
01 Jan 1986

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Recommended Citation

S. Friberg et al., "A Non-aqueous Lamellar Liquid Crystal With An Ionic Surfactant-long Chain Alcohol Combination," *Colloids and Surfaces*, vol. 19, no. 2 thru 3, pp. 249 - 253, Elsevier, Jan 1986.

The definitive version is available at [https://doi.org/10.1016/0166-6622\(86\)80339-0](https://doi.org/10.1016/0166-6622(86)80339-0)

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A NON-AQUEOUS LAMELLAR LIQUID CRYSTAL WITH AN IONIC SURFACTANT—LONG CHAIN ALCOHOL COMBINATION

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(Received 3 January 1986; accepted 4 February 1986)

ABSTRACT

A non-aqueous lamellar liquid crystal of sodium dodecyl sulfate, decanol and glycerol was prepared and compared with its aqueous counterpart.

The results show that the stability of the liquid crystal with glycerol is critically dependent on the surfactant/alcohol ratio, whereas the liquid crystal with water is stable over a wide range of this ratio.

The interlayer spacing was smaller for the glycerol system than for the water system at finite amount of solvent, but the value extrapolated to zero solvent content was identical for both systems. This result indicates that glycerol perturbs the amphiphilic layer more than water, but that the organization of the amphiphilic chains per se is identical in the glycerol and the water systems.

INTRODUCTION

Lyotropic liquid crystals based on water as solvent have been well characterized regarding composition [1], structure and dynamics [2–4]. Corresponding systems with a non-aqueous solvent have recently been introduced [5] and investigations have been limited to lecithin systems [6–10], with one exception [11].

This means that comparisons with the water/ionic surfactant/long chain alcohol systems of Ekwall [1] have not been possible; an obvious impediment to progress in the field.

With this note we present the first comparison of water and glycerol lamellar liquid crystals stabilized by a combination of an ionic surfactant (sodium dodecyl sulfate) and a long chain alcohol (decanol).

EXPERIMENTAL

Materials

Sodium dodecyl sulfate (BDH) was recrystallized twice from ethanol; decanol [Aldrich (99%)] was used without further purification; glycerol (Aldrich) was of 99.5% grade, from which water was removed by azeotropic distillation to a level of 0.05% according to Karl Fisher titration; water was twice distilled.

Determinations of phase regions

The extent of the liquid crystalline phase was determined by careful optical inspection by microscope, using polarized light. The high water limit was confirmed by observing the change from the two-phase area of glycerol plus alcohol solutions, to the three-phase glycerol plus alcohol solutions plus liquid crystal to the left of the diagram. This tie-line separating the two- and three-phase areas is detected exactly from the appearance of optically anisotropic species in the microscope. Hence, the maximum water or glycerol content of the liquid crystal is given a safe lowest value.

Small-angle X-ray diffraction

Small-angle X-ray diffraction measurements were obtained by use of a Kiessig small-angle camera from Richard Seifert. Ni filtered Cu radiation was used, and the reflection determined by a Tennelec position sensitive detector system (Model PSD-1100).

RESULTS

The regions of stability are given in Fig. 1. The aqueous system provided a huge liquid crystalline area approximately covering a region with a water/surfactant ratio greater than 0.5, a surfactant/cosurfactant ratio greater than 0.4 and a cosurfactant content in excess of approximately 10%. The maximum amount of water was 91%. The liquid crystalline phase with glycerol, on the other hand, showed a small crescent-shaped area with a cosurfactant/surfactant weight ratio of approximately 2. Its maximum glycerol content was 96%.

The small-angle X-ray diffraction patterns gave the interlayer spacings for both systems, depicted in Fig. 2. The glycerol system gave smaller interlayer spacings than the aqueous system for identical decanol/sodium dodecyl sulfate ratio, and the increase of spacing was also smaller. However, the value extrapolated to zero solvent content was identical for the aqueous and the glycerol systems.

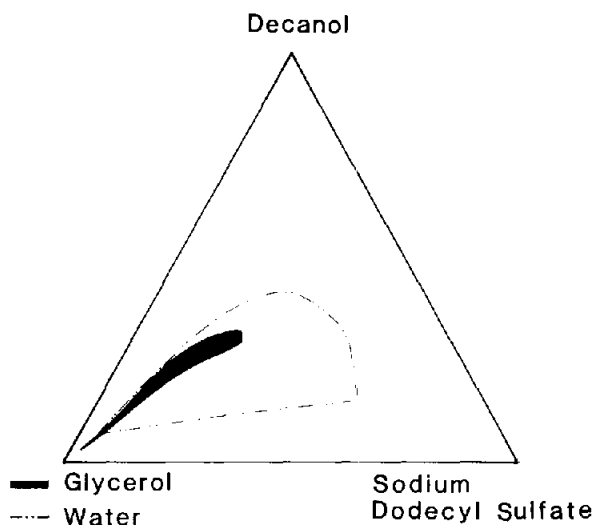


Fig. 1. The region for the lamellar liquid crystal in the sodium dodecyl sulfate/decanol system with water (---) was huge, while the region with glycerol (black) was limited.

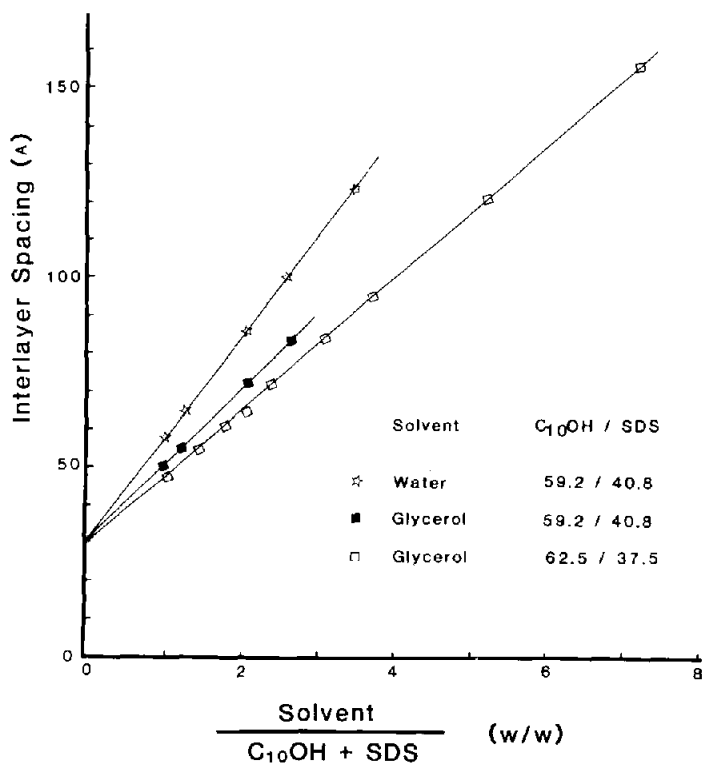


Fig. 2. The interlayer spacing of the lamellar liquid crystal with glycerol as solvent is less than that in the aqueous system ($C_{10}OH$ = decanol; SDS = sodium dodecyl sulfate).

DISCUSSION

The results provide evidence of non-aqueous liquid crystals with a polar solvent stabilized by an ionic surfactant/long chain alcohol. The necessary condition appears to be an extended chain length both for the alcohol and the surfactant in comparison with the aqueous systems. In these latter, a hydrocarbon chain of six carbons is sufficient for the formation of a liquid crystal; the glycerol system obviously requires approximately double that number.

The reason for this lower stability of the glycerol system may be found in the different interactions of glycerol and water with the liquid crystal, as indicated by the X-ray results. The glycerol system gave a smaller increase in the interlayer spacing with added solvent than the water system, Fig. 2. A smaller increase with added solvent indicates an enhanced disorder of the amphiphilic chains due to higher penetration of the solvent. The latter factor per se means a reduction in interlayer spacing, but it is difficult to perceive that factor operating without an accompanying disordering of the amphiphilic chains. The lower degree of order in the glycerol system may be a contributing factor to the instability of the glycerol systems with short chain amphiphiles.

The results also show that the stability of the lamellar liquid crystal with glycerol as a solvent is more strongly dependent on the ratio between cosurfactant and surfactant. Several factors may be put forward to explain the narrow range of cosurfactant/surfactant ratio for stability. One obvious influence is the changed electric-double-layer characteristics experienced when glycerol replaces water as solvent. To date, the treatment of these phenomena is comparatively limited [12,13] and not sufficient to apply in the present case. Another factor is the fact that enhanced content of alcohol led to a reduction of the interlayer spacing, Fig. 2. This indicates a pronounced change in solvent penetration with alcohol/surfactant ratio; a destabilizing factor. A final factor is the difference in surfactant solubility in glycerol and water. Water and sodium dodecyl sulfate display mutual solubility to approximately 60% by weight of the surfactant, while the solubility in glycerol is less than 1%. This means that the right-hand limit of the liquid crystalline regions for the aqueous system also retains the high surfactant/water ratio when the cosurfactant concentration is low and the liquid crystalline region displays the shape shown in Fig. 1. In the glycerol system, on the other hand, the surfactant solubility is rapidly reduced at high surfactant/cosurfactant ratios giving the crescent-shaped region for the glycerol liquid crystal shown in Fig. 1.

Another interesting feature of the glycerol diagram is the extremely high solvent content of the lamellar liquid crystal. The stability of a lamellar system with 96% glycerol and with interlayer spacings in excess of 200 Å is an interesting problem.

ACKNOWLEDGMENT

This research was supported by NSF Grant No. NSF CPE 8213378.

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