Phase Behavior of Some Sucrose Surfactants with Water and n-Decane

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The phase behavior of some sucrose esters in water and n-decane is reported. The type of liquid crystal formed and the extent of a particular phase region are correlated with the hydrocarbon chain length of the fatty acid.

Sucrose surfactants are widely used as emulsifying agents and detergents. Like other nonionic surfactants with water micelles are formed and lyotropic liquid crystals at higher concentrations. Some nonionic compounds which form lyotropic crystals, however, do not form thermotropic liquid crystals when heated in the pure state, but melt to form a truly isotropic liquid. Pure monoglycerides (1) and the n-alkylpolyoxyethylene monoethers (2) are examples exhibiting this type of behavior. It has been reported recently that curtain alkyl glycosides and 1-thioglycosides (3) display thermotropic liquid crystalline behavior between room temperature and their melting points. In this work a number of sucrose esters have been investigated in the pure state and in the presence of aqueous and nonaqueous solvents. They display lyotropic properties in both water and n-decane as well as thermotropic properties in the anhydrous state.

There are three well-established classes of lyotropic liquid crystalline phase; these are lamellar, hexagonal and cubic. In the lamellar-phase (L_α) surfactant molecules are arranged in bilayers separated by solvent layers. A lamellar structure with "solid-like" chains may occur at temperatures below the lamellar phase region; this is termed the lamellar gel phase and designated L_β. There are two well-established classes of hexagonal phase structures, the hexagonal phase and the reversed hexagonal phase. The hexagonal phase (H_1) consists of rod-shaped micelles packed in an hexagonal array with the polar head groups in contact with the continuous polar phase, whereas in the reversed hexagonal phase (H_2) the hydrocarbon chains occupy the spaces between hexagonally packed cylinders of solvent. Cubic phases, in contrast to the lamellar and hexagonal phases, are isotropic and not birefringent when observed between crossed polars. Two different classes of cubic phase have been identified. The I type occurs at compositions between a micellar solution (L_1) and the hexagonal (H_1) phase; this consists of an ordered packing of spherical micelles and is designated I_1. The second (V) class is considered to be a "bicontinuous" network; it occurs between L_α and H_1 and is designated V_1, and as the reversed "bicontinuous" phase it occurs between L_α and H_2 and is designated V_2.

EXPERIMENTAL

The sucrose esters were prepared using a transesterification procedure from sucrose and methyl laurate or oleate and purified by liquid chromatography (4,5). Purity was estimated by gas and thin-layer chromatography as >99.5%. The esters as prepared are mixtures of isomers; the sucrose molecule is most readily esterified at the primary hydroxyl groups at the 6,1′ and 6′ positions; the 6 and 6′ positions are more reactive than the 1′ position (4). GLC and NMR on methylated derivatives of the monoesters showed that the isomers 6′:6:1′ were present in the proportions of 6:3:1. Sucrose monotallowate was prepared by purifying commercial sucrose tallowate (Tate and Lyle Industries Ltd., Reading, U.K.) using silica gel column chromatography (5). All reagents and solvents used were AR grade.

Phase structures were identified by polarizing microscopy using a Leitz microscope with fitted hot-stage. Hexagonal and lamellar phases were identified by comparing their textures with literature photomicrographs (6) and by their characteristic conoscopic figures. Cubic phases and micellar solutions may be distinguished by large differences in viscosity and refractive discontinuity. Phase structures were confirmed using low angle X-ray diffraction and bilayer thicknesses obtained for the lamellar phase. Differential scanning calorimetry (DSC) was used to confirm the transitions observed by optical microscopy.

Phase diagrams were determined by measurements on 40-50 binary mixtures. Homogeneity was attained using a vibromixer for the lower concentrations and repeated centrifugation through a narrow constriction for more concentrated samples. The phase behavior was observed between cross polars both for heating and cooling cycles of the sealed, stirred samples in a water bath. Phase boundaries are accurate to better than ±2% (by wt) and ±2 C. The phase sequence in the more complex regions of the phase diagram was checked by the microscope penetration technique.

RESULTS

The thermotropic transitions of the sucrose esters are reported in Table 1. With the exception of sucrose monooleate and dioleate all the esters possess a crystalline phase at 20 C. Microscopic observations show that at room temperature sucrose monolaurate is a white, apparently crystalline solid; at 55 C definite loss of birefringence occurs and a rigid gel-like phase is formed. Mosaic textures of the lamellar phase were observed above 138 C. A DSC scan showed a small transition at 55 C (0.4 kJ mol^{-1}). X-ray data at 21 C and

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H_1, hexagonal phase; H_2, reversed hexagonal phase; I_1, cubic phase of close-packed spherical micelles; L_1, water continuous isotropic phase of low viscosity; L_2, hydrocarbon continuous isotropic phase of low viscosity; L_α, lamellar phase; L_β, gel phase; V_1, normal bicontinuous cubic phase; V_2, reversed bicontinuous cubic phase; S, solid phase; T_i, temperature at which the disappearance, on slow heating, of last trace of solid occurs; T_c, temperature of formation of a liquid isotropic to polarized light.

TABLE 1

Transition Temperatures of the Sucrose Esters

	Transition temperature (°C)		
	Solid-L_β	L_β-L_α	L_α-Isotropic liquid
Sucrose monolaurate	55	138	163
Sucrose monooleate	33[a]	94	154
Sucrose dilaurate	38	81	156
Sucrose dioleate	—	52	89

[a] Semi-solid.

60 C were consistent only with a layer structure. At 21 C there was a strong first order spacing at 37 Å and a weaker second order at 18.5 Å; the weakness of the second order could indicate a lack of crystallinity or thermal motion. At 60 C the pattern was unchanged except that the second order peak had vanished, indicating either further thermal motion or decreased crystallinity. Pulsed NMR data showed more thermal motion than usual. At 26 C there were two different proton mobilities; this is probably indicative of different mobilities of headgroups and tails as the ratio of the peaks representing wt% is 1:1 and independent of temperature (protons of headgroups to tails are approximately equal). The actual mobilities were unusual; the tails appeared to be mobile as in a gel, while the headgroups were less mobile, indicating that an extremely mobile solid is most likely. Two mobilities were found at 60 C; at this temperature the headgroups had the mobility of a gel, whereas the tails were more mobile than a gel, but less mobile than in a liquid crystal, indicating a highly mobile gel phase. Thermogravimetric analysis showed that the apparent onset of thermal degradation was 179 C for the monolaurate and 181 C for the monoleate, but in all cases a darkening in color occurred between 110 and 120 C. Below 60 C the X-ray, DSC and NMR results for the monolaurate are consistent with a layer structure. The enthalpy of the transition at 55 C is small for a solid to gel transition and indicates that the solid is already of high energy; probably disordered solid (rotator phase) to gel (L_β) occurs at 55 C. Sucrose dilaurate shows similar behavior.

Sucrose monooleate is a semisolid of stiff consistency, which has a transition at 33 C to form the gel-like L_β phase. X-ray data confirm a layer structure of 43 Å; NMR and DSC data indicated a less-ordered low temperature structure. Optical microscsopy of the dioleate at room temperature shows lamellar textures although the viscosity is too high for this phase, but by 55 C the viscosity has decreased and this, together with the textures, indicates the L_α phase. Pulsed NMR data are consistent with a mobile gel phase at 26 C and a lamellar phase at 60 C. No sign of a solid to gel transition was observed in the region -50 C to 20 C, indicating that the gel phase exists to below -50 C. A very broad peak indicated that the gel to L_α transition was gradual and took place over a wide temperature range. A small endothermic peak at 89 C gave an enthalpy of 0.85 kJ mol^{-1} for the L_α to isotropic liquid transition.

Sucrose monolaurate + water. Sucrose monolaurate is very soluble in water and forms the L_1 phase to fairly high surfactant concentrations (Fig. 1). At greater than 30 wt% mixtures show streaming birefringence. Above 57 wt% at 20 C an optically transparent viscous phase, LC2, is formed which is highly birefringent. A freshly sheared preparation exhibited nongeometric textures typical of the H_1 phase, changing to angular fan-like textures on raising the temperature and remaining stable on cooling. Conoscopic observations gave a flash figure, but it was not possible to determine the optic sign. Low angle X-ray confirmed the hexagonal phase. Compositions greater than 82% were viscous semisolids at 20 C. Above 55 C some homeotropic alignment occurred. Freshly sheared samples gave

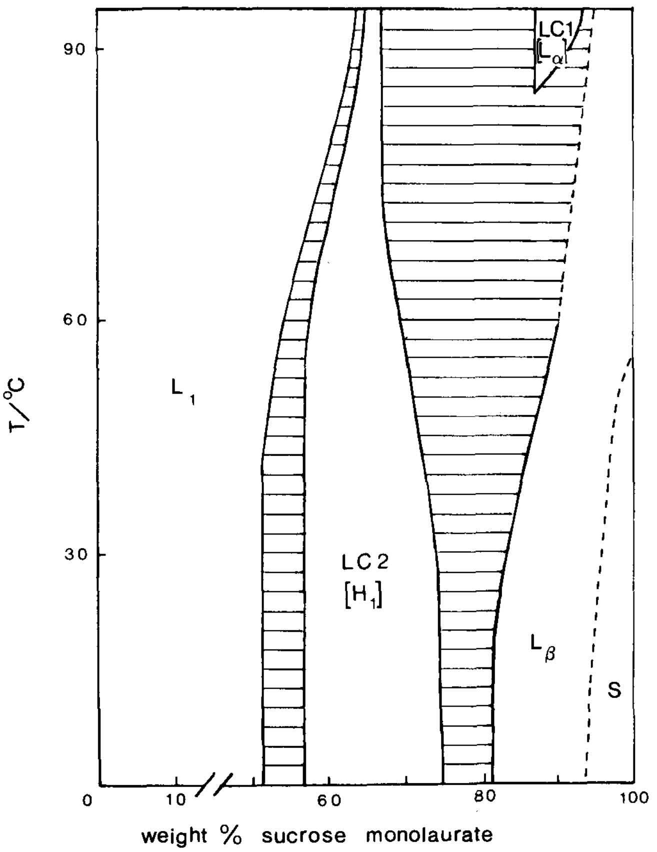

FIG. 1. Phase diagram of the sucrose monolaurate + water system over the temperature range 0-100°C. Dotted lines indicate boundaries not determined accurately.

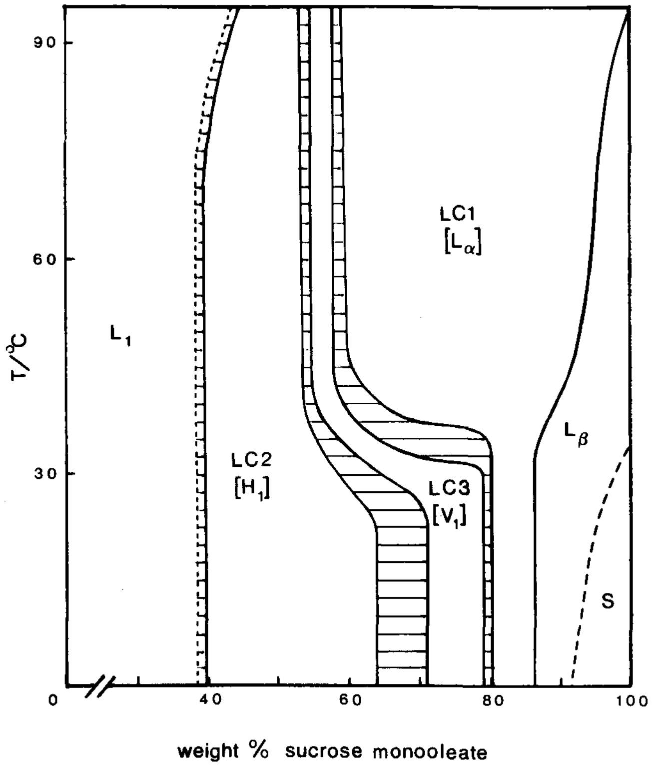

FIG. 2. Phase diagram of the sucrose monooleate + water system over the temperature range 0-100°C.

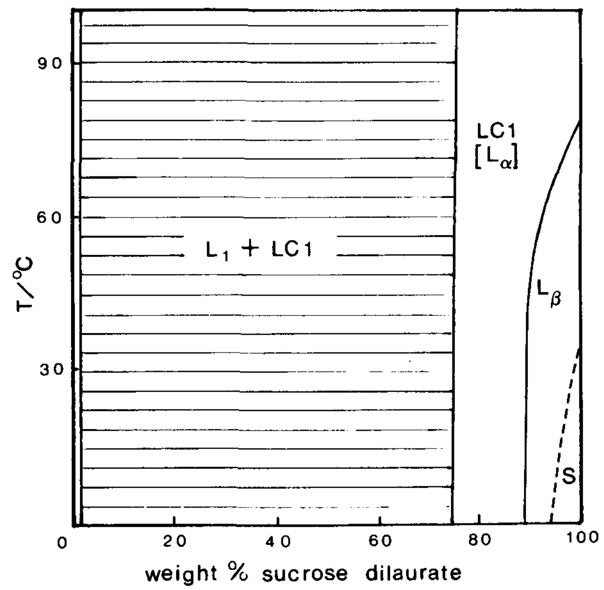

FIG. 3. Phase diagram of the sucrose dilaurate + water system over the temperature range 0-100°C.

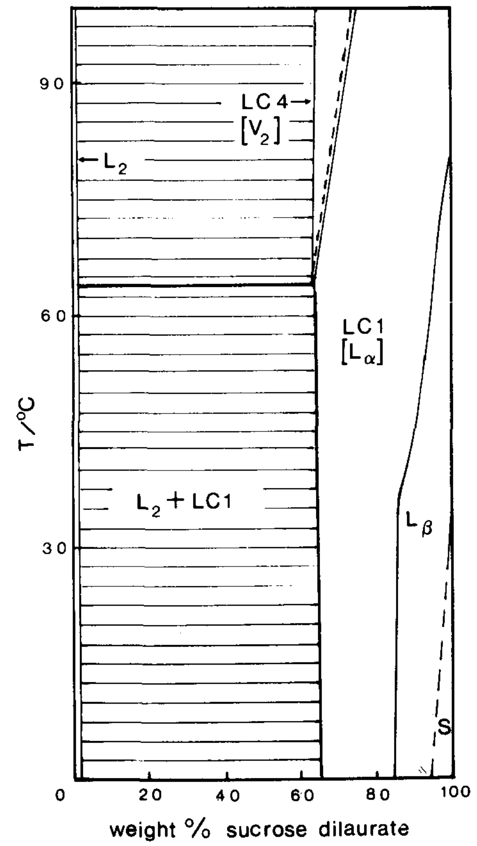

FIG. 4. Phase diagram of the sucrose dilaurate + n-decane system over the temperature range 0-100°C.

primitive textures similar to the mosaic textures of the lamellar phase; conoscopy identified the phase as uniaxially positive. Compositions above 87 wt% of this gel phase (L_β) changed to the LC1 phase on heating, identified as lamellar, L_α.

Sucrose monooleate + water. Sucrose monooleate possesses high water solubility, up to 39 wt% at 20 C, and an extensive L_1 region was observed (Fig. 2); compositions from 21-39 wt% showed streaming birefringence. On increasing the surfactant concentration, after a small two-phase region (~ 3 wt%), a highly viscous brightly birefringent phase (LC2) was found, which displayed fan-like textures; conoscopy gave a "flash figure" of negative optic axis. LC2 was identified as the hexagonal, H_1, phase. At higher surfactant concentrations, a highly mobile phase (LC1) was found which displayed textures typical of the lamellar phase (oily streaks and mosaic textures) and gave a positive uniaxial interference figure. Sandwiched between the LC1 and LC2 birefringent liquid crystalline phases at intermediate compositions, a non-birefringent phase of stiff consistency (LC3) was present. Conversion from LC2 to LC3 was extremely slow, sometimes taking many hours to complete. From the position of LC3 on the phase diagram, its highly viscous nature and that it was isotropic between crossed polars, LC3 was inferred to be the viscous isotropic phase V_1.

Sucrose dilaurate + water. Pure sucrose dilaurate is a white waxy solid, sparingly soluble in water; a narrow L_1 region occurs adjacent to the temperature axis (Fig. 3). Compositions up to 74 wt% exist as two phases in equilibrium over the temperature range investigated. Between 74-88 wt% at 20 C a single optically transparent highly birefringent phase of low viscosity (LC1) is present. This showed the oily streaks and mosaic textures of the lamellar phase, and its designation as L_α was confirmed by conoscopy and low

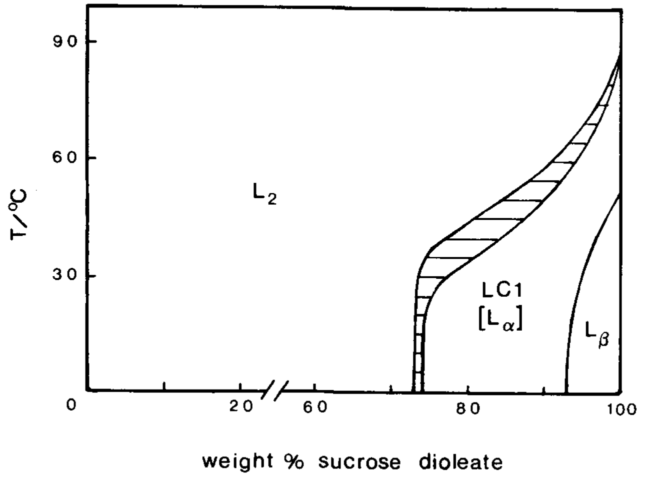

FIG. 5. Phase diagram of the sucrose dioleate + n-decane system over the temperature range 0-100°C.

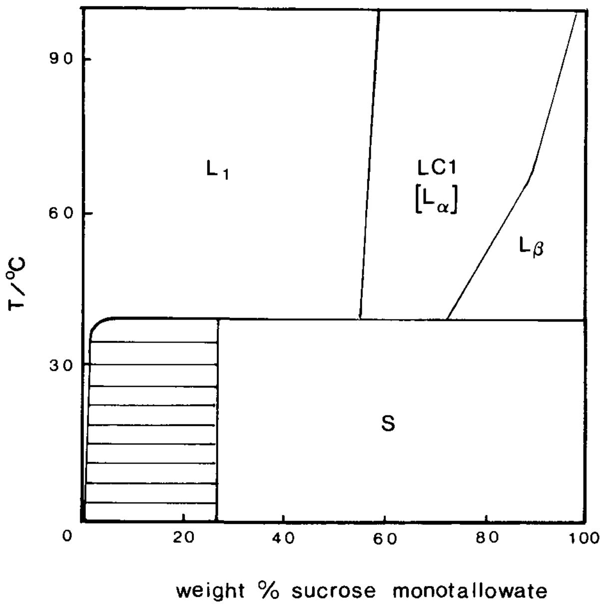

FIG. 6. Phase diagram of the sucrose monotallowate + water system over the temperature range 0-100°C.

angle X-ray diffraction. The gel phase, previously described, was present at surfactant concentrations greater than 90 wt%.

Sucrose dilaurate + n-decane. Sucrose dilaurate is sparingly soluble in n-decane at 20 C (0.09 % by wt), and the L_2 region is very narrow over the temperature range investigated (Fig. 4). Up to 63 wt%, two phases coexist; the lower phase is highly mobile and anisotropic. Above 64 C, two immiscible isotropic phases coexist (L_2 and LC4). At 20 C compositions between 63-85 wt% form a single highly birefringent liquid crystalline phase of low viscosity, displaying a mixture of oily streaks in a planar matrix and a mosaic texture. A positive uniaxial interference figure together with the observed textures indicated the L_α phase, confirmed by X-ray analysis. Above 64 C, the L_α phase started to form the isotropic LC4 phase, designated V_2. A phase adjacent to the surfactant axis displayed the characteristic properties of the gel phase, $L\beta$.

Sucrose dioleate + n-decane. Sucrose dioleate is very soluble in n-decane, and a large region of continuous isotropic phase, L_2, was observed (Fig. 5). At 20 C, the first phase change occurred at 72 wt% and birefringence was detected. After a small two phase region (~ 2 wt%) a single highly birefringent phase occurred (LC1); this was optically transparent, possessed low viscosity and had a uniaxially positive interference figure. It was confirmed as L_α by low angle X-ray. The gel phase, $L\beta$, was present at high surfactant compositions.

Sucrose monotallowate + water. Sucrose monotallowate has the fatty acid profile: 35% oleic, 31% palmitic, 25% stearic, small amounts of palmitoleic and linoleic acids. At ambient temperatures it is a white powder. Figure 6 shows the observed macroscopic changes. A Krafft boundary is indicated at 39 C. Below this temperature the surfactant is only slightly soluble and a two phase region occurs up to a concentration of 27 wt%; above this a hydrated solid phase is formed. Above the T_C line at 39 C, a single isotropic phase is formed at compositions up to 54 wt%; mixtures between 18 and 54 wt% exhibit streaming birefringence. On increasing the surfactant concentration, after a small two-phase region, an anisotropic phase, LC1, of low viscosity appears displaying oily streaks and mosaic textures. Conoscopic observation showed the phase to be uniaxially positive, and it was identified as the lamellar phase, L_α. Further increase in surfactant concentration gives a highly viscous phase of low birefringence, displaying the mosaic textures of the LC1 phase. This phase was designated as the gel phase, $L\beta$. DSC scans of 34, 67, 80 and 100 wt% compositions all showed a broad endothermic peak between 22 and 45 C.

The high Krafft temperature for sucrose monotallowate suggests the presence of some diester; that 5% of diester is present was confirmed by GLC. However, above the Krafft temperature the solubility is greater than would be expected from the anticipated phase behavior of the pure components, suggesting that mixed micelle formation is advantageous.

DISCUSSION

Sucrose monolaurate and sucrose monooleate show analogous thermotropic behavior to octyl, nonyl and decyl β-D-glucopyranosides (3). Crystals of the latter have a transition to an "intermediate" phase at temperatures from 57 to 68 C, and to a "smectic" liquid crystal phase from 68 to 72 C, which melts to form the isotropic liquid at temperatures from 110 to 133 C. The dialkyl esters by analogy with ionic surfactants would be predicted to form L_α, V_2 or H_2 mesophases. Aqueous solutions of the dialkyl polyoxyethylene surfactant, $(C_{10}H_{21})_2CHCH_2(OCH_2CH_2)_{10}OH$, show an extensive L_α phase changing to V_2 above 91 C in contrast to the predicted extensive H_1 phase, with possibly some V_1, for $C_{12}H_{25}(OCH_2CH_2)_{10}OH$ (7). Sucrose dilaurate and dioleate show lower transition temperatures both for the $L\beta$ to L_α and the L_α to isotropic liquid transitions than the monoalkyl esters. With water, sucrose dilaurate shows a more extensive L_α phase and no sign of the hexagonal phase exhibited by the monolaurate. However, the V_2 phase is found only by adding decane.

The factors determining the effect of headgroup size and alkyl chain length on the type of mesophase expected may be deduced from a consideration of those governing micelle shape (8). Possible micelle shapes are spheres, rods or discs. The volume per alkyl chain, v, surface area per chain, A_c, and the longest extension of the alkyl chain, 1_t, are related by

$$A_c > 3v/1_t \qquad \text{(sphere)}$$

$$A_c > 2v/1_t \qquad \text{(rod)}$$

$$A_c > v/1_t \qquad \text{(disc)}$$

Taking $1_t/\text{Å} = 1.5 + 1.265\ n_c$, where n_c is the number of carbon atoms embedded in the micelle core (n_c = 11 for sucrose monolaurate) (9) and calculating v from the density of undecane (10), then the limiting values for sucrose monolaurate are

$$A_c > 68.6\ \text{Å}^2 \quad \text{(spheres)}$$

$$68.6\ \text{Å}^2 > A_c > 45.7\ \text{Å}^2 \quad \text{(rods)}$$

$$45.7\ \text{Å}^2 > A_c > 22.9\ \text{Å}^2 \quad \text{(bilayers)}$$

$$22.9\ \text{Å}^2 > A_c \quad \text{(reversed phases)}$$

Thus, for the mesophases transitions would be expected in the order cubic (I_1)-hexagonal (H_1)-cubic (V_1)-lamellar-reversed phases.

If micelles are considered as hard-core particles, then packing constraints will determine the phase transitions. As the volume fraction of micelles is increased, so order/disorder transitions will be observed. Spherical micelles will pack into a cubic array, while long rod-shaped micelles will form a hexagonal array. The limiting volume fractions are 0.74 for face-centered cubic and 0.91 for a hexagonal phase. Discotic micelles will form the lamellar phase, but as this phase does not require the presence of solvent, the transition can take place between a volume fraction of zero and one. The actual volume fractions for order/disorder transitions are found experimentally to be in the range 0.7–0.8 of the close-packed values. These considerations do not take into account the fact that in reality there is a soft-core repulsion between micelles and also that the micellar aggregation number will affect the Gibbs energy of the system. However, the phase diagrams are consistent with the general picture outlined above. Surfactant-rich isotropic solutions of both the monolaurate and the monooleate show streaming birefringence, which is considered to indicate the presence of long rod micelles and herald the onset of the hexagonal phase (8). The isotropic phase of sucrose monotallowate also shows streaming birefringence, but no hexagonal phase was detected.

For the polyoxyethylene surfactants, $C_nH_{2n+1}(OCH_2CH_2)_mOH$, ($C_nEO_m$), the effect of increasing the alkyl chain length, n, for given headgroup size, m, can be studied in their phase diagrams with water (7). Thus, in the temperature range 0 to 30 C, whereas a small H_1 region is shown by C_8EO_6, a much larger region of H_1 is found for $C_{10}EO_6$, and for $C_{12}EO_6$ large areas of H_1 and L_α (with a small area of V_1 cubic sandwiched between) are shown. Similarly, $C_{12}EO_8$ exhibits H_1, V_1 and a small region of L_α phase, whereas $C_{16}EO_8$ shows H_1, V_1 and a large region of L_α in the same temperature range. Similarly, sucrose laurate forms a more extensive H_1 region than the oleate of longer alkyl chain length. However, for the monoglycerides, increasing the length of the alkyl chain apparently decreases the stability of the lamellar phase (1). Over the temperature range 40 to 100 C, the viscous isotropic phase appears with increasing temperature for monostearin, whereas it is not shown by monolaurin, and monoolein shows both a viscous isotropic and a small hexagonal region as temperature increases, but these may be the reversed cubic, V_2, and reversed hexagonal, H_2, phases. Most of the C_nEO_m series show a lower consolute temperature, implying that the headgroup hydration decreases with increasing temperature for a given alkyl chain length; this would favor the lamellar phase at higher temperatures, and this is supported by the phase diagrams (7). The sucrose surfactants showed no sign of a cloud point in the temperature range studied consistent with the strongly hydrophilic character of the sucrose head group. For the sodium soaps, as the alkyl chain length increases, the L_1/H_1 and H_1/L_α transitions move to lower surfactant concentrations as exemplified by sodium laurate and stearate (octadecanoate) (10,12); however, although this is also true for sodium oleate (*cis*-9-octadecanoate), the transitions are much closer to those of the laurate, and the upper stability limit of the L_α phase is some 40 C lower.

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