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Water incorporation into a micellar-lamellar phase (dodecyl maltoside-water)

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Many alkylated sugars are surfactants, and show lamellar phases which prove to be identical to those of more conventional surfactants. Most, if not all, previous investigations focus on the behaviour of these compounds in pure form. Dodecyl maltoside shows the same lamellar phase as when dry, but on the addition of water the layer spacing expands, and on addition of more water, a hexagonal phase forms. The area per head group increases substantially with water addition, indicating that the water is incorporated into the layers, possibly at the head groups. We suggest that the hexagonal phase is the system's answer to the frustration caused by a large head group area compared with that of the tails.

1. Introduction

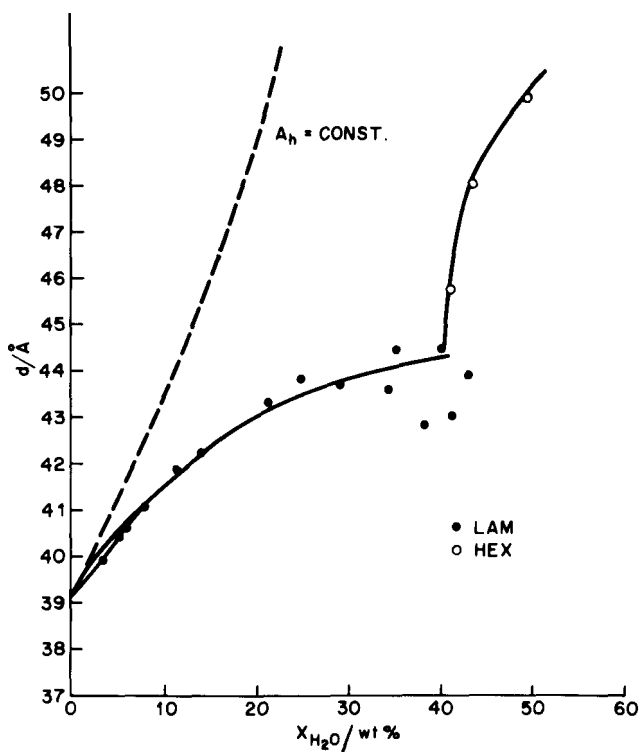
Recently, there has been some interest in the mesophases exhibited by alkylated carbohydrates, such as dodecyl glucoside. These compounds consist of a sugar or sugar-like head group attached to an alkyl tail of at least six carbons in length. The sugar heads are hydrophilic, and the tails are hydrophobic, thus giving rise to surfactant properties. These compounds often form lamellar mesophases [1], which have been shown to be identical to those of traditional surfactant-water systems [2].

In pure form, dodecyl maltoside has a mesophase which is identical to that of dodecyl glucoside [3]. The unusual thing about this compound is that the head group has two sugar rings, not just one. This large head group seems to make the mesophase more stable than those of single-ring glucosides. Given a surfactant that has been characterized in pure form, the traditional thing to do next is to add water. The results of this addition are what we shall discuss in this paper.

2. Experiments

Dodecyl maltoside (DM) was purchased from Fluka, and used as received. Mixtures were made by adding water and DM to vials, which were then sealed and allowed to sit at 90°C for a day. The resulting material appeared to be uniform, and had sharp small-angle scattering features, indicating uniformity of composition.

Small angle X-ray scattering (SAXS) was done on a rotating anode tube with a curved-crystal focusing monochromator and a position-sensitive detector. Spectra were taken at room temperature. Some of the wetter samples were stable at room temperature, and the rest were metastable, staying in the lamellar phase long enough for spectra to be taken. We measured the d spacings for the lamellar phase, and confirmed that the hexagonal samples were hexagonal by seeing two peaks, with distances in the ratio of $1 : \sqrt{3}$. Optical textures were also characteristic of hexagonal phases. We see no evidence for cubic phases in contact preparations by optical microscopy.



d spacing versus composition for the DM-water system. Filled circles represent samples in the lamellar phase. Open circles are for the hexagonal phase. For the hexagonal samples, the plotted value is the average of the longest spacing and $\sqrt{3}$ times the second-longest.

3. Results and discussion

The figure shows the d spacing versus composition plot. Compositions are in wt % water. The three points past the slope change represent the data for the longest d spacing in the hexagonal phase. The dashed line represents what the d spacing for the lamellar phase would be if the area per head group remained constant. It is clear that the area per head group increases with increasing water content. The hexagonal phase occurs when there are about 21 water molecules per head. Each head can form about eight hydrogen bonds, so the heads are fully hydrated at this composition.

Where does the water go? If it went between the layers, it would swell the structure to the extent shown as the dashed line. Thus, a large part of the water must stay in the layers. The obvious place for the water is in the area of the head groups. It is believed [3] that the head groups are inter-digitated in the dry material. The water may cause the heads to overlap less, thus increasing the layer spacing. This effect may be why the layer spacing increases at all. Another possibility is that there may still be some water between the layers.

As more water enters the layers, the area per head group increases, forcing the tails to spread out over larger areas. At some point, the tails must become too spread out for a flat layer to be stable. We suggest that the hexagonal phase is the result of this frustration. In a direct hexagonal phase, the heads can take up more area than the tails. This structure can thus accommodate bulky, hydrated heads and thin tails at the

same time. An elegant mathematical treatment of frustration effects has been given by Charvolin and Sadoc [5].

Suppose the hexagonal phase consists of cylinders of fixed size embedded in water. As the water content increases, so does the spacing between the cylinders. Now assume that the volume of the cylinders equals the volume of surfactant, and that the cylinders have a density of 1. Then, the radii of the cylinders must be 18.41 Å, 19.11 Å and 18.51 Å, for surfactant contents of 58.85, 56.46 and 49.67 per cent, respectively. That these numbers are so close to each other suggests that the model of fixed structures separated by varying amounts of water is correct. Now how do we interpret these numbers? The cylinder radius is very close to half the d spacing for the dry sugar, $d_{\text{um}} = 37.64$ Å. In the interdigitated model of the lamellar phase, the d spacing is twice the tail length plus the length of a head group. Half of this is the tail length plus half a head length. Consider a model in which the tails form a tightly-packed rod, and the heads stick out, with water penetrating into the head layer. The resulting micelle is an oily rod, studded with sugar groups. Depending on the details of how the water and heads mix, this could easily have an effective radius equal to the tail length plus half the head length, the latter term being due to the surface, which is part heads and part water.

How do these results compare with those found for other surfactants? Lamellar \leftrightarrow hexagonal transitions, usually with an intervening cubic phase, are known from studies of hydrated lecithins [5, 6], and from the AOT-water system [7]. In most of these systems, there is a cubic phase between the lamellar and hexagonal phases, though there are exceptions to this rule [8]. We see no such phase in this system, at least near room temperature.

Lamellar phases fall into two classes with respect to their behaviour on water addition: swelling and non-swelling [9]. Members of the former class, for example AOT, have constant area per head group, thus showing a lattice spacing which varies linearly with the reciprocal of the surfactant volume fraction. The latter class shows nearly constant lattice spacings, thus indicating that most of the water is found within layers. Potassium alkanoate soaps fall into this class. Dodecyl maltoside falls in between these two limits, in that neither the lattice spacing nor the head group area is constant.

4. Conclusions

We have performed the first investigation of the effect of water on an alkylated sugar surfactant. The effect of water on the mesophase of the non-ionic surfactant dodecyl maltoside is to increase the area per head group. One of the consequences of this increase is the formation of a hexagonal phase. This system, and others like it, may be useful as test systems in which the head group area can be varied, especially since it is non-ionic, so there is no added complication from electrostatic forces. Therefore, this system exhibits the effect of head-tail frustration in a particularly pure, uncluttered manner.

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