals over the range 82–88°C. However, the liquid surfactant supercools to L_α which melts at 60·5°C. We suspect that the crystals in the L + crystals region in C_8G and C_9G are a different head group isomer. Because of the tiny fraction present and the limited amounts of materials available no attempt to purify the compounds further was made.

n-Decanoyl-, *n*-undecanoyl- and *n*-dodecanoyl derivatives melt to the isotropic liquid via a lamellar phase, the lamellar phase first being observed at 80, 89 and 95°C respectively. The mesophase then melts to the isotropic liquid at 92, 111 and 127°C respectively. In each case both the liquid and the lamellar phase can be supercooled to room temperature. Once formed the lamellar phase may still contain a number of needle-like crystals which will dissolve on further heating.

n-(Oleoylmethyl amino)-1-deoxy-D-glucitol) ($C_{18=}G$) has not been reported previously. It is a soft solid at room temperature, forms a lamellar phase at 60°C which then melts to a liquid at 140–142°C. Both the liquid and lamellar phase can be supercooled to room temperature.

Differential scanning calorimetry was used to follow the phase transitions of each anhydrous surfactant. The transition heats are listed in the table. In general the results are in good agreement with those of Goodby *et al.* [17], but some complications occurred due to super-cooling of the melt. For example, the first heating run of the nonanoyl derivative shows a single sharp, endothermic transition at 91°C. This melting transition is at a higher temperature than that observed by microscopy (82–88°C). After cooling, a second heating run produced a thermogram with two peaks, the first, a broad exothermic transition at 60°C with a shoulder at 57°C and the second, a sharper, endothermic transition at 85°C. Successive thermograms had the same features. The exothermic transition is the recrystallization of the solid from the supercooled liquid and the second endothermic peak is the solid→liquid melting transition. Optical microscopy showed the liquid C_9G supercooling to the lamellar phase at room temperature which then melted to a liquid at 60·5°C. The lamellar melting transition is masked by the recrystallization of the solid and is seen only as a shoulder on the first peak. With both C_8G and C_9G there was no sign of any peak due to the small fraction of crystals melting above the main peak, confirming that this is a very minor

Transition temperatures (°C) of anhydrous 1-(alkanoylmethyl amino) 1-deoxy-D-glucitols.

	$S \rightarrow L_\alpha + XTLS$	$L_\alpha + XTLS \rightarrow L_1$
(Octanoylmethyl amino) 1-deoxy-D-glucitol	80	83
	(40·56)†‡	—
(Nonanoylmethyl amino) 1-deoxy-D-glucitol	82	88
	(41·42)†	—
	$S \rightarrow L_\alpha$	$L_\alpha \rightarrow L_1$
(Decanoylmethyl amino) 1-deoxy-D-glucitol	80	92
	(52·9)†	—
(Undecanoylmethyl amino) 1-deoxy-D-glucitol	89	111
	(45·6)	(1·3)
(Dodecanoylmethyl amino) 1-deoxy-D-glucitol	95	127
	(31·2)	(1·2)
(Oleoylmethyl amino) 1-deoxy-D-glucitol	60	140–142
	(38·5)	(1·7)

† Single melting transition observed on thermogram.
‡ Endothermic transitions from DSC in kJ/mol.
S, solid; L_1, isotropic liquid; L_α, lamellar; XTLS, solid crystals.

component. Similar results were observed for the C_{11} and C_{12} derivatives. The first heating run gave sharp peaks for the S/L_α and L_α/L transitions while subsequent runs also showed exothermic transitions arising from the supercooled liquid: C_{10}G exhibited like behaviour except that the heat of the L_α/L transition was too small to be observed.

$C_{18=}$G produced a thermogram with two peaks. The first, a large endothermic transition at 64°C and the second, a small exotherm at 142°C correspond to the S/L_α and L_α/L transitions respectively. The cooling scan had a single exotherm at 139°C indicating a single reversible phase transition from isotropic liquid to lamellar phase. This phase supercooled to ambient temperature. A second scan had only one endotherm at 134°C, the transition from liquid crystal to liquid. On leaving the sample overnight the DSC scan regained the solid$\rightarrow L_\alpha$ transition.

3.2. *Lyotropic phases*

The results of the lyotropic phase behaviour are represented schematically in figures 1–6. These show the separate phases observed by optical microscopy in the form of bar charts. The shaded areas indicate two-phase co-existence regions. The *n*-octanoyl derivative (see figure 1) forms a hexagonal phase when contacted with water. The hexagonal phase, which was present down to 0°C, melted at 39°C to the isotropic micellar solution. An isotropic liquid first appears between H_1 and S at 34·5°C. No other mesophases occurred at higher surfactant concentrations, even after supercooling a melt.

In contrast to this, C_9G (see figure 2) forms an extensive range of mesophases. H_1 is observed above 15°C ($T_{pen} = 15$°C) followed by V_1 ($T_{pen} = 36$°C) and L_α ($T_{pen} = 44$°C) (T_{pen} is the minimum temperature at which a particular mesophase forms—see [6]). The mesophases melt at 69, 56 and 76°C respectively. Note that the metastable L_α phase of the anhydrous surfactant becomes stable and has an increased melting point in the presence of water. The solid surfactant remains to 90°C. Above 54°C a band of isotropic liquid was observed between the H_1 and V_1 regions, i.e. the sequence is S–L_α–V_1–L_1–H_1–L_1. The cubic phase melts at 56°C leaving S–L_α–L_1–H_1–L_1.

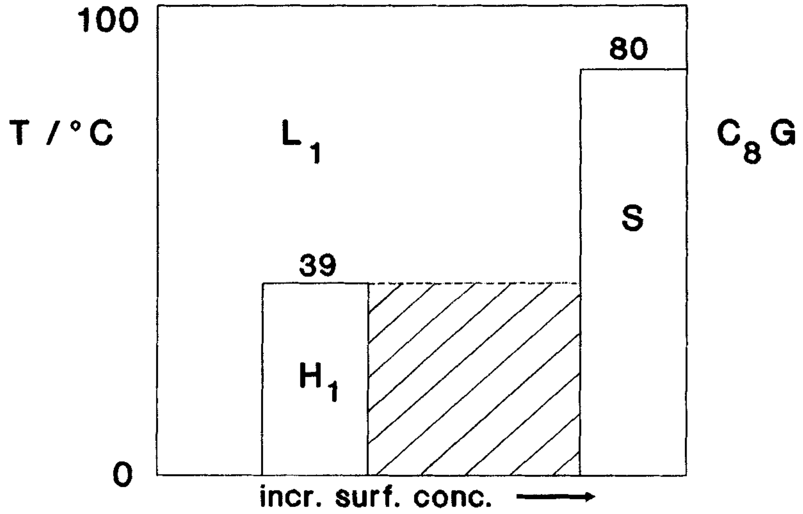


Figure 1. Schematic diagram showing the lyotropic phase behaviour of (*n*-octanoylmethyl amino) 1-deoxy-D-glucitol in water. L_1, micellar solution; H_1, hexagonal phase; S, solid surfactant.

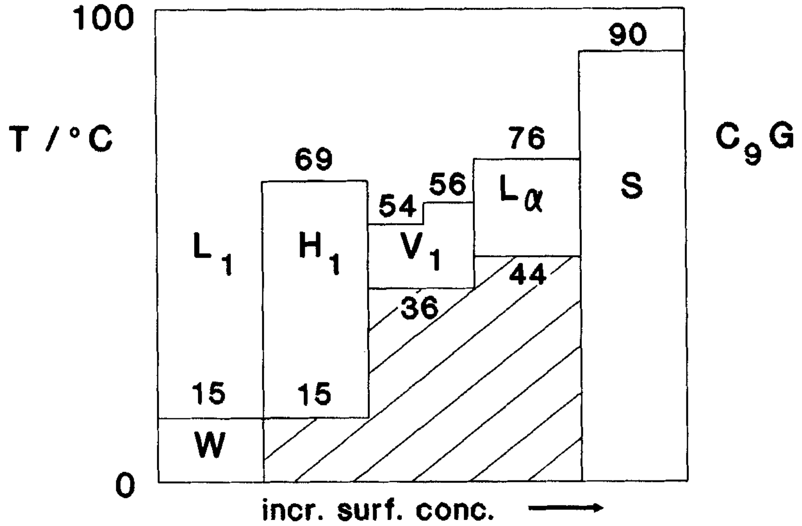


Figure 2. Schematic diagram showing the lyotropic phase behaviour of (*n*-nonanoylmethyl amino) 1-deoxy-D-glucitol in water. L_1, micellar solution; H_1, hexagonal phase; S, solid surfactant; W, dilute surfactant solution; V_1, bicontinuous cubic phase; L_α, lamellar phase.

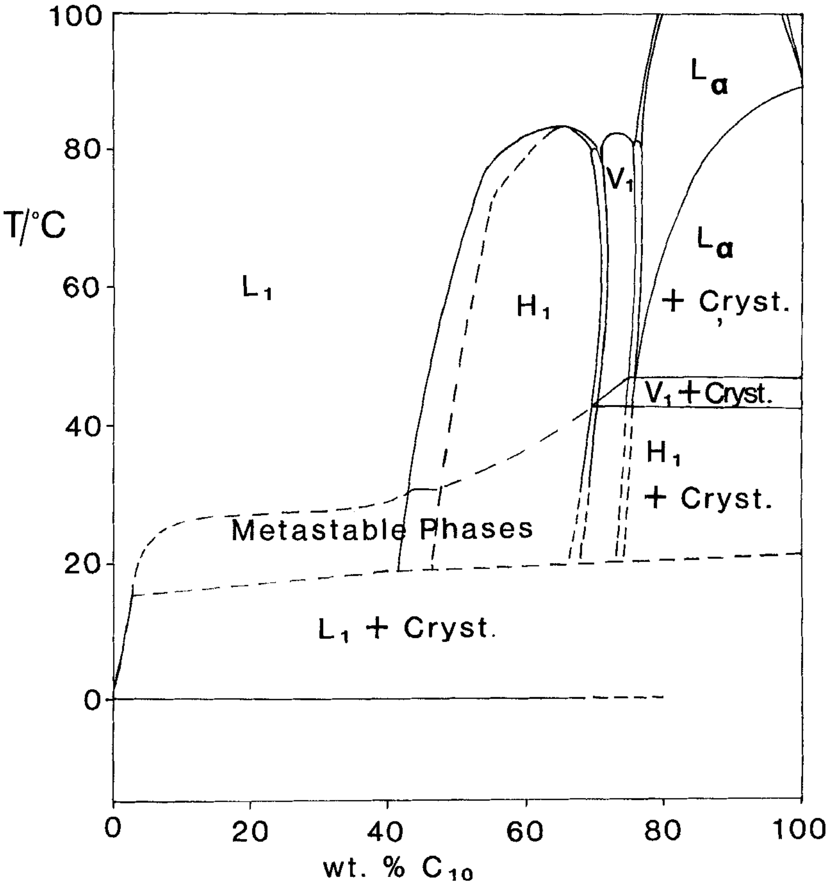


Figure 3. Full phase diagram showing the lyotropic phase behaviour of (*n*-decanoylmethyl amino) 1-deoxy-D-glucitol/water system. L_1, micellar solution; H_1, hexagonal phase; V_1, bicontinuous cubic phase; L_α, lamellar phase; S, solid surfactant; Cryst, solid crystals.

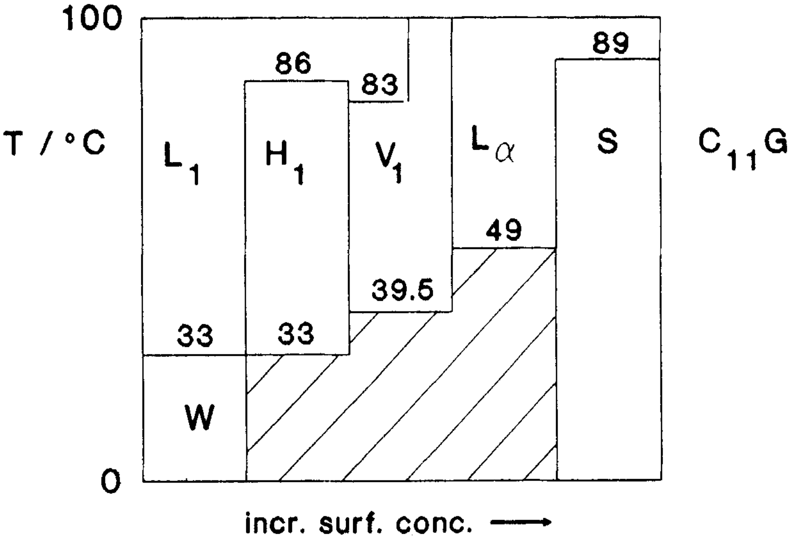


Figure 4. Schematic diagram showing the lyotropic phase behaviour of (*n*-undecanoylmethyl amino) 1-deoxy-D-glucitol in water. L_1, micellar solution; H_1, hexagonal phase; V_1, bicontinuous cubic phase; L_α, lamellar phase; S, solid surfactant.

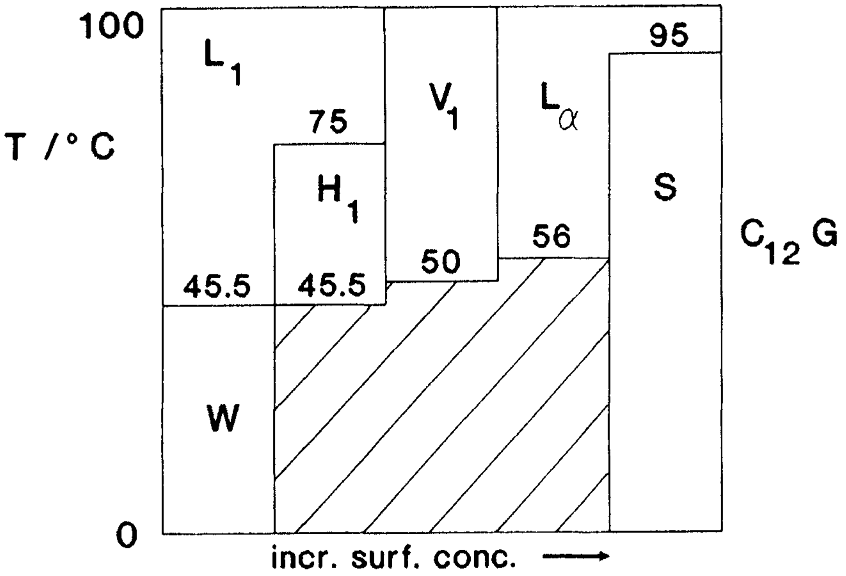


Figure 5. Schematic diagram showing the lyotropic phase behaviour of (*n*-dodecanoylmethyl amino) 1-deoxy-D-glucitol in water. L_1, micellar solution; H_1, hexagonal phase; V_1, bicontinuous cubic phase; L_α, lamellar phase; S, solid surfactant.

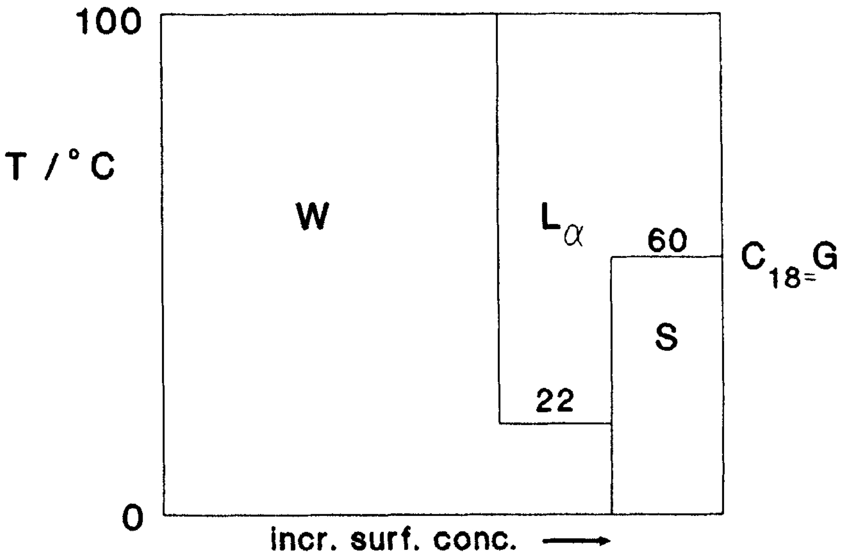


Figure 6. Schematic diagram showing the lyotropic phase behaviour of (oleoylmethyl amino) 1-deoxy-D-glucitol in water. W, dilute solution; L_α. lamellar phase; S, solid surfactant.

1-(Decanoylmethyl amino)-1-deoxy-D-glucitol (see figure 3) forms a hexagonal phase above 30°C and V_1 and L_α at 42°C and 46°C, respectively. H_1 and V_1 melt at 81 and 80°C, respectively, with the sequence S–L_α–L_1–H_1–L_1 being observed briefly from 80 to 81°C. The phase diagram for this surfactant, determined by microscope examination of about 40 samples, is given in figure 3. Accurate measurement of the boundary between solutions or liquid crystals and a two-phase region also containing crystalline surfactant was prevented by the ease with which metastable, supercooled, mesophase or solution states occurred. Hence dotted boundaries are shown in this region. The concentrations at the phase boundaries between L_1 and the mesophases, or between the different mesophase types, are similar to those observed for many other non-ionic and ionic surfactants [4, 5].

For the *n*-undecanoyl derivative, T_{pen} for H_1 has increased to 33°C. The hexagonal phase melts at 86°C, with the sequence S–L_α–V_1–L_1–H_1–L_1 being observed from 83 to 86°C. The cubic and lamellar regions remain until > 100°C. $C_{12}G$ (see figure 5) forms a hexagonal phase above 45·5°C. Cubic (V_1) forms at 50°C and L_α at 56°C. H_1 melts at 75°C from the L_1 side and no V_1–L_1–H_1 sequence is seen. The H_1 melting temperature is lower than that of either $C_{10}G$ or $C_{11}G$, but that of the V_1 phase is > 100°C, as for $C_{11}G$. Krafft temperatures (T_k) were not measured for these surfactants. However, microscope observations indicate that T_k must be only slightly lower than T_{pen} (H_1). Below T_{pen} (H_1 the surfactant appears to be insoluble in the water. This is followed by a dramatic increase in solubility at about the same temperature as that for hexagonal phase formation.

For the oleoyl derivative ($C_{18=}G$) the phase behaviour is much simpler. Only a lamellar phase is observed above 22°C and this remained to > 100°C (see figure 6). Preparation of bulk samples demonstrates that the lamellar phase forms a cloudy dispersion at low concentrations (< 10 per cent) which appears as an emulsion of L_α in water under the microscope. Thus, the surfactant does not appear to form micelles. (No attempt was made to determine the maximum water content of L_α.)

4. Discussion

While the behaviour of these poly-hydroxy surfactants does resemble that of conventional monoalkyl, non-ionic and ionic surfactants in that H_1, V_1 and L_α are the most common mesophases [4, 5], there are some important differences. First, unlike the polyoxyethylene surfactants they form thermotropic L_α phases on initial melting, the stability of the mesophase increasing with alkyl chain length. This is clearly a consequence of the strong inter-headgroup attractions, resembling the behaviour of ionic surfactants. That the hydrogen bonding between polyhydroxy headgroups is much weaker than the headgroup interactions in ionic systems is indicated by the much lower L_α/isotropic transitions observed here (60–140°C compared to >300°C). It is very probable that inter-headgroup hydrogen bonding is also present in the liquid surfactant, hence the liquid (L) does contain aggregates. The chain length (C_{n-1}) dependence of the L_α/L transition temperature presumably reflects the increase in aggregate size in the L phase as C_{n-1} increases. Liquid surfactants are often described as reversed micellar phases. However, from known densities [29] the size of the sugar headgroup is estimated to be 258 Å^3 ($-C-N(CH_3)CH_2- = 90$ Å^3; $-CHOH- = 33{\cdot}1$ Å^3. $-CH_2OH = 35{\cdot}3$ Å^3). This is about the same size as a C_8–C_9 hydrocarbon chain. Hence the volume fraction of polar groups in the C_8–$C_{10}G$ derivatives is the same as or larger than that of the alkyl chains. In addition, the liquids are relatively mobile (fairly low viscosity compared to the mesophases) hence they do not contain large aggregates. It is probably more accurate to think of the surfactant liquids as consisting of separated polar and non-polar regions having dimensions of *c.* 10 Å, with the shape and size of the regions varying according to alkyl chain size and the temperature. The molecular aggregates will be small, polydisperse, and transient, with aggregation numbers of less than about 10, which decrease with increasing temperature.

Secondly, an important practical observation is that the liquid surfactant, the liquid crystals and the aqueous solutions can often be supercooled by up to 100°C or more to form metastable states from which the surfactant does not crystallize for several days or longer. This is presumably a consequence of the hindered rotational isomerization of the head group. Rotation about R–CHOH–CHOHR bonds is much more difficult than that of alkyl or ethylene oxide groups due to the larger steric interactions of –OH compared to –H. Hence the rate of formation of the initial crystal nuclei is lower, because only one of many rotational isomers is required to form the nucleus. Most surfactants have very flexible head groups (EO chains) or compact ones, and so this problem does not occur.

The initial addition of water obviously increases surfactant aggregation since the L_α phase extends to higher temperatures than in the pure compounds. This is likely to arise from an increased contrast between polar and non-polar regions, i.e. an increased surface tension between polar and hydrocarbon regions. Further water addition gives the phase sequence L_α–V_1–H_1–L_1. A gradual increase in the effective size of the headgroups resulting from the onset of hydration-induced repulsive forces would be expected here, consistent with the observed phase sequence.

Since H_1 is the high concentration surfactant phase we conclude that the *a* value for the D-glucitol derivative group is in the range 47–70 Å^2, possibly being closer to the lower limit than otherwise (see later). This is roughly equivalent to a hexa-oxyethylene (EO_6) head group at 25°C. For the series of surfactants $CH_3(CH_2)_{n-1}$ EO6 (C_nEO_6), the hexagonal phase is first observed with the C_8 derivative, where a low melting H_1 phase (11–14°C) is formed. For longer chain homologues L_α and V_1 are also observed [4]. Despite the temperature sensitivity of the headgroup, the upper temperature limit of H_1 is constant at *c.* 35±2°C, over the range C_{10}–C_{16} [4]. In this study the H_1 phase occurs for a C_7 chain (C_8G), but H_1 is surrounded by isotropic liquid (wherever crystalline surfactant does not occur) as for C_8EO_6. This again supports the idea that poly OH surfactants form mesophases more readily than poly EO surfactants.

It is notable that the upper temperature limits of both V_1 and L_α increase sharply with chain length, with V_1 melting below H_1 for C_9G and well above it for $C_{11}G$ (see figures 2–4). In particular, the maximum in the H_1 melting temperature at $C_{11}G$, and the disappearance of the L_1–H_1–L_1–V_1 sequence for $C_{12}G$ demonstrates that alkyl chain length has a much stronger influence on phase behaviour for the glucitols than for EO surfactants. (Note that for an L_1–H_1–L_1–V_1 sequence the two L_1 phases are thought to contain micelles having different shapes [4].) There are no H_1 or V_1 phases at all for the oleoyl derivative. Indeed, the presence of an L_α dispersion at low surfactant concentrations indicates that micelles do not form. Thus increasing the chain length from C_{12} to C_{18} has increased the negative curvature to such an extent that only a zero curvative micelle (i.e. L_α) can form. There is the additional marked influence of the *cis*-double bond, which is well known to disrupt efficient packing in the crystal, leading to lower S/L_α and T_{pen} (L_α) transition temperature, compared to linear surfactants.

The explanation for this remarkable sensitivity of phase type to alkyl chain length is probably related to the shape of the head group. For a given head group, increasing alkyl chain length tends to reduce positive curvature of micelles. The unfavourable entropy associated with the all-trans conformations tends to make the maximum chain length smaller than that of the all-trans, hence the sphere/rod/disc micelle transitions listed previously occur at larger *a* values. For poly-CHOH surfactants, the chain is much more sterically hindered than an EO or paraffin chain. The C–C–C–C skeleton will tend to adopt an all-trans conformation, or *C*–C–C–*O* will be trans to each other, according to local steric requirements. This will result in a more extended head group than in EO surfactants. Assuming that two water molecules bind to each OH group, and that two water molecules bond to the amide link, then the hydrated head group volume is 617 Å^3. This gives an average cross sectional area of *c.* 54 Å^2 for all-trans head group. Compare this with $C_{12}EO_6$, taking the EO size from recent measurements [30] (395 Å^3) and assuming that two water molecules are bound per oxygen, the hydrated head group volume is 814 Å^3. For a random coil conformation the average cross section area is *c.* 120 Å^2. This is clearly much larger than what is observed in practice, but does illustrate that EO surfactants have a much larger propensity to positive curvature than poly-CHOH materials. Thus the alkyl chain contribution to negative curvature, which becomes more important with increasing chain length, has a much stronger influence on the phase behaviour of these acyclic polyhydroxy surfactants than with conventional non-ionics.

A further difference between the EO and D-glucitol surfactants is the existence of an L_1/V_1 boundary over 20°C or more for $C_{11}G$ and $C_{12}G$, as compared to *c.* 2–4°C for the EO surfactants [4]. Previously we have attributed the V_1/L_1 transition in EO surfactants to a decrease in EO hydration with increasing temperature, which decreases *a* and leads to L_α formation. The extensive L_1/V_1 boundary for the glucitols indicates that head group hydration does not change strongly with temperature, hence the sensitivity of phase behaviour to chain length is unlikely to arise from changes in head group hydration.

Finally, we compare the phase behaviour of the open chain glucitol with that of monoalkyl glycosides, where the sugar moiety is cyclic. Chung and Jeffrey [24] report H_1, V_1 and L_α phases for the C_8 derivative, but only an L_α mesophase for the C_7, C_9 and

C_{10} compounds (all at room temperature). The C_7 compound shows H_1, V_1 and L_α at 0°C [24]. We have observed H_1, V_1 and L_α with the C_8 and C_9 derivatives, but not with C_{10}–C_{12} [31]. Even where they do occur the H_1 and V_1 phases melt below 50°C. Again, chain length has a strong influence on mesophase formation. Not surprisingly, the greater conformational freedom of the glucitol headgroup leads to more positive curvature at the micelle surface. Hence H_1 and V_1 are observed over a wider range of chain lengths and temperatures.

To summarize, the major differences between glucitol and conventional EO surfactants are that chain length has a far greater influence on the glucitol phase behaviour, the glucitols have a greater propensity for mesophase formation, and both their solutions and mesophases exist readily in supercooled states for extended periods. These differences arise mainly from the hindered conformational isomerisation and stronger inter-head group interactions of the glucitol moiety.

References

[1] Noller, C. R., and Rockwell, W. C., 1938, *J. Am. chem. Soc.*, **60,** 2076.

[2] Jeffrey, G. A., 1986, *Accts chem. Res.*, **19,** 168.

[3] Israelachvili, J. N., Mitchell, D. J., and Ninham, B. W., 1976, *J. chem. Soc. Faraday Trans. II*, **72,** 1525.

[4] Mitchell, D. J., Tiddy, G. J. T., Waring, L., Bostock, T., and McDonald, M. P., 1983, *J. chem. Soc. Faraday Trans. I*, **79,** 975.

[5] Tiddy, G. J. T., 1985, *Modern Trends of Colloid Science in Chemistry and Biology*, edited by H. F. Eicke (Birkhauser-Verlag), p. 148.

[6] Lawrence, A. C. S., 1969, *Liquid Crystals*, Vol. 2, edited by G. H. Brown (Gordon & Breach), Part 1, p. 1.

[7] Larsson, K., 1968, *Z. phys. Chem.*, **56,** 173.

[8] Lutton, E. S., 1965, *J. Am. Oil Chem. Soc.*, **42,** 1068.

[9] Lindblom, G., and Rilfors, L., 1989, *Biochim. biophys. Acta*, **988,** 221.

[10] Jeffrey, G. A., and Bhattacharjee, S., 1983, *Carbohyd. Res.*, **115,** 53.

[11] Goodby, J. W., 1984, *Molec. Crystals liq. Crystals*, **110,** 205.

[12] Jeffrey, G. A., and Yeon, Y., 1987, *Carbohyd. Res.*, **169,** 1.

[13] Dahlhoff, W. V., 1987, *Synthesis*, p. 336.

[14] Dahlhoff, W. V., 1987, *Z. Naturf.* (*b*), **42,** 661.

[15] van Doren, H., Buma, T. J., Kellogg, R. M., and Wynberg, H., 1988, *J. chem. Soc. Chem. Commun.*, p. 460.

[16] Pfannemuller, B., Welte, W., Chin, E., and Goodby, J. W., 1986, *Liq. Crystals*, **1,** 357.

[17] Goodby, J. W., Marcus, M. A., Chin, E., Finn, P. L., and Pfannemuller, B., 1988, *Liq Crystals*, **3,** 1569.

[18] Eckert, A., Kohne, B., and Praefcke, K., 1988, *Z. Naturf.* (*b*), **43,** 878.

[19] Dorset, D. L., and Rosenbusch, J. P., 1981, *Chem. Phys. Lipids*, **29,** 299.

[20] Herrington, T. M., and Sahi, S. S., 1988, *J. Amer. Oil Chem. Soc.*, **65,** 1677.

[21] Warr, G. G., Drummond, C. J., Grieser, F., Ninham, B. W., and Evans, D. F., 1986, *J. phys. Chem.*, **90,** 4581.

[22] Marcus, M. A., and Finn, P. L., 1988, *Liq. Crystals*, **3,** 381.

[23] Sagitani, H., Hayashi, Y., and Ochiai, M., 1989, *J. Amer. Oil Chem. Soc.*, **66,** 146.

[24] Chung, Y. J., and Jeffrey, G. A., 1989, *Biochim. biophys. Acta*, **985,** 300.

[25] Vanlerberghe, G., Handjani, R. M., and Rondot, B., 1980, *Rev. fr. Cps gras*, **27,** 237.

[26] Pfannemuller, B., and Welte, W., 1985, *Chem. Phys. Lipids*, **37,** 227.

[27] Hildreth, J. E. K., 1982, *J. Biochem.*, **207,** 363.

[28] Rosevear, F. B., 1954, *J. Amer. Oil Chem. Soc.*, **31,** 628.

[29] 1973, *CRC Handbook of Chemistry and Physics*, 54th edition (CRC Press).

[30] Herrington, T. M., Sahi, S. S., and Leng, C. A., 1985, *J. chem. Soc. Faraday Trans. I*, **81,** 2693.

[31] Tiddy, G. J. T., and Hall, C. (unpublished results).