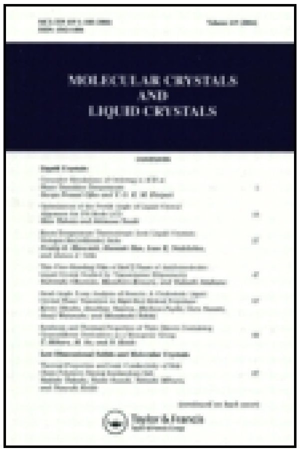

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Preparation of Sodium Decylsulphate: Physical Chemical Measurements and Elaboration of a Ternary and a Quaternary Lyotropic Phase Diagram

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Preparation and analysis of sodium decylsulphate, as well as the elaboration of a ternay and a quaternary phase diagram are here presented. The lyomesophases were studied by: polarizing microscopy, small angle X-ray scattering, densimetry and refractometry. The results will be used as basis of comparison in subsequent articles for the related surfactants sodium decylphosphate and sodium decylsulphonate in lyotropic systems.

Keywords: Sodium decylsulphate; phase diagrams; density; refractometric and X-ray analysis

INTRODUCTION

The first lyotropic nematic, susceptible to alignment by a magnetic field, was describe by Lawson and Flautt [1]. The surfactant used was sodium decylsulphate (SDS) and the original system was quaternary (SDS + *n*-Decanol + Na_2SO_4 + H_2O). Since then, SDS systems have been studied by many researchers [2 – 6] using different techniques (microscopy, X-rays, NMR, etc.). SDS in binary, ternary, quaternary or more complex systems has been used and almost all types of measurements performed, but the phase diagrams for SDS systems are rare. Hendrikx and Charvolin [2] have recently presented a ternary (SDS + *n*-Decanol + water) phase diagram, but limited to only one temperature (23 ± 1) C. Yu and Saupe [5] also presented a ternary system but in this case the solvent was D_2O and the decanol concentration was constant (7.0 wt %). We think that the probable causes the rarity of phase diagrams for the SDS systems are the thermal instability [7] of the surfactant and the difficulty of preparing SDS pure enough to reproduce a coherent topology on the phase diagram. Our objective was to prepare large quantities of sufficiently pure surfactant to obtain reliable phase diagrams.

Phase diagrams are useful because they provide information about the thermodynamic conditions under which a given mesophase exists, enabling the researcher to choose the sample which results in a specific desired phase in a known composition\temperature range. Here independent and complementary techniques namely polarizing microscopy, small angle X-ray scattering, densimetry and refractometry were used to determine the phases and the phase behaviour at the boundaries between phase transitions.

EXPERIMENTAL SECTION

Surfactant Preparation

The surfactant SDS was prepared as described by Dreger *et al.* [8]. The *n*-decanol (DeOH), purchased from Merck, was double distilled prior to sulfonation. To extract the surfactant, after the inorganic salts were removed by filtration, we distilled the remaining butanol under vacuum and controlled temperature (around 30 mm of Hg and 60 C). The crude surfactant was solubilised in hot ethanol (50 – 60 C), filtered and twice recrystalized from ethanol. We maintained temperature at values as low as possible, during all preparation and drying process as it is an important point to avoid the undesirable hydrolysis of the surfactant and ^{1}H NMR (D_2O, 200 MHz): $\delta = 0.9(t, CH_3)$; $1.3(m, 7CH_2)$; 1.7(quint., CH_2); $4.1(t, CH_2—O)$ have confirmed the surfactant prepared. A CHN analysis was made and the result (C(%) – Measured: 46.00/Calculated: 46.15 and H(%) – Measured: 08.19/Calculated: 08.08), were considered acceptable and were reproducible within a range of 0.5%. Also the measured CMC of $3.2\ 10^{-2}$ M (Analion Condutivimeter Mod. C-701 at 25,0 C) is in agreement with the literature [8].

Sample Preparation

Sample components were weighed in culture tubes using a Mettler balance with a precision $\pm 5.10^{-5}$ g. The tubes were sealed and the components were mixed for 48 to 72 hours, depending on the viscosity of the sample, until a homogeneous sample was formed.

Microscopy Study

To examine the texture and determine phase transition temperatures, sealed microslides were prepared and checked using a hot stage (Mettler FP-52) and polarised light microscopy (Leitz Wetzlar-Ortholux).

X-ray Study

For X-ray diffraction studies we developed as small angle diffraction camera with $|s|_{MIN} = 1.2.10^{-2}$ Å^{-1} (where $|s| = 2\sin\theta/\lambda$) using filtered Cu K_α radiation. Temperature control was better than 100 mK. The samples were sealed in glass capillaries ($\phi = 0.7$ mm) and X-ray diffraction patterns were obtained using flat film technique.

Density Study

The density was determined from the oscillation period of a U tube using a PAAR DMA 60 densitometer. The sample temperature was controlled (better than 5 mK) by a Heto-CB7 ultrathermostat.

Refratometry Study

The refractive indices were measured using a Abbe refratometer (Atago/3T) with an accuracy of 2.10^{-4} and the sample temperature control was 200 mK.

RESULTS AND DISCUSSION

The phase diagrams were determined by examination of at least three independent samples at each concentration in sealed microslides. The transition temperatures were normally measured at 2 K/min (heating) and slower/faster rates were used when necessary. We were careful to avoid leaving the sample at: 1) temperatures corresponding to a two phase region which can cause the development of concentration gradients; 2) high temperatures for more than a couple of minutes because the thermal instability of the surfactant might induce hydrolysis and consequent changes in sample composition [7].

To built the phase diagram of a ternary system (SDS + DeOH + H_2O) we maintained a constant ratio of $SDS/H_2O = 0.74(0.05)\%$, weight (molar) and varied the concentration of DeOH from 0 to 7.5 (1.50)% Figure 1 shows the phase diagram. There are four single lyomesophases present in this SDS ternary system: (I) isotropic; (H) hexagonal; (N_C) nematic calamitic and (G) coagel, and two phase region: (H + I) and $(N_C + H)$. Above 5.2 (1.02)% of DeOH a nematic calamitic (N_C) single phase region appear. The (N_C) region is present at lower temperatures and on increasing temperature passes through a two phases region $(N_C + H)$ and then to the H phase, the temperature most stable phase. The (N_C) phase was identified as a nematic phase by texture and the optical sign was negative as determined using a gypsum compensator. The transition $(N_C) \rightarrow (N_C + H)$, as a function of temperature, was checked by examining the characteristic patterns of small angle scattering. The limits of DeOH concentration in the phase diagram are determined by the appearance of only an isotropic phase at low concentration and at high concentration we could not prepare homogeneous samples.

Figure 2 shows the phase diagram for the quaternary system (SDS + DeOH + H_2O + Na_2SO_4). Here we maintained constant the ratio (SDS + DeOH)/H_2O [0.87(0.066)%] and varied the salt concentration from 0 to

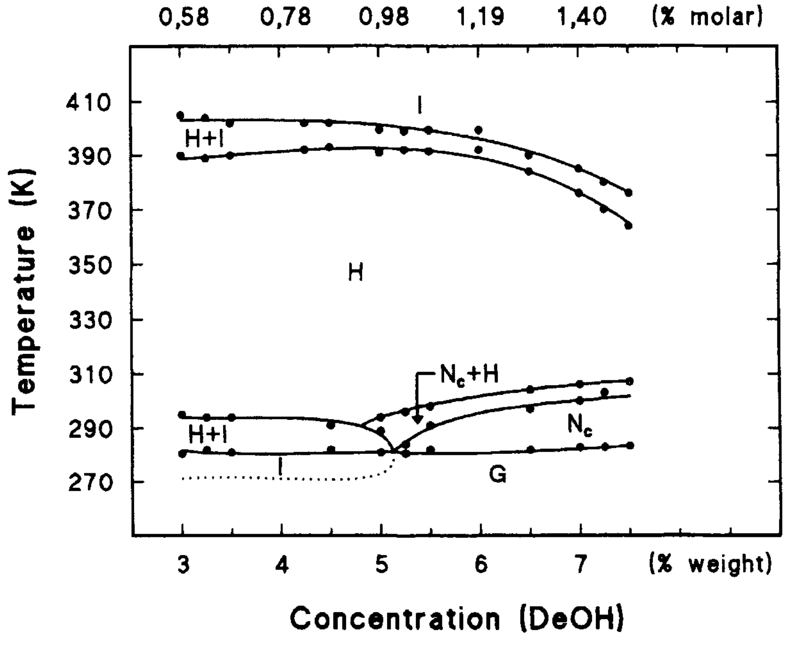

FIGURE 1 Phase diagram for (Sodium Decylsulphate) + (*n*-Decanol) + (Water) ternary system. (I) isotropic; (H) hexagonal; (N_C) nematic calamitic and (G) coagel. Observe that the molar concentration scale is not linear.

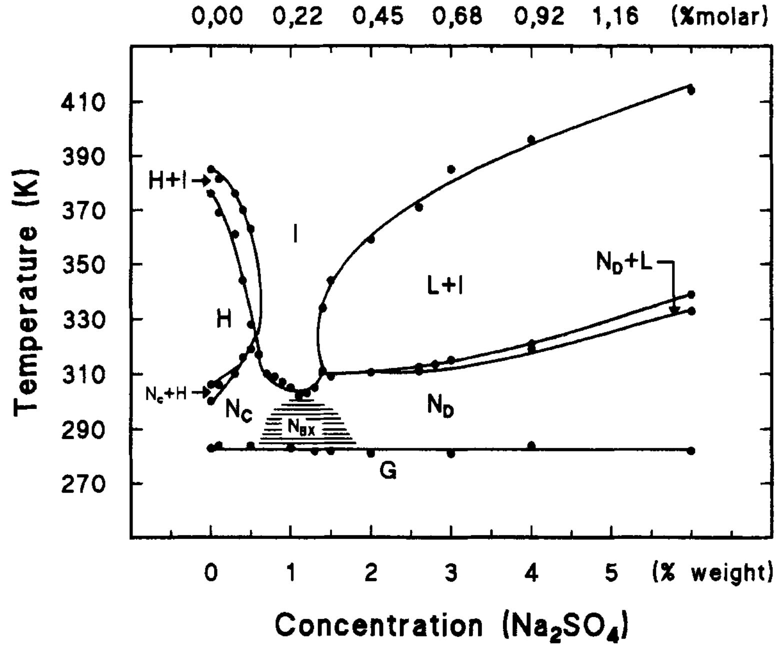

FIGURE 2 Phase diagram for (Sodium Decylsulphate) + (*n*-Decanol) + (Water) + (Nasalt) quaternary system. (I) isotropic; (H) hexagonal; (N_C) nematic calamitic; (N_D) nematic discotic; (N_{BX}) nematic biaxial; (L) lamellar and (G) coagel. Observe that the molar concentration scale is not linear.

6.0 (1.4)%. At lower salt concentration the quaternary phase diagram reproduces the high concentration part of the ternary diagram as expected. On increasing the salt concentration new phases appear: (N_D) nematic discotic, (N_{BX}) nematic biaxial and two phase regions with the lamellar phase (L); $(N_D + L)$ and $(L + I)$. Distinction between the (N_C) and (N_D) phases was made by: texture, magnetic alignment $[(N_C)\ \Delta\chi > 0$ and $(N_D)\ \Delta\chi < 0]$; optic sign $[(N_C)\ \Delta n < 0$ and $(N_D)\ \Delta n > 0]$ and small angle X-ray scattering. The small angle diffuse scattering is more intense in the (N_D) then in the (N_C). The existence of the biaxial phase (N_{BX}) was identified clearly only by conoscopic observation and the boundary of it's region of existence is suggested by the hachured region in Figure 2. The (L) phase was identified by texture and the characteristic pattern of small angle X-ray scattering.

Figure 3 shows density versus temperature for the ternary system (with DeOH 7.0 (1.4)%) on heating at a constant rate of 500 mK/10 min. Our experimental error is $\pm 2.10^{-5}$ g cm^{-3} and we can see that the density decreases almost linearly with increasing temperature over all the range studied. The calculated expansion coefficient for each phase was:

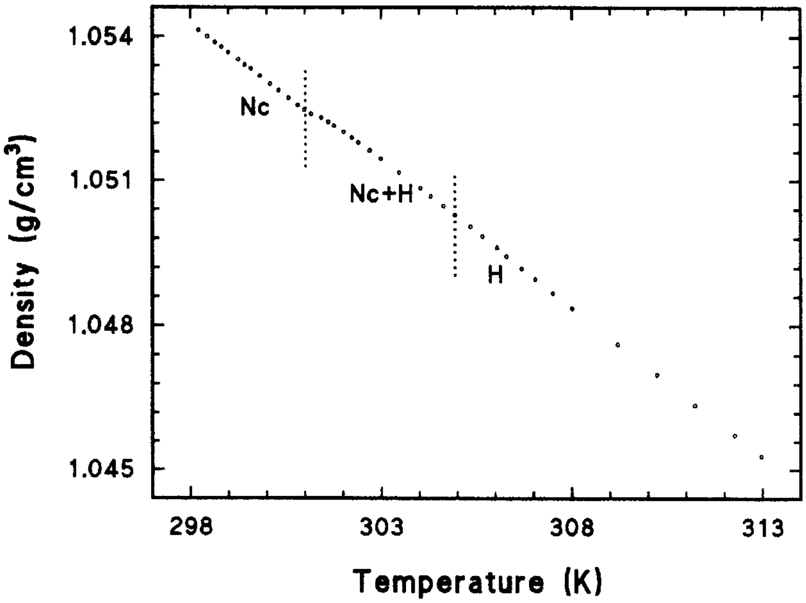

FIGURE 3 Density as function of temperature for the (Sodium Decylsulphate) + (*n*-Decanol) + (Water) ternary system with *n*-Decanol concentration of 7.0 (1.40) by weight (molar)%.

[$\alpha_{(NC)} = (5.67 \pm 0.02).\ 10^{-4}$ and $\alpha_{(H)} = (5.72 \pm 0.01).10^{-4}]K^{-1}$. We also measured a binary system (ratio of SDS/H_2O [0.74(0.05)%] isotropic phase), to compare the expansion coefficients in different systems, $\alpha_{(I)} = (5.63 \pm 0.02).\ 10^{-4}\ K^{-1}$, with $\rho_{(I)} = 1.07\ g\ cm^{-3}$ at 300 K. The small differences in α in different structural systems suggests that, at our limit of experimental error, we can not infer any structural changes in lyotropic system by examining the behaviour of α as a function of temperature. The presence of surfactant significantly decreases the temperature dependence of the coefficient of expansion of water although the molar concentration of the water in all those systems is greater than 93% (in the temperature range studied, $\alpha_{(H_2O)}$ increases by almost a factor of two).

Figure 4 shows the refractive indices (n_e and n_o) as a function of salt concentration at constant temperature (23 ± 1) C. Samples were prepared in sealed planar microslides and aligned in a magnetic field; the alignment was checked examining the interference figure by conoscopic observation. Using the refractive indexes and density data, we calculated the molecular refractivity [R_M] [10] of the systems. To calculate [R_M] of a lyotropic system we compute the 'molecular weight M of the system' as the sum of the molecular weight of components weighted by the weight fraction of each component. The ratio of the refractivity of the system to the water refractivity

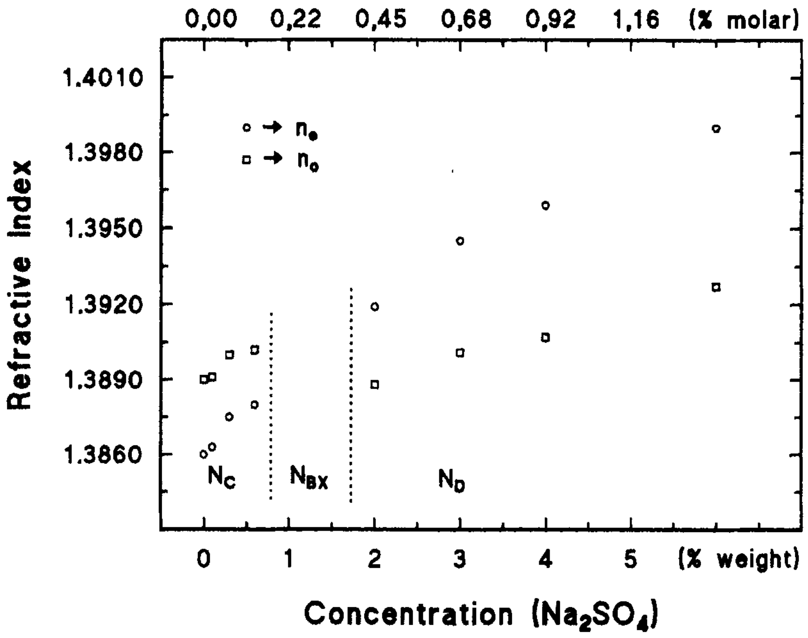

FIGURE 4 Refractive indexes (n_e/n_o) as function of salt concentration. (N_C) nematic calamitic; (N_D) nematic discotic; and region without data points corresponds to the nematic biaxial phase (N_{BX}) region. Observe that the molar concentration scale is not linear.

$[R_M]_{()}/[R_M]_{H_2O} = R$ is for the isotropic phase 7.11 while for the nematic and hexagonal phases it is 7.46. The fact that the refractivity ratio for the ternary system is greater then that for the binary system indicates a difference in relative polarizabilities of these systems. Actually we have some evidence that slight differences in relative polarizability may be relevant to the existence or non-existence of the mesomorphic state in lyotropics systems.

COMMENTS

When using SDS, synthesis and preparation of lyotropic systems, it is relevant to avoid the hydrolysis of surfactant and preserve purity of the system, to maintain the temperature of the system as low as possible. It is well known how hard it is to reproduce topological detail in SDS system the phase diagrams. Our feeling is that the principal reason for these difficulties must be credited to failure in controlling the temperature of the surfactant during preparation, storage or preparation of phases. If we prepare a system with pure surfactant and keep the system at 90°C for a few minutes we will not be able to reproduce the former limits of the phase existence. If it were possible to know the molar composition, after the hydrolysis, probably we would find changes in R, important enough, to justify the phase alteration.

In closing we want to mention the possibility that measurement of α could be sensitive to changes in micellar form but it is a poor instrument to indicate structural alteration between mesomorfic transitions.

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