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Preparation of Sodium Decylphosphate: Physical Chemical Measurements and Elaboration of the Binary Lyotropic Phase Diagram

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Preparation and analysis of sodium decylphosphate, and elaboration of the binary phase diagram with water as solvent are presented. Lyomesophases isotropic, nematic calamitic and hexagonal are present and were studied by polarizing microscopy, small angle x-ray scattering, densimetry and refratometry. The results are compared with a related surfactant system, sodium decylsulphate.

Keywords: Sodium decylphosfate; phase diagram; density; refractometry; x-ray analysis

INTRODUCTION

Lyotropic mesophases are formed by surfactant molecules in a suitable solvent and can exhibit a variety of ordered phases depending on temperature, surfactant and solvent concentration. The first lyotropic nematic, susceptible to alignment by a magnetic field, was described 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, the SDS system has been studied by many researchers [2–4] 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.

Our objective was to prepare a surfactant whose molecular structure was similar to the SDS molecule but different enough to be distinct. We choose to prepare sodium decylphosphate (SDP), where a phosphorus atom substitutes the sulphur atom on the polar head of the molecule. The modifications of lyomesophases properties are compared with data of the SDS system.

In the construction of binary phase diagram (SDP + H_2O), Figure 1, we began at 50% by weight concentration of surfactant. This results in a two component immiscible mixture. Thus, increased the water concentration until we obtained a homogeneous phase which was observed to be a lyomesophase by texture observation using polarizing microscopy. The complementary techniques used to characterise the lyomesophases were x-ray scattering, density and refratometry measurements. The summary of our results and conclusions are presented here.

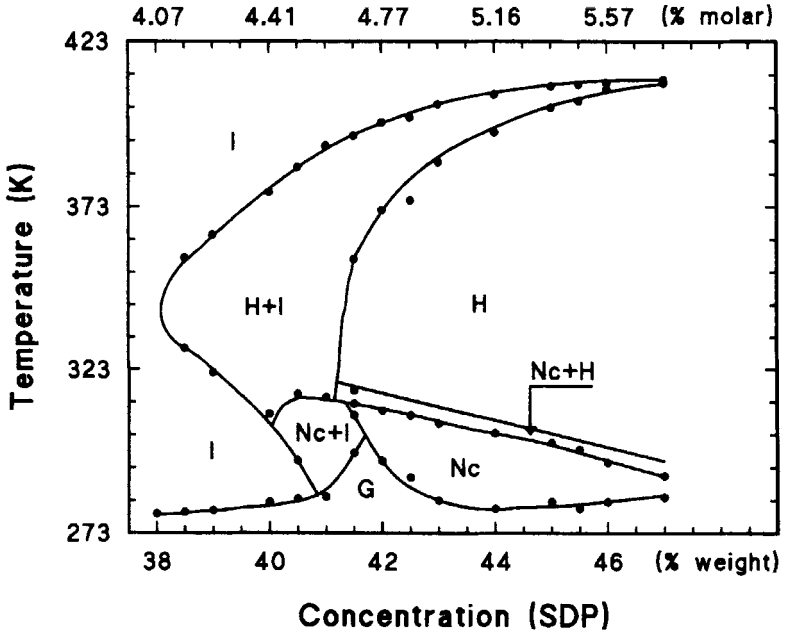

FIGURE 1 Phase diagram for Sodium Decylphosphate/H_2O binary system; (I) isotropic; (H) hexagonal; (N_C) nematic calamitic; (G) coagel. Observe that the molar concentration scale is not linear.

EXPERIMENTAL SECTION

Surfactant Preparation

The surfactant (SDP) was prepared as described by Nelson and Toy [5]. The crude surfactant was solubilised in hot ethanol, filtered and twice recrystalized from ethanol. The ^{1}H NMR[D_2O, 200MHz]: $\delta = 0.9$ (t, CH_3); 1.3(mm, $7CH_2$); 1.6 (quint., CH_2); 3.9(q, CH_2—O) have confirmed the surfactant prepared. A CHN analysis was made and the results (C(%) – Measured: 46.02/Calculated: 46.15, and H(%) – Measured: 8.66/ Calculated: 8.52), were considered acceptable and were reproducible in a range of 0.5%. The measured CMC 3.4 10^{-2} M (Analion Condutivimeter Mod.C-701) is in good agreement with the literature [6].

Samples preparation and physical chemical measurements follow the same procedure as presented elsewhere [8].

RESULTS AND DISCUSSION

The phase diagram for the binary system (SDP + H_2O) is presented in Figure 1. The phase diagram was determined by examination of 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. Special care was taken to avoid leaving the sample: 1) at temperatures corresponding to a two phase region which can cause the development of concentration gradients in these regions; 2 at high temperatures for more then a couple of minutes because thermal instability of the surfactant, as in the case of sodium decylsulphate [7], might induce hydrolysis and consequent changes in sample composition. (In regard to the composition changes induced by the degree of hydrolysis, see the discussion below and Fig. 2.)

The first mesophase to appear, as surfactant concentration increases is a hexagonal plus isotropic (H + I) two phase region. This mesophase forms at about 4.1 mole% of the surfactant and only above 4.6 mole% of surfactant does a nematic calamitic (N_C) and/or hexagonal (H) single phase region appear. The (N_C) region is present at lower temperatures and on increasing the temperature the system passes thru a two phase region (N_C + H) to a hexagonal (H) single phase region. The low temperature part of the phase diagram is dominated by coagel (G). A remarkable aspect of the phase diagram is the existence of the nematic phase in a binary system, a rare occurrence.

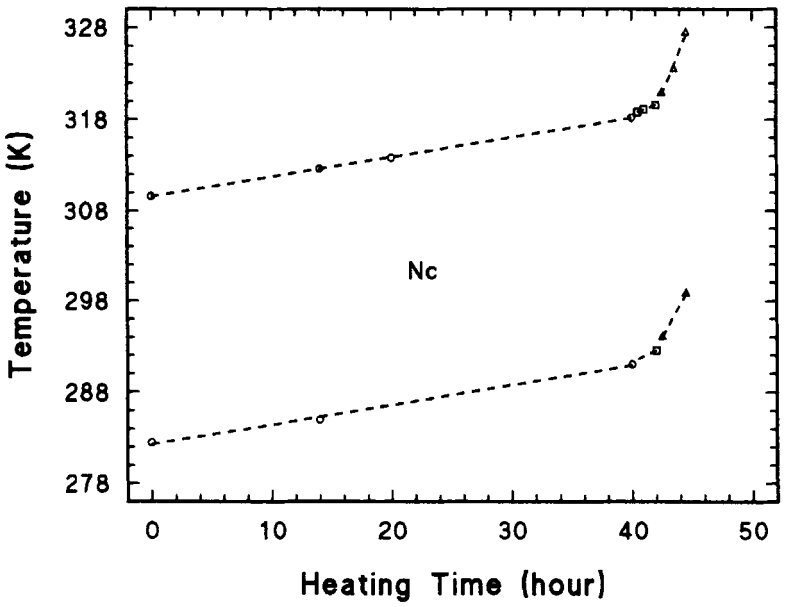

FIGURE 2 Change of the range of existence of the nematic phase (N_C), at a concentration of 43.0(4.96) by weight (molar)%, as a function of time and temperature. (○) = 353 K; (□) = 363 K and (Δ) = 373 K.

Figure 2 shows the temperature range of existence of the nematic phase, at 43% by weight concentration, as a function of time and temperature. To obtain the data we prepared samples in flame sealed microslides and the cells were placed in a constant temperature oven (controlled to within $\pm$ 100 mK). Every three hours, the samples were taken out of the oven, cooled to room temperature and the phase transition temperatures determined by texture examination. After the phase transition temperatures were determined the cells were returned to the oven for another three hour period. Up to a temperature of 353 K we could not observe any changes in the temperature range of nematic existence. At a temperature of 353 K, it is possible to observe changes in the nematic range and the change in temperature is approximately linear with time (Fig. 2). After forty hours (at an oven temperature of 353 K), the range of existence of the nematic phase has changed by almost 10 K. At higher oven temperatures the changes increase quickly. Thus we arrive at a special feature of this system; Under hydrolysis it preserves, approximately, the topological interval of the nematic region, as shown in the Figure 2.

From Figure 3, we can see that the angular position of the maximum in the diffraction patterns do not show any temperature dependence. Our

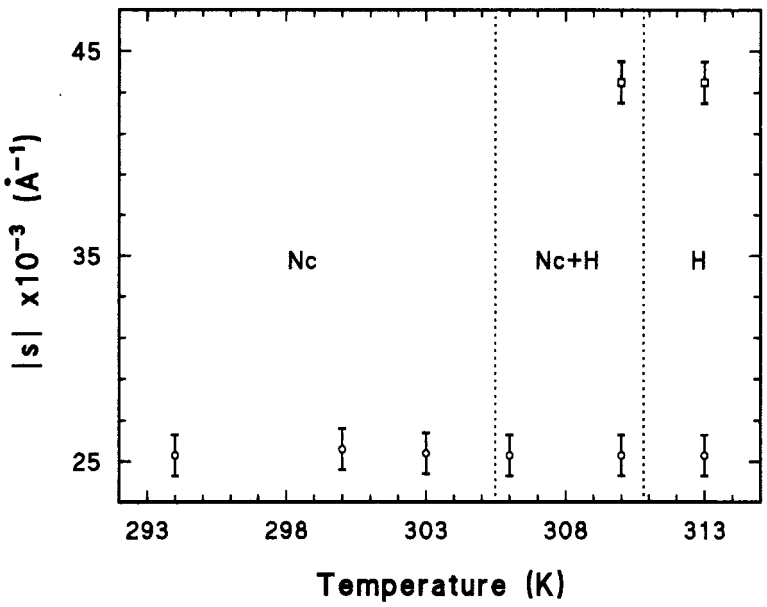

FIGURE 3 Diffraction patterns as function of temperature for the SDP system at concentration of 43.0(4.96) by weight (molar)%. (H) hexagonal; (N_C) nematic calamitic and where: $|\mathbf{s}|_{(\square)} \approx \sqrt{3}\,|\mathbf{s}|_{(\bigcirc)}$.

conclusion is that, within the limit of our experimental error, temperature variation does not change significantly the mean distance between the micelles in the nematic and hexagonal phases ($|\mathbf{s}|^{-1} \approx 40$ Å). When we explore the diffraction patterns as a function of the concentration of SDP, (between 42% and 45% by weight) in the range of the nematic phase, we also could not detect any changes, within our experimental error.

Figure 4 shows density versus temperature for the system (SDP 42.5% by weight) on heating. The heating rate was constant at 500 mK/10 min. We can see that within our experimental error ($\pm 2 \cdot 10^{-5}$ g cm^{-3}) the density decreases almost linearly with temperature. With the same assumptions as Photinos and Saupe [9] we calculated the surfactant density at 300 K and found $\rho_{SDP} = 1.23$ g cm^{-3}. This value can be compared with that of sodium decylsulphate (SDS), measured in a binary (isotropic phase) system [8] $\rho_{SDS} = 1.19$ g cm^{-3} at the same temperature. Unlike the studies of Photinos and Saupe [9] of decylammonium chloride (DAC*l*) and cesium perfluorooctanoate (CsPFO) systems but in agreement with our results [11], we could not detect any step like feature marking the phase transition in this system. This also is in agreement with our x-ray data.

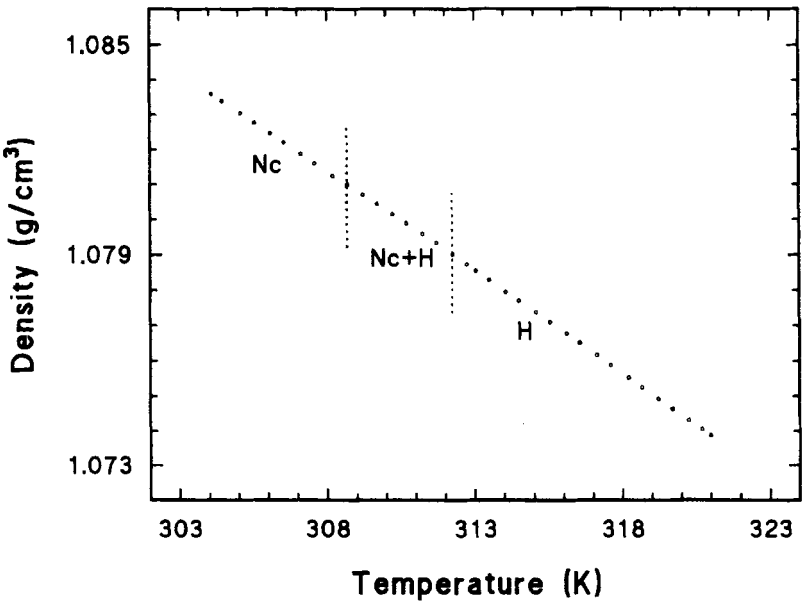

FIGURE 4 Density as function of temperature for SDP system at concentration of 43.0(4.96) by weight (molar)%.

The calculated expansion coefficient for the system, in the nematic (N_C) region is $\alpha_{(N_C)} = 5.3\ 10^{-4} K^{-1}$ and in the hexagonal (H) region is $\alpha_{(H)} = 5.5\ 10^{-4} K^{-1}$. Those values are essentially equal to those obtained in SDS systems [8] and the DAC*l* and CsPFO systems studied by Photinos and Saupe. This observations seems to support the general conclusion that in the majority of lyotropic systems where the molar ratio of water/surfactant is $\gg 1$ (here ~ 19.5), the value of the expansion coefficient reflects the behaviour of the water/surfactant mixture better than that any particular characteristic of the lyomesophase strucutre.

The mean value of refractive indexes ($n = 1/3\ (n_e + 2n_o)$) as measured in the (N_C) phase at 300 K, was $n = 1.393$. In the SDS ternary system [8] at the same temperature and in the nematic phase we have $n = 1.388$. Both systems are hard to align and n_0/n_e are not easy to measure but the birefringences are estimated to be of the order 1 to $3 \cdot 10^{-3}$. Using these data and those of density we could calculate the molecular refractivity [10] [R_M] for the SDP and SDS binary systems. If we take the ratio of these values to the molecular refractivity of water, $[R_M]_{H_2O}$, we should have a measure of the relative polarizability of the systems. For the SDP Systems; $[R_M]_{SDP}/[R_M]_{H_2O} = 7.16$ and for SDS: $[R_M]_{SDS}/[R_M]_{H_2O} = 7.11$. The fact that the ratio

for SDP is greater than that, for the SDS system, agrees with the polarizability inferred by electronegativity. Thus there is a possibility than that the slight difference in relative polarizabilities is the cause of the existence of the nematic and hexagonal phases in the SDP binary system, whereas only nematic and hexagonal phases appear in the ternary SDS system [8] where the ratio is measured to be 7.46.

CONCLUSION

We belive that the most remarkable aspect of the phase diagram is the fact that a nematic phase is obtained in a binary ststem. Like the SDS system this system also presents hydrolysis with temperature/time but unlike the SDS [8] system the nematic phase is not destroyed and all that happens is a shift of temperature of the nematic region. Our x-ray and density data, around the nematic to hexagonal transition do not show any abrupt changes as a function of temperature. We conclude that there is no evidence indicating a change in the mean distance between micelles at the transition.

Finally, refratometric results seem to show that the relation between the molar polarizabilities could be the reason that the SDP system presents a nematic phase in a binary system but in SDS the simplest system that shows a nematic phase is ternary.

Acknowledgements

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