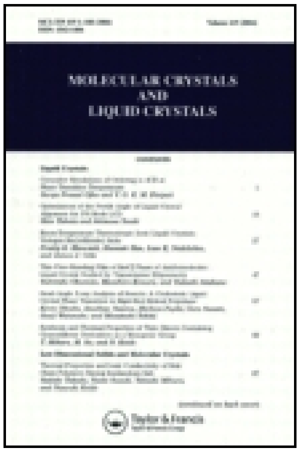

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Preparation of Sodium Decylsulphonate: Physical Chemical Measurements and Elaboration of a Ternary and a Quaternary Lyotropic Phase Diagram

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

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Preparation and analysis of sodium decylsulphonate (SDS_{NATE}), as well as the elaboration of the ternary and quaternary phases diagram are here presented. The lyomesosphases were studied by: polarizing microscopy, small angle X-ray scattering, densimetry and refratometry. We compare the present results on the SDS_{NATE} systems to sodium decylsulphate systems and perhaps the most important point is that the SDS_{NATE} is free of hydrolysis for all mesomorphic purposes, i.e. the SDS_{NATE} is thermally stable.

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

INTRODUCTION

Lyotropic liquid crystals, in nematic phases were discovered by Lawson and Flawtt [1] in the quaternary system: [Sodium decylsulphate (SDS) + *n*-Decanol (DeOH) + Sodium Sulphate (NaSalt) + Water]. An approximative phase diagram for a ternary system (SDS + DeOH + H_2O) was first presented by Hendrikx and Charvolin [2]. In 1992 they presented a more compelte form to the phase diagram of the SDS system in the neighbourhood of the nematic domain [3]. Other authors have been developed mixtures which have nematic lyomesophases [4–6].

The different systems of SDS, especially the quaternary, are attractive because they present a complete set of well-known lyomesophases. (Nematic calamitic N_C, nematic discotic N_D, nematic biaxial N_{BX}, hexagonal H, and lamellar L, phases). However, a important drawback with SDS is it's thermal stability. Hydolysis [7] of the surfactant has a tendency to make results irreproducible, at high temperatures because of changes in composition of the system [8]. With objective of preserving the desirable characteristics and removing the difficulty with the hydrolysis we have prepared a more stable surfactant that has a molecule similar to the SDS molecule. For that end we choose to prepare sodium decylsulphonate (SDS_{NATE}). The bonding of the sulphur atom of the polar head directly to the first carbon atom of the carbon is known to be more stable and hydrolysis resistant, then the bonding of a sulphur atom through an oxygen atom (as in the sulphate case). We will show that, in SDS_{NATE}, the thermal stability in the mesomorfic phases is indeed very good.

Following the phase diagrams for ternary and quaternary SDS systems [8] we constructed similar phase diagrams with SDS_{NATE} and determined the existence of lyomesophases be examining and comparing the textures in polarizing microscopy. Complementary techniques used to characterise the lyomesophases were: X-ray small angle scattering, density and refratometry measurements.

EXPERIMENTAL

The surfactant, SDS_{NATE}, was prepared by the method of Strecker, as described in ref. [9]. The crude surfactant was recrystallized three times from ethanol and ^1H-NMR[D_2O, 200 MHz]: $\delta = 0.9$(t, CH_3); 1.3 (m, $7CH_2$); 1.8(quint., CH_2); 2.9 (t, CH_2—O) have confirmed the surfactant prepared. A CHN analysis was made and the results are presented in Table I. The divergence between the measured and calculated values was too large to be acceptable. Purification was continued by heating the crude product in hot ethanol (~ 340 K), which gives a turbid solution. The hot solution was filtered twice and after this treatment was not turbid. After recrystallization,

TABLE I CHN elemental analysis of SDS_{NATE}(Before* and after** filtering)

Carbon (%)			Hydrogen (%)		
Measured	*Calc.*	*Diff.*	*Measured*	*Calc.*	*Diff.*
(*)48.25	49.16	−0.91	8.58	8.66	−0.08
(**)49.08	49.16	−0.08	8.86	8.66	+0.20

the final product was tested again and the final results were considered acceptable (Tab. I). The critical micelle concentration (CMC) was measured CMC 4.0 10^{-2} M (at 25 C) (Analion Condutivimeter Mod.C–701) is in good agreement with the literature [10].

Sample preparation and physical chemical measurements are the same procedure as described previously [8].

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram of the ternary $\mathrm{SDS_{NATE}}$ system. All the phases were determined by examining at least three independent samples at each concentration in sealed microslides. The transition temperature was normally measured at 2 K/min (heating) and slower rates were used when necessary. To build the phase diagram we fixed a constant ratio of ($\mathrm{SDS_{NATE}}/H_2O$) [0.69(0.05)% weight (molar)] and varied the DeOH concentration from 0 to 8.0(1.57)%. There are four single lyomesophases present:

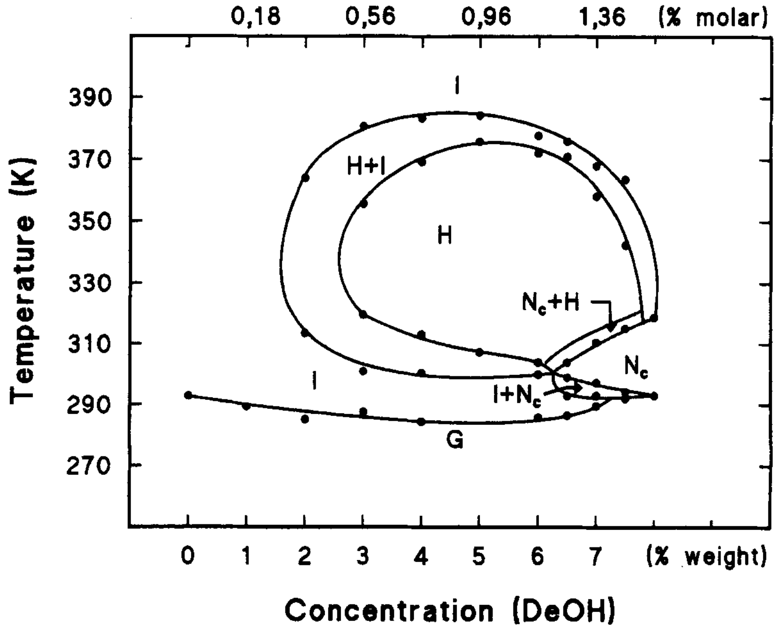

FIGURE 1 Phase diagram for (Sodium Decylsulphonate) + (*n*-Decanol) + (Water) ternary system. (I) isotropic; (H) hexagonal; (N_C) nematic calamitic and (G) coagel. Observe that molar concentration scale is not linear.

hexagonal (H), nematic calamitic (N_C), isotropic (I) and coagel (G); and three mixed lyomesophases: (H + I), (I + N_C), and (N_C + H). For DeOH concentrations greater than 8.0 (1.57)% it is hard to solubilize the componets to obtain a homogeneous sample.

The phase were identified by texture and the (N_C) was also checked by it optical sign, (negative) as determined using a gypsum compensator. Complementary check to confirm the transition $(N_C) \rightarrow (N_C + H)$ and $(N_C + H) \rightarrow (H)$ in temperature was made by examining the characteristic patterns of X-ray small angle scattering, as shown in Figure 3A.

For the phase diagram of the quaternary system, Figure 2, we used the same ratio surfactant/water used in the ternary system [$(SDS_{NATE}/H_2O) =$ 0.69(0.05)%] and also constant DeOH concentrations 7, 2(1.40)% and the Na_2SO_4 concentration varying from 0(0) to 3.5 (0.78)%. We can see that at very lower salt concentration the diagram reproduces the final part of ternary phase diagram, as expected for minor salt concentration. For higher salt concentration, higher than 1.0(0.22)%, we see the appearance of the nematic discotic (N_D) and also the lameller (L) phase. The appearance and

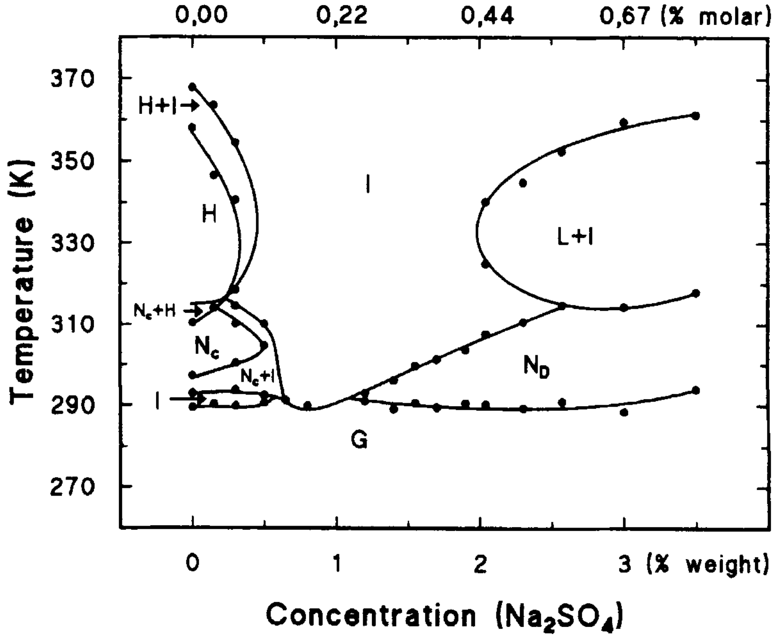

FIGURE 2 Phase diagram for (Sodium Decylsulphonate) + (*n*-Decanol) + (Water) + (Nasalt) quaternary system. (I) isotropic; (H) hexagonal; (N_C) nematic calamitic; (N_D) nematic discotic; (L) lamellar and (G) coagel. Observe that molar concentration scale is not linear.

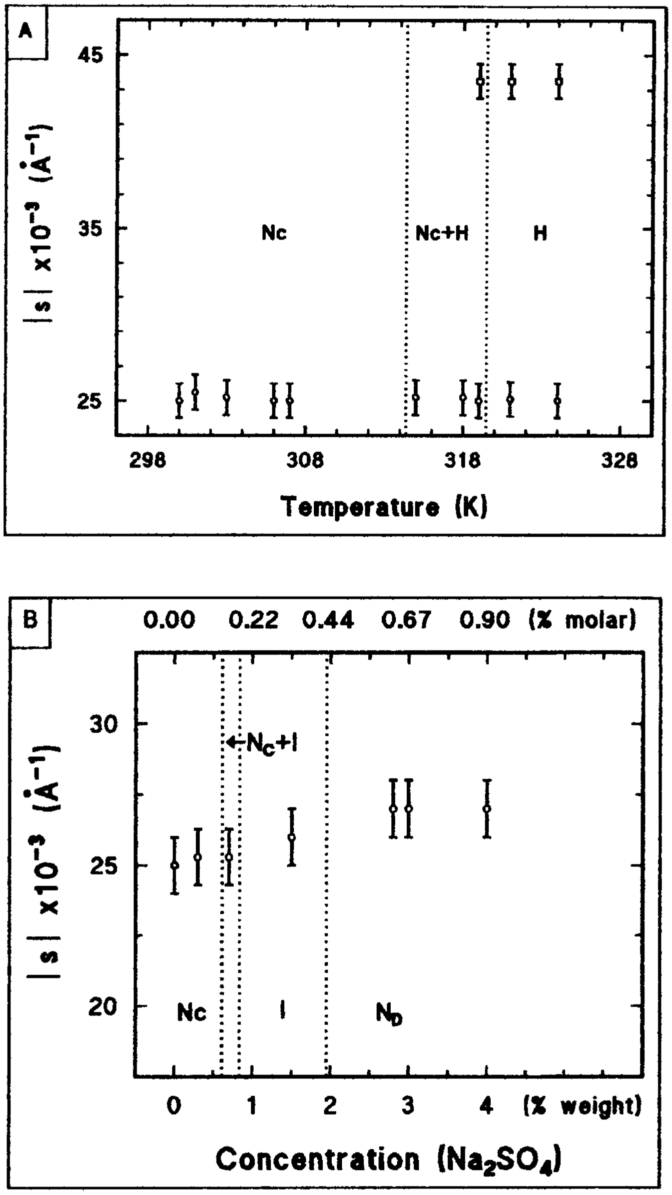

FIGURE 3 Position of maximum intensity as a function of the scattering vector $|s|$ (where $|s| = 2\sin\theta/\lambda$). A) ternary SDS_{NATE} system with *n*-Decanol 7.2(1.40)% by weight (molar) close to the N_C to H transition. B) quaternary SDS_{NATE} system as function of Na_2SO_4 concentration at 303 K. Note the step like behaviour of $|s|$ at the N_C to N_D transition.

growth of (N_D) and (L) regions, with increasing salt concentration, seems to indicate a gradual and significant change of the micellar structure. The changes of the optical sign from negative in (N_C) to positive in (N_D) and the more intense small angle diffuse scattering in (N_D) as compared to (N_C), internal patterns more intense to (N_D) then to (N_C), as function of salt concentration, Figure 3B, suggests strongly the idea of some type of structural transformation, as were discussed below. Another relevant aspect of the phase diagram is that the anisotropic phases are separated by an isotropic phase. This appears indicate a change in the micelle form and not a mixture of two anisometric objects (cylinder and disc). If we look with care, Figure 3B suggests that the parameter $|s|$ (where $|s| = 2\sin\theta/\lambda$), related to structural periodicity in the phases (N_C) and (N_D), has a step like behaviour through isotropic phase, so that the hypothesis of a discontinuous modification appear be deserved.

Figure 4 shows density versus temperature for the ternary system (with DeOH 7.2(1.40)%) on heating. The heating rate was constant at 500 mK/10 min. Our experimental error is $\pm 2 \cdot 10^{-5}$ g cm^{-3} and we can see that density

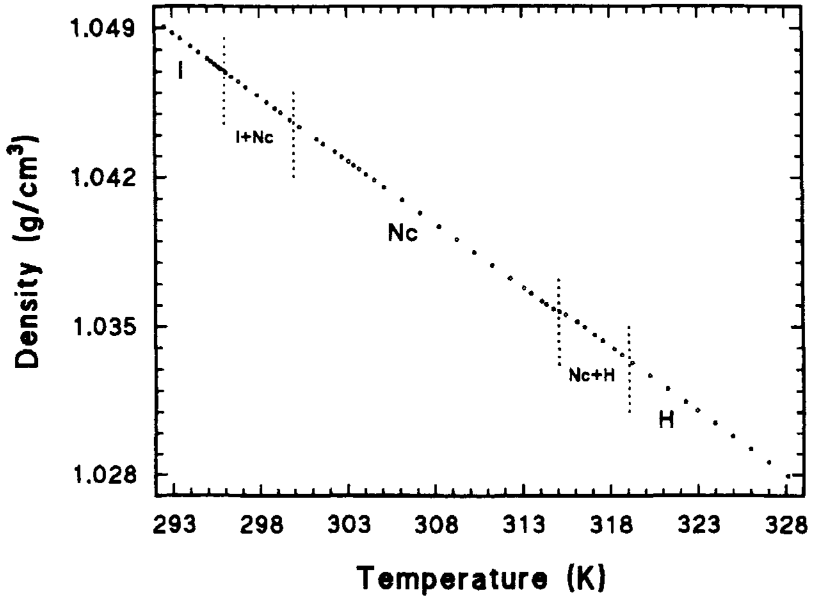

FIGURE 4 Density as function of temperature for the ternary system with n-Decanol concentration of 7.0(1.40) by weight (molar)%.

decreases almost linearly with temperature over all the range studied. The calculated expansion coefficient for each phase was: $[\alpha_{(I)} = (5.69 \pm 0.02) \cdot 10^{-4}$, $\alpha_{(N_c)} = (5.72 \pm 0.01) \cdot 10^{-4}$ and $\alpha_{(H)} = (5.84 \pm 0.01) \cdot 10^{-4}]K^{-1}$. Also in the ternary system but with DeOH 8.0 (1.57)%, the density ranges between 1.030 (I) to 1.034 (N_C), and the expansion coefficients are: $[\alpha_{(I)} = (5.40 \pm 0.02) \cdot 10^{-4}$, and $\alpha_{(N_c)} = (5.81 \pm 0.02) \cdot 10^{-4}]K^{-4}$. As in the SDS and SDP systems [8], small variation of α with temperature within the same phase or in different phases suggests that a general characteristic of water/surfactant systems is the virtual independence of expansion coefficient.

The refractive indexes (n_e and n_o) as a function of temperature for the ternary system with DeOH 8, 0(1.57)% are presented in Figures 5A and 5B shows birefringence versus temperature. The samples were prepared in sealed planar microslides and aligned in a magnetic field. The sample alignment was checked by examining the interference figure in conoscopic observation. In the measurements using a Abbe refractometer the aligned sample, in a sealed microslide, was treated as a solid and for optical coupling Canada balsam was used ($n = 1.530$). For the quaternary system (ternary composition plus Na_2SO_4 2.7% by weight) the dependence of

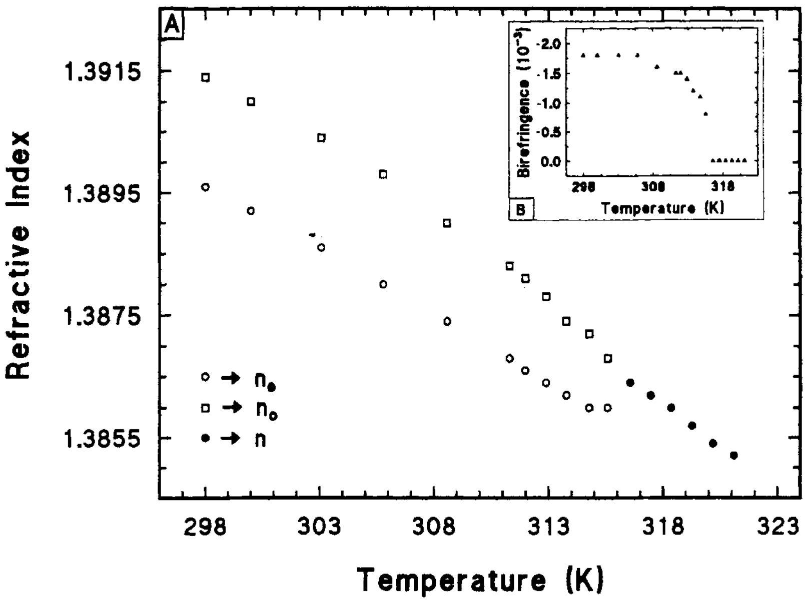

FIGURE 5 Ternary SDS_{NATE} system with *n*-Decanol concentration of 8.0(1.57) by weight (molar)%: A) Refractive indexes (n_e/n_o) as a function of temperature; B) birefringence as function of temperature.

indexes with temperature was similar to that in Figure 5 but the birefringence is positive.

The sign and the absolute values of the birefringence in ternary and quaternary systems reflect essentially the symmetries of the micelle and are compatible with the cylindrical and discotic micellar systems. Thus refratometry corroborates the previous classification of the nematic phases as (N_C) and (N_D).

Lastly it should be remarked that SDS_{NATE} is very stable to hydrolysis. During the sample preparation to obtain the phase diagrams, we did not detect any alteration that would evidence thermal instability in time or temperature. Also samples sealed in microslide and/or culture tubes, were placed in a temperature controlled oven. Samples were left at 400 K for up 200 hours and no alteration of phase transition temperatures were observed by texture in polarizing microscope. Our assumption is that for all practical purposes the surfactant does not hydrolysis in solution.

CONCLUSION

We have presented ternary and quaternary phase diagrams for SDS_{NATE} systems. We believe that a important point is that these new systems present a phase topology very similar to the SDS systems. All phases present in the SDS systems are present in SDS_{NATE} systems at corresponding concentrations. A most remarkable fact is that systems with SDS_{NATE} are free of hydrolysis.

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