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01 Sep 1987

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### Recommended Citation

S. Friberg et al., "Dynamic Structure Of A Nonaqueous Lamellar Liquid Crystal: Comparison With The Aqueous Case," *Langmuir*, vol. 3, no. 5, pp. 735 - 737, American Chemical Society, Sep 1987.

The definitive version is available at <https://doi.org/10.1021/la00077a028>

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is the following: the  $P$  value of 1-PeOH is larger in POE23 than in POE4 solutions when expressed on the mole fraction scale (460 and 280, respectively) but the reverse is found if the molar scale is considered (7.4 and 13.3).

Similar situations when different concentration scales are considered are not uncommon in the literature.<sup>41,42</sup> Interpretations have been proposed which take into account the relative size and number of monomers per aggregate for nonionic surfactants with the increase of the oxyethylene chain length.<sup>42</sup> However, the specific problem to deal with is that of the ill-defined notion of the micellar volume phase which might lead to calculation artifacts. An alternative to previous approaches is suggested below.

Studies of the cmc of nonionic surfactants series with various oxyethylene (OE) chain lengths<sup>42,43</sup> have led to the suggestion that beyond a number equal to 6, the oxyethylene groups' free energy properties are identical with

that of the monomer surfactant. We may apply crudely this finding to micellar solubilization in the case of POE23 by assuming that beyond the value of 6, the EO groups do not participate to the solubilization process. This hypothesis is not physically unsound for the particular solute studied considering the close  $P(x)$  values with the two nonionic surfactants studied. POE23 might be considered then as a hypothetical POE6 surfactant (keeping of course the same experimental  $P(x)$  value): using the corresponding partial molar volume we obtain  $P(c) = 18.1$ . The  $P$  trend for POE4 and POE6 (or POE23) is now the same on both mole fraction and molar concentration scales, a more reasonable situation than the previous one.

Thus one of the main advantages of gas chromatography over other methods of solubilization determination is the direct measurement of vapor activity in the mole fraction scale, avoiding the complex evaluation of the micellar volume phase necessary for molar basis partition coefficients.

**Registry No.** LiDS, 2044-56-6; LiFOS, 29457-72-5; SDS, 151-21-3; POE23, 9002-92-0; SDeS, 142-87-0; POE4, 5274-68-0; 1-PeOH, 71-41-0; C<sub>10</sub>Br, 2082-84-0.

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## Dynamic Structure of a Nonaqueous Lamellar Liquid Crystal: Comparison with the Aqueous Case

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*Received November 1, 1986. In Final Form: January 16, 1987*

The lamellar phase of sodium dodecyl sulfate/decanol/glycerol has been compared to the analogous water-based system. Results of NMR studies of deuteriated alcohol and surfactant showed the bilayer to be more disordered in the nonaqueous case than in the phase made with water. The order profiles of the two systems, however, were of the same form, implying that the same essential packing requirements applied to each case. The overall increase in dynamic disorder observed in the glycerol system is a result of a transversely more disordered bilayer/solvent interface.

### Introduction

Recent attention has been focused upon the associated surfactant phases formed in nonaqueous media.<sup>1-9</sup> The structure and dynamics of these systems have not been characterized to the extent found for comparable aqueous systems.<sup>10-12</sup> It is obvious that a direct comparison with a well-characterized aqueous system<sup>13</sup> such as water/ionic surfactant/long-chain alcohol would give insight to some of the consequences of changing the solvent. This preliminary paper presents, to the best of our knowledge, the first comparison of water- and glycerol-based lyotropic lamellar liquid crystals stabilized by a combination of an ionic surfactant (sodium dodecyl sulfate) and a long-chain alcohol (*n*-decanol). <sup>2</sup>H NMR spectroscopy has been utilized to give the order parameter profiles of the bilayer interiors of both systems.

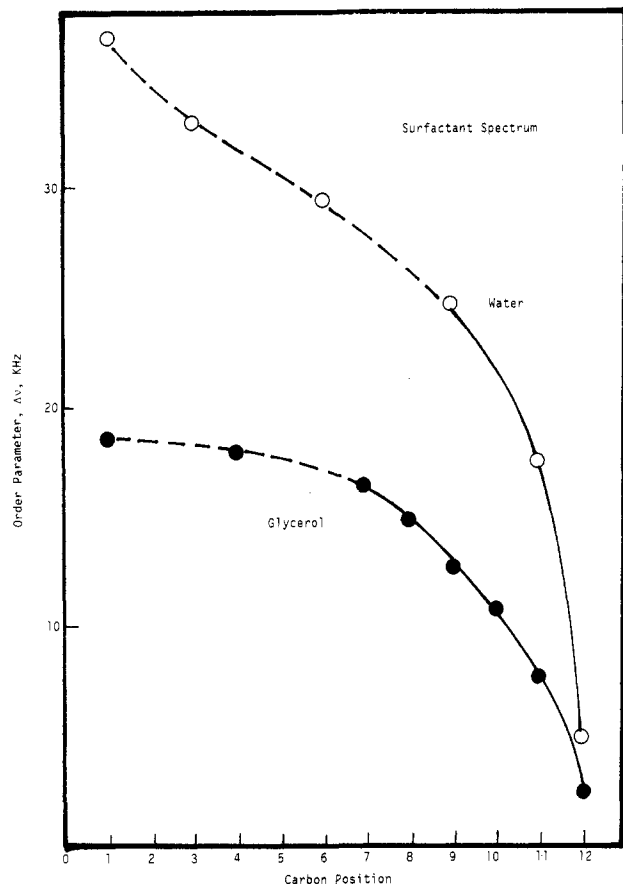
### Experimental Section

Sodium dodecyl sulfate (SDS) from BDH Chemicals was recrystallized twice from ethanol and the *n*-decanol (Aldrich

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**Figure 1.** Order parameter for deuterated sodium dodecyl sulfate in a lamellar liquid crystal with volume ratios decanol/sodium dodecyl sulfate/solvent of 28/17/55. Solvent: (O) water; (●) glycerol.

Chemical Co. (99%) used without further purification.

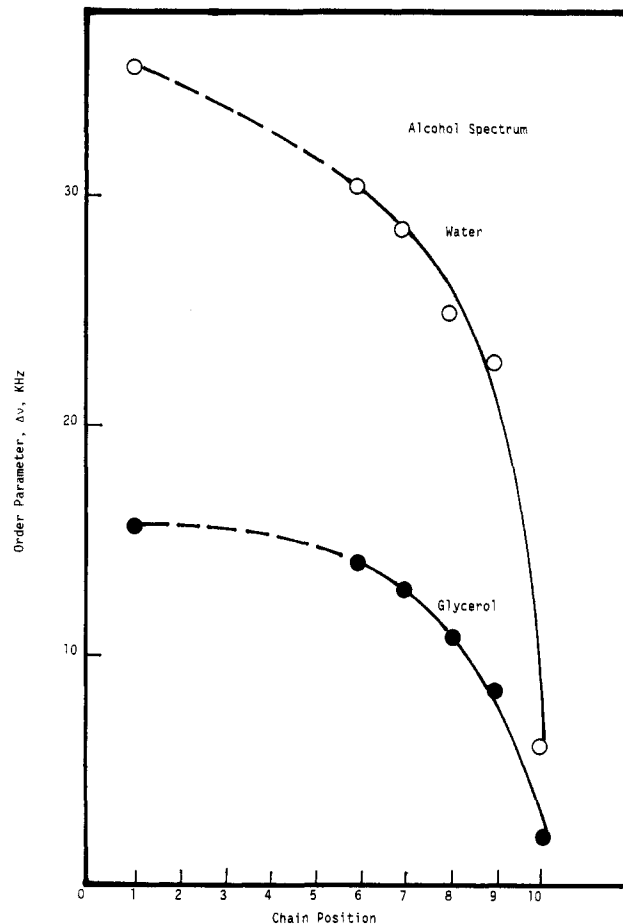
Water was removed from the glycerol (Aldrich (99%)) by azeotropic distillation with benzene to ca. 0.05% as determined by Karl Fischer titration. The water used to make the aqueous phase was deionized and twice distilled.

Lamellar samples were mixed as previously described<sup>14</sup> until they had a homogeneous appearance when viewed through crossed polars.

Perdeuterated surfactant (SDS-*d*<sub>25</sub>) and alcohol (decan-*d*<sub>21</sub>-ol) were from Cambridge Isotopes (MA) and used without further purification. Samples containing deuterated material were made with ca. 5% of the total component as the deuterated analogue in order to reduce the possibility of altering the phase behaviour. <sup>2</sup>H NMR measurements were made by using Nicolet and Varian XL-300 pulsed spectrometers operating at 41 MHz. Limitations of the probe and transmitter bandwidths lead to distortions of the spectra due to the large splittings involved (ca. 40 KHz.). These were reduced as much as possible by use of either the quadrupolar echo or quantum cycling sequence.<sup>15,16</sup> All measurements were made at 303 K and required between 500 and 5000 pulses to give satisfactory signal/noise ratios.

## Results

The <sup>2</sup>H NMR spectra of SDS-*d*<sub>25</sub> in the lamellar phase of water/surfactant/decanol comprised 12 overlapping "powder" patterns from which nine quadrupolar splittings in the range 5–40 KHz can be distinguished; whereas, for decan-*d*<sub>21</sub>-ol, six such splittings in the range 2–38 KHz are



**Figure 2.** Order parameter for deuterated decanol in a lamellar liquid crystal with volume ratios decanol/sodium dodecyl sulfate/solvent of 28/17/55. Solvent: (O) water; (●) glycerol.

seen. Similar spectra were observed for the glycerol/surfactant/decanol system with again nine splittings resolved for the surfactant and six for the alcohol all falling in the range 2–20 KHz. Order parameters for the two systems are given in Figures 1 and 2. It was not possible to assign a number of chain segments with a given order parameter as the instrumental distortion of the spectra did not allow simulations of the intensities.

The order parameters for the aqueous system, Figures 1 and 2, were at the level of and varied with the carbon location along the chain in accordance with earlier results<sup>11,12</sup> with the values for the alcohol and the surfactant identical. In the glycerol system, on the other hand, the order parameters of the surfactant were consistently 0.55–0.45 times those in the aqueous system and those of the alcohol 0.45–0.35 times the ones for the alcohol in the aqueous system. The lower values were for the methyl group and adjacent methylene groups.

## Discussion

There are two features of the results, which should be related to the lamellar liquid-crystalline structure in the glycerol system.

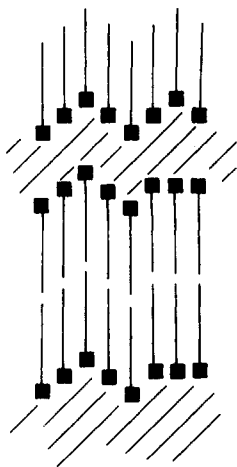
In the first instance the order parameters of the amphiphiles are at values less than one-half of those in the aqueous system, and, second, in the glycerol system the values for methylene groups close to the polar group were significantly lower ( $\approx 15\%$ ) for the alcohol than for the surfactant.

A first assumption that the difference in order parameter ought to be ascribed to an increase in the available area per molecule<sup>17</sup> is not sufficient to explain the data. A

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**Figure 3.** Staggered conformation in a lamellar liquid crystal would allow a low order parameter without a corresponding increase of the area per molecule: (|) hydrocarbon chain; (■) polar group; (//) glycerol.

comparison with the area-order parameter variation found for the potassium laurate/water lamellar phase<sup>18</sup> shows a reduction of the order parameter to approximately one-half the value to require an increase of 30–40% in the area/polar group. But low-angle X-ray scattering studies of the glycerol/SDS/decanol system<sup>19</sup> have indicated only a small (<10%) increase in the area per amphiphile when replacing water by glycerol. The present decrease of approximately 50% in the order parameters as observed in Figures 1 and 2, when water is replaced by glycerol at the same volume ratio, is obviously too large to be accounted for in terms of changes in the area/polar group. With this in mind we assume the difference to be related to another phenomenon resulting in lower values in the glycerol system.

Calculation of the effective length of the alkyl chains from the order parameters<sup>20</sup> would give bilayer thicknesses of 22.2 Å in the aqueous case and 10.6 Å for the glycerol system. These values are less than the value obtained from the X-ray studies which give a bilayer thickness of ca. 30 Å.<sup>19</sup> The reason for this discrepancy is that the calculation is valid only for the case of no motion in a direction parallel to the director.<sup>20</sup>

A motion parallel to the director will not per se change the order parameter, but it appears reasonable to assume that the resulting staggered configuration as in Figure 3 would give enhanced disorder. Such a staggered organization will not cause a significant difference in the area per amphiphile but would allow a considerably enhanced disorder.

This assumption agrees well with the following facts. Preliminary determinations<sup>21</sup> of the counterion binding in

the system showed considerably enhanced splitting, indicating enhanced counterion binding for glycerol systems compared to water values. Such a difference would mean both a weakened electric double layer repulsion and a greater number of nondissociated ionic surfactant molecules. These results are reasonable and expected because glycerol has considerably lower solubility of salts than water. In addition it should be noted that both these changes would facilitate translational movement parallel to the director.

The more "hydrophobic" properties of glycerol in comparison with those of water should allow more of this transverse movement. In this context, it is essential to observe that the reduction of order parameters for the alcohol was greater than that of the ionic surfactant. It appears reasonable to assume more enhanced transverse movement of the alcohol with reduced difference in hydrophobicity between the polar solvent and the hydrocarbon chain moiety of the amphiphilic bilayers.

Hence, the data indicate that there is some added flexibility of the bilayer surface because of translational motion along the long-chain axis when the solvent is changed from water to glycerol. This results, in turn, in an overall increase in disorder of the bilayer interior although the organization of the amphiphilic chains per se are similar.

It should be observed that the reduction in order parameter is more pronounced for the methylene groups closer to the methyl group. This fact is in accordance with the staggered configuration in Figure 3, in which the transverse change of the methyl group should not reduce its order parameter, but the corresponding movement of the polar groups should.

An enhanced disordering of this kind has recently been found in systems containing nonionic surfactants.<sup>22</sup> Enhanced interface flexibility and a reduced repulsive interaction across the bilayers of the solvent regions may be the source of the nonaqueous system's sensitivity to the cosurfactant/surfactant ratio.<sup>7</sup>

The results also offer a timely explanation for the fact that the nonaqueous systems with sodium dodecyl sulfate as cosurfactant do not form lamellar liquid crystals when combined with hexanol in contrast to the aqueous systems.<sup>23</sup>

In addition it may be observed that recent investigations<sup>23,24</sup> into nonaqueous "microemulsions" strongly indicated these not to be microemulsions with a well-defined glycerol/hydrocarbon interface but unstructured solutions. An added transverse flexibility would have the effect of transforming a microemulsion with defined oil/water interface to a structureless critical solution.

In summary, it appears that a suggestion of enhanced flexibility parallel to the director should be a useful concept in order to understand the differences between aqueous and glycerol systems.

**Registry No.** SDS, 151-21-3; *n*-decanol, 112-30-1; glycerol, 56-81-5.

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