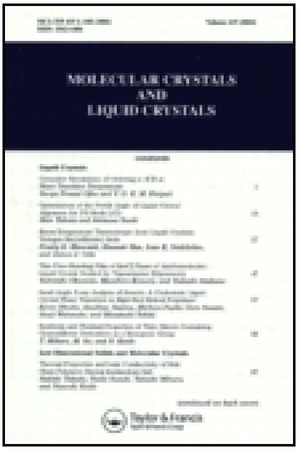

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New Nematic Phase in Lyotropic Binary Liquid Crystals Detected by Positron Annihilation Techniquest

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New Nematic Phase in Lyotropic Binary Liquid Crystals Detected by Positron Annihilation Techniques†

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A new nematic phase in lyotropic binary liquid crystalline systems consisting of sodium dodecyl sulfate-water was detected, for the first time, in the absence of additives by utilizing positron annihilation techniques. Lyotropic and thermotropic phase transitions were also investigated by the same methods. The positron annihilation parameters have also indicated a better definition of the concentration ranges at which each phase exists in the system studied. Crossed polarized light microscopy was applied to substantiate these results.

INTRODUCTION

Liquid crystals have revolutionized the electronic industry. They are used as displays in calculators, watches and other devices. Additionally, liquid crystals have been utilized to provide insight into the organization of biological membranes.[1–3]

Lyotropic nematic phases readily dissolve both polar and apolar substances. This is a great advantage over thermotropic crystalline

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§ Present address: Department of Chemistry, Syracuse University, Syracuse, NY 13244-1200 systems.[4] Lyotropic nematics have been suggested to be very suitable for photophysical studies using polarized light spectroscopy.[5] Another important application of lyotropic nematics is their uses as order matrices in NMR studies,[6] and in the determination of electrical transition dipole moments of chromophores.[7] Lyotropic nematics have been observed in classical surfactant-water systems only in the presence of an electrolyte or a long chain alcohol.[4–11] In the absence of additives only hexagonal or middle, cubic or viscous isotropic, complex hexagonal and lamellar or neat phases are observed at different surfactant compositions.

The systematic investigation of the phase behavior of a simple binary system has been the objective of the present study. The behavior of sodium dodecyl sulfate (SDS)-water systems in the absence of additives has been examined in the 15–85% surfactant concentration range between 10 and 85 °C by utilizing positron annihilation techniques. Positron annihilation has proved to be an extremely sensitive method for investigating aggregation mechanisms in micelles and in microemulsions as well as in polyelectrolyte-couterion interactions.[13–29] Positron annihilation techniques were previously applied to detect phase transitions in thermotropic liquid crystals.[30,31] The application of this technique is based on the very high dependence of the positronium atom, (Ps) (the bound state of a positron and an electron) formation and its subsequent reactions on phase changes occurring in the aggregates.

Positronium formation and positronium reactions can both be observed by measuring the positron lifetimes.[26] The positron annihilation parameters can be correlated with changes occurring in the systems as a function of their composition.

Distinct correlations between the positron lifetime parameter, τ_2 and the phase behavior of liquid crystalline structures in well characterized systems of SDS are reported in the present work.

This allowed the first observation of a nematic phase in a binary system (surfactant-water) in the absence of any additives. Crossed polarized light microscopy has been used for the substantiation of the presence of a nematic phase.

EXPERIMENTAL SECTION

Sample preparation

Sodium dodecyl sulfate (SDS, Eastman) was purified by conventional methods.[32] Samples corresponding to different phases were prepared in specially designed cylindrical sample vials (pyrex glass, 25 mm long and 10 mm i.d. with a 4 mm constriction in the middle). Appropriate amounts of SDS were weighed into each vial. Solutions were made *in situ* by adding 10–20 μCi of carrier free $^{22}NaCl$ (New England, Co.) along with the necessary volumes of triply distilled water. The vials were degassed on a vacuum line by repeated freeze-pump-thaw cycles and were sealed in vacuum. Contents of the vials were mixed by shaking in a water bath set at 90 °C and by repeated transfers through the constriction from one part of the vial to the other. Samples prepared in this way were stable at room temperature for several weeks. At least four independent determinations were carried out on each sample.

Positron lifetime measurements

These measurements were carried out by a fast coincidence technique as described previously.[19] The resolution of the system, measured by the prompt time distribution of a ^{60}Co source, was found to be 0.390 ns fwhm. Corrections for the positron absorption on the tube wall, which had an intensity of less than 3%, were made by the usual way by using conventional computational methods.[29] Each series of measurements were carried out every 5 °C in the temperature range of 25–85 °C.

General method of data analysis

Positron lifetime and distributions were obtained by standard computational techniques.[13–29] The lifetime spectra was resolved as previously described[13–29] into two components, a short-lived component, which is the result of *p*-Ps annihilation, free positron annihilation, and epithermal positronium interactions, and the long-lived component, with a lifetime τ_2 and its associated intensity I_2 which originates from the reactions and subsequent annihilation of thermalized or nearly thermalized *o*-Ps.[26]

Optical microscopic experiments

The optical microscopic observations were performed by using a Leitz crossed polarized light microscope with a magnification of (1 × 60) coupled to a photographic camera charged with a colored 135 Kodak ASA 100 film. One of the inner walls of a rectangular quartz cell (50 mm long, 10 mm wide and 10 mm thick) was covered with a film of the corresponding liquid crystalline phase which was prepared as described previously (without positron source) (*vide supra*). The cell nozzle was sealed off in vacuum in the same conditions as in the positron annihilation experiments. Subsequently it was set up on the platinum heating stage of the microscope which temperature was controlled by means of a specially designed thermostat to ±0.5 °C. All experiments were carried out at 75 °C.

RESULTS AND DISCUSSION

The systematic investigation of the phase behavior of a simple binary system has been the objective of the present study. The behavior of the SDS-water system on the absence of additives has been examined in the 15–85% surfactant concentration range between 10 and 85 °C by using positron annihilation techniques.

Effects of the surfactant concentration and temperature on the onset of phase transitions in SDS-water system will be discussed sequentially.

Effect of SDS concentration

Figure 1 shows a plot of the positronium lifetime parameter, τ_2, *vs.* SDS concentration at 75 °C. Increasing the surfactant concentration is seen to result in an initial increase of τ_2 values up to 38% SDS. This range corresponds to a micellar isotropic phase.[33] At 38% concentration, τ_2 experiences a drastic decrease, indicating the onset of a phase change, there is an apparent plateau value (indicated by A in Figure 1). Increasing the surfactant concentration results in the onset of a new transition covering the 55–63% range (indicated by B in Figure 1). It is important to point out that these two distinct phase transitions in the 38–63% range in the absence of additives have not been previously noted. The only phase recognized in this region was attributed to that corresponding to the hexagonal or middle phase.[34–36] Increasing the surfactant concentration still further (63%), τ_2 increases abruptly as far as it reaches a plateau in the 65–67% range (indicated by C in Figure 1). This narrow concentration range corresponds to the complex hexagonal phase.[34] At still higher SDS concentration (70%) the system assumes a lamellar structure (indicated by D in Figure 1).

These data are summarized and compared to those previously reported by using other techniques in Table I.[12,34,36] The structure of the liquid crystalline phases in the SDS-water system was prior es-

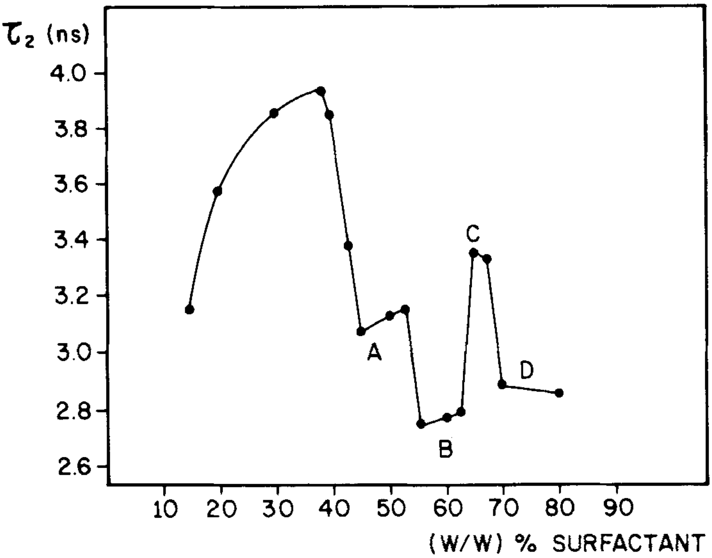

FIGURE 1 Variation of τ_2 as a function of surfactant concentration at 75 °C.

tablished by Husson et al. by using X-ray diffraction methods.[34] The macroscopic appearance of the same liquid crystalline phases is described as reported by Ekwall.[12] As it is shown in the same Table, the nematic phase, described by Lawson and Flautt[37] as rod-shaped aggregates parallel to the main symmetry axis of the liquid crystals, was not reported by Husson[34] in the 55–63% concentration range since these values are involved in that range in which the hexagonal and the complex hexagonal phases were observed in their X-ray diffraction experiments.

Polarized light microscopic studies

The phase behavior established by positron annihilation was substantiated by crossed polarized light microscopy. Micrographs taken at 75 °C for each phase are shown in Figures 2, 3, 4, and 5. The micrograph taken at 50% SDS concentration, shown in Figure 2, exhibits a fan-like texture, as compared with those taken by other authors.[36] This texture is related to the hexagonal phase which consists of surfactant molecules grouped into rod-like normal clusters of indefinite length which are arranged, in turn, side by side, in a hexagonal packing[35,36] (indicated by A in Figure 1).

TABLE I

Concentration ranges at which the various phases exist in the SDS-water system detected by positron annihilation as compared with those observed by X-ray diffraction.

Phase	Positron annihilation concentration range % (w/w)	X-ray diffraction		Macroscopic appearance[15]
		Concentration range % (w/w)	Determined structure	
Isotropic	up to 38	up to 38	Micelles in water	Aqueous and transparent solution
Hexagonal (A)	45–53	38–62	Amphiphilic molecules grouped into rod-like clusters of indefinite length which are arranged, in turn, side by side in a hexagonal packing.[35]	
Nematic (B)	53–63	non reported	Rod-shaped aggregates parallel to the main symmetry axes of the liquid crystal. The average length of the aggregates is much shorter than in that in the hexagonal phase.[37]	Viscous, opaque and isotropic fluid.
Complex Hexagonal (C)	65–67	62–69	Indefinitely long mutually parallel rods consisting of a double layer of amphiphilic molecules surrounding a core of hydrated polar groups and water. The rods are in hexagonal array in a water continuum.[35]	Stiff gel clear transparent and isotropic.
Lamellar (D)	70–100	69–100	Water is between double layers of amphiphilic molecules with lamellar packing may be perpendicular to the plane or tilted.[35]	Semiliquid and mucous consistency slightly translucent and anisotropic.

FIGURE 2 Micrograph of the hexagonal phase texture in SDS-water system (50% w/w) taken at 75 °C (indicated by A in Figure 1).
See Color Plate I.

FIGURE 3 Micrograph of the nematic phase texture in the SDS-water system (60% w/w) taken at 75 °C (indicated by B in Figure 1) and first detected by positron annihilation techniques.
See Color Plate II.

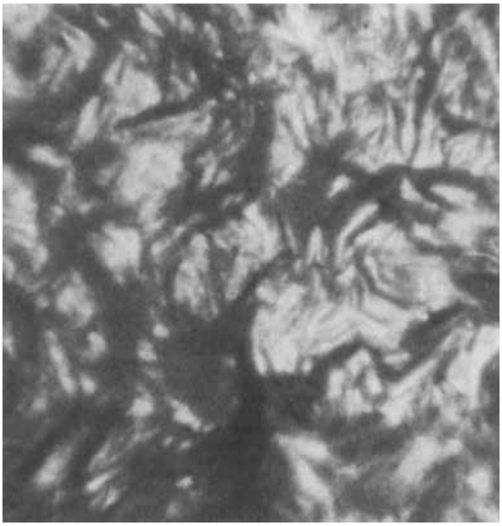

FIGURE 4 Micrograph of the complex hexagonal phase texture in the SDS/water system (66% w/w) taken at 75 °C (indicated by C in Figure 1).
See Color Plate III.

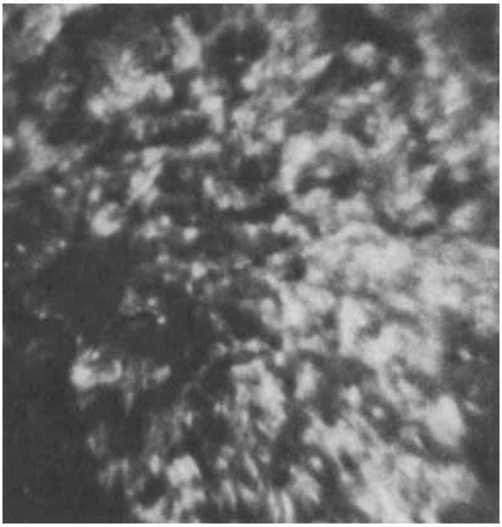

FIGURE 5 Micrograph of the lamellar phase texture in the SDS/water system (70% w/w) taken at 75 °C (indicated by D in Figure 1).
See Color Plate IV.

Figure 3 shows a micrograph taken at 66% SDS concentration, and exhibits a deformed conic texture, as previously reported by Luzzati.[35] This texture corresponds to a complex hexagonal phase which structure has been described as indefinitely long parallel rods consisting of a double layer of surfactant molecules surrounding a core of hydrated polar groups and water. The rods are in a hexagonal array in a water continuum[35] (indicated by C in Figure 1).

The micrograph shown in Figure 4 reveals a focal conic texture which was prior identified as a lamellar phase by utilizing X-ray diffraction techniques[35] (signaled by D in Figure 1).

The observed texture at 60% SDS in the micrograph, shown in Figure 5 (indicated by B in Figure 1), resembles to that attributed to a nematic phase by Figueiredo et al.[36] in the system consisting of 33.19% $C_{12}H_{13}COOK$, 1.35% KCl and 65.5% water (salt containing KDS system). This phase has not been previously reported in binary systems since the 55–63% surfactant concentration range in which the nematic phase was observed by positron annihilation techniques is almost totally included in the 38–62% SDS concentration range at which other authors have only observed the hexagonal phase.

Conversely, the light micrographs taken in the 45–53% SDS region (indicated by A in Figure 1) correspond well to those taken for 38% KSD in the absence of additives and attributed to the hexagonal phase.[36]

Influence of temperature

In another series of experiments, temperature dependence of each phase A, B, C and D (Figure 1) was examined.

The annihilation parameters were determined again in the same samples studied at 75 °C (*vide supra*) but now in the 25–85 °C range. Above 85 °C the phases in the system became separated probably forming isotropic phases. The isometric diagram obtained by using a specially developed computing program (Figure 6) represents the variation of τ_2 as a function of both temperature and SDS concentration.

These results suggest that in the 25–55 °C temperature range only hexagonal, nematic and lamellar phases (A, B and D, respectively in Figure 1) may exist, or can be clearly observed. The most favorable temperature range to observe all phases in the SDS-water crystalline system in a well defined way is 65–75 °C.

Previously, Figuereido et al.[36] investigated the behavior of the nematic phase in a ternary system (i.e.; salt containing KSD-water

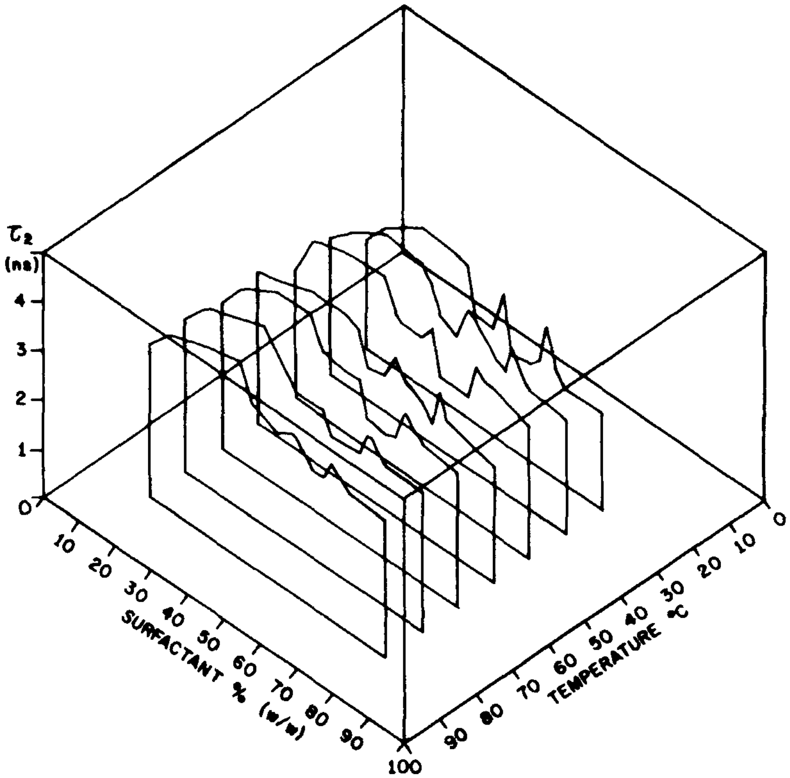

FIGURE 6 Isometric diagram. τ_2 *vs.* surfactant concentration at various temperatures.

mixture) as a function of temperature: at 22 °C they only observed the nematic phase. Increasing the temperature up to 55 °C there was a mixture of nematic and hexagonal phases which changed completely to a hexagonal structure at 61 °C. At higher temperature (75 °C) the transition of the hexagonal structure to an isotropic phase occurred.

The complex hexagonal phase (65–67%) seems to be very well defined along the temperature range of 65–75 °C in the present experiments. This demonstrates the sensitivity of the positron annihilation technique for detecting phase transitions in binary systems, since several authors have reported the difficulty of determining this phase by using different techniques.[12,35,36] According to these authors the complex hexagonal phase always appears mixed with the hexagonal one. This might be due to small concentration and temperature ranges at which this phase exists.

Binary phase diagram

The data obtained in the present experiments allowed the construction of a binary diagram (Figure 7). This diagram indicates the behavior of each liquid crystalline structure of phases A, B, C and D in the SDS-water system (Figure 1) as a function of increasing temperature and shows graphically the results obtained by positron annihilation techniques substantiated by crossed polarized microscopy.

Preliminary phase diagrams of binary systems (surfactant-water)[12] show the existence of only the hexagonal and the lamellar phases. Subsequent X-ray diffraction experiments performed by Luzzati

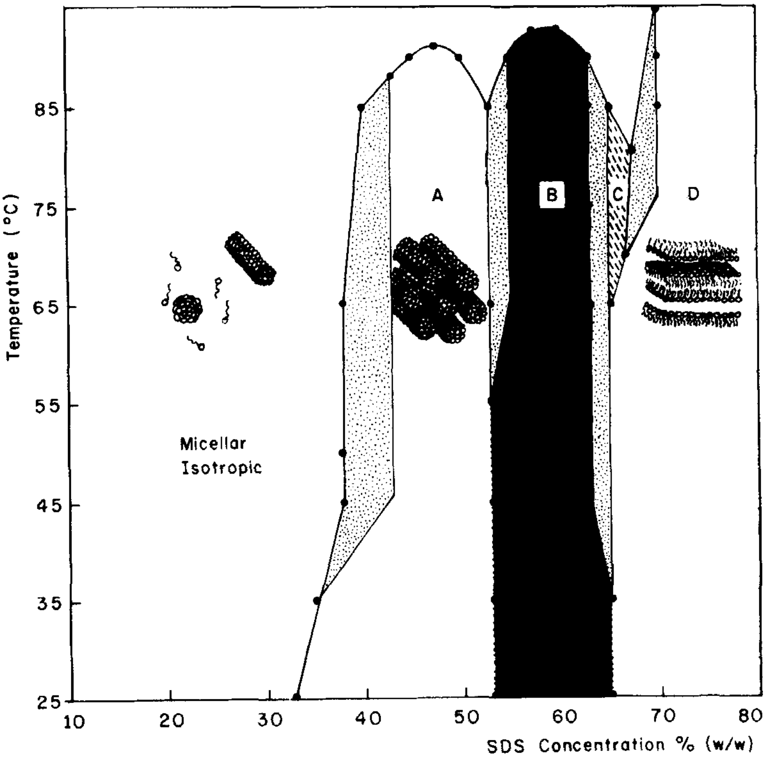

FIGURE 7 Binary phase diagram for the SDS-water liquid crystalline system.

et al.[35] revealed the presence of a complex hexagonal phase at 68% SDS concentration at 70 °C between the hexagonal and the lamellar phases. However, in their studies of the hexagonal phase carried out by using crossed polarized light microscopy, these authors reported that in addition of observing a strongly birrefringent fan-like texture, they saw oil threads in some of the sample regions.[35] This suggests that in those samples, nematic and hexagonal phases might be coexisting since oil thread-like textures are typical of nematic phases.

Comparing the results obtained for the binary system (surfactant-water) in the present study with those reported for ternary ones (surfactant-water-alcohol or salt), i.e.; sodium decyl sulfate (SDS)-water-decanol[38] and KSD-water-KCl,[36] it can be seen that the surfactant/water ratio at which the nematic phase was observed (0.68–0.76) for the system containing decanol and 0.50 for the salt-containing mixture) is lower than that required for forming the same phase in the SDS-water system (1.20–1.70) (Table II). This suggests the existence of an effect of the additive on the surfactant concentration range at which the lyotropic nematics is formed. In case of the SDS-water-decanol system,[38] the range of the surfactant/water ratio in which the nematic phase was observed might be extended from 0.68 to 1.70 if the alcohol content decreased approximately from 7.0 to 0%.

Experiments carried out in the temperature range of 22–75 °C in salt-containing ternary systems[36] revealed that the nematic structure changes to a hexagonal one and subsequently, it reaches an isotropic phase. Conversely, in the binary system studied by positron annihilation, the lyotropic nematics seems to be stable along all the temperature range of 25–85 °C.

The most remarkable result of this study is the observation, for the first time, of a lyotropic nematic phase in a binary system (surfactant-water), showing that some of these systems can present a

TABLE II

Surfactant/water ratio at which the lyotropic nematics has been observed by positron annihilation in binary systems (surfactant-water) as compared with ternary mixtures (surfactant-water-alcohol or salt) studied by X-ray diffraction.

System	Lyotropic nematic phase surfactant/water ratio
SDS-water	1.22–1.70
SDS-water-decanol	0.68–0.77
KDS-water-KCl	0.50

nematic phase without the presence of additives. In addition, the positron annihilation parameters have also indicated a better definition of the concentration range at which each phase exists in the binary liquid crystalline system studied.

These results demonstrate the superiority of the positron annihilation technique to detect phase transitions in lyotropic liquid crystalline systems.

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