

Mesomorphic Behavior of Dioctyl Sodium Sulfosuccinate in Hydrocarbon Solvents

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Abstract □ The formation of mesomorphic (liquid crystalline) systems by highly concentrated solutions of dioctyl sodium sulfosuccinate in an homologous series of five even-numbered chain length *n*-aliphatic hydrocarbon solvents was studied. It was determined that dioctyl sodium sulfosuccinate concentration, solvent chain length, and temperature significantly affect the formation of a mesomorphic phase. At constant temperature, the concentration of dioctyl sodium sulfosuccinate required to produce a mesomorphic phase increased as the solvent chain length increased from octane to dodecane and then decreased to hexadecane. At constant dioctyl sodium sulfosuccinate concentration in each of the five solvents, the mesomorphic-to-isotropic phase transition temperature reached a minimum at dodecane; however, the phase transition temperatures for dioctyl sodium sulfosuccinate systems in tetradecane and hexadecane were higher than those for decane and octane, respectively.

Keyphrases □ Dioctyl sodium sulfosuccinate—mesomorphic behavior in five hydrocarbon solvents, effects of concentration, solvent chain length, and temperature □ Mesomorphic phases—dioctyl sodium sulfosuccinate in five hydrocarbon solvents, phase transition temperatures, effects of concentration, solvent chain length, and temperature □ Phase transition, mesomorphic—dioctyl sodium sulfosuccinate in five hydrocarbon solvents

Under suitable conditions, certain solid organic compounds can exist in intermediate anisotropic states between true crystals and true isotropic liquids (1). The term mesomorphic or liquid crystal is used to describe the intermediate phase, which is a birefringent fluid of rheological properties ranging from viscous liquids to wax-like semisolids. As a result of their birefringence, mesomorphic phases may be characterized and identified by observation between crossed polarizers in an optical microscope (2). Rosevear (3) identified characteristic textures and birefringence that are related to the molecular arrangement within the phase.

Thermotropic mesomorphic phases are produced by heating a solid to a particular temperature, whereas lyotropic mesomorphic phases occur upon the addition of a solvent to a solid. Lyotropic systems can also be thermotropic in behavior, depending on the amount of solvent added and the temperature. The optical properties and sharp X-ray diffraction patterns indicate a degree of structural order in both types of mesomorphic systems (4, 5).

A number of concentrated solutions of viruses, lipids, polymers, and surfactants form lyotropic mesomorphic phases (6). Balmbra *et al.* (7) indicated that dioctyl sodium sulfosuccinate¹, a surface-active compound, is mesomorphic in the anhydrous state and in high concentration, forms lyotropic mesomorphic phases with water and toluene. At constant temperature, as the dioctyl sodium sulfosuccinate concentration in aqueous systems was increased, the systems underwent phase

changes in the order: isotropic → neat phase → viscous isotropic → middle phase. The neat and middle phases were in reversed order from that seen with most other compounds except the phospholipids. The dioctyl sodium sulfosuccinate-toluene systems existed only as middle phase at high dioctyl sodium sulfosuccinate concentrations and were isotropic at lower concentrations. The middle and neat phases are both associated with the smectic mesomorphic phase, one of the three major mesomorphic structural arrangements, the others being nematic and cholesteric. The neat phase consists of a lamellar arrangement of bimolecular layers of surfactant with layers of solvent; the middle phase has a hexagonal structure of long cylindrical micelles (4). There is evidence for additional fine structure in the middle phase, indicating that the hexagonally arranged units may be linear chains of spherical micelles (5).

The purpose of this study was to investigate the formation of lyotropic mesomorphic phases in dioctyl sodium sulfosuccinate-*n*-aliphatic hydrocarbon solvent systems. The parameters evaluated included the influence of surfactant concentration, hydrocarbon solvent chain length, and temperature on the behavior of the lyotropic phases.

EXPERIMENTAL

Materials—Dioctyl sodium sulfosuccinate was synthesized and purified according to the procedure of Balmbra *et al.* (7). The final product, obtained as a hygroscopic waxy solid, gave the correct elemental analysis. Surface tension measurements indicated no minima at the CMC in water, and the CMC value was in good agreement with previously reported values (8, 9).

The hydrocarbon solvents *n*-octane², *n*-dodecane², *n*-hexadecane², *n*-decane³, and *n*-tetradecane³ were treated according to the method of Gillap *et al.* (10). Specific gravities determined for all solvents were in excellent agreement with previously reported values (11, 12).

Instrumentation—Microscopic observations were made with a polarizing microscope⁴ equipped for photomicroscopy. Sample temperature was maintained on a microscope hot stage⁵ regulated with a variable transformer to an approximately 2° rise in temperature per minute. Observations were made at 100×.

Procedure—The binary dioctyl sodium sulfosuccinate-hydrocarbon solvent systems were prepared on a weight/weight percentage basis. The samples, contained in Teflon-lined screw-capped culture tubes, were gently heated with agitation until they fused. The tubes were then slowly cooled to room temperature and allowed to stand for 24–48 hr. prior to observation. This latter step was necessary to ensure equilibration of the samples and thus avoid irreproducibility of the microscopic observations due to possible effects of prior thermal history.

A small portion of the sample was then placed on a microscope slide and formed into a wedge with a cover glass. The slide was

¹ Aerosol OT, American Cyanamid Co.

² Aldrich Chemical Co.

³ Eastman Organic Chemicals.

⁴ Nikon model S.

⁵ Koeffler, A. H. Thomas Co.

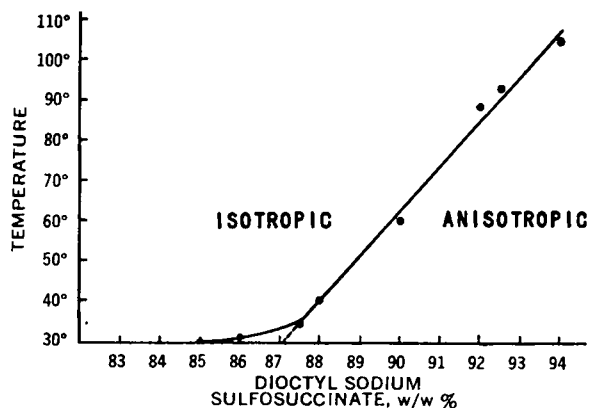


Figure 1—Anisotropic- (liquid crystalline) to-isotropic transition temperatures for dioctyl sodium sulfosuccinate-dodecane systems.

placed on the hot stage at about 30°, and the center portion of the sample was observed as the stage temperature increased. The liquid crystalline systems were anisotropic and showed various birefringent colors and characteristic liquid crystal textures (9). The isotropic samples were dark with no birefringence when observed through the crossed polarizers. The anisotropic-to-isotropic transition temperature was determined to be the first significant darkening of the sample. Three samples for microscopy were taken from different portions of each mixture. Agreement between these runs was good ($\pm 0.2^\circ$), indicating good mixture homogeneity. Duplicate mixtures agreed within $\pm 1^\circ$.

RESULTS AND DISCUSSION

In the absence of solvent, dioctyl sodium sulfosuccinate is a white, waxy, mesomorphic solid at room temperature. When observed between crossed polarizers in a microscope, it is birefringent and has a tightly packed mosaic texture. With increasing concentration of an *n*-aliphatic hydrocarbon solvent, at constant temperature, the system gradually changes to a mesomorphic, turbid, gray-white viscous liquid and finally to a clear, colorless, viscous liquid at the anisotropic-to-isotropic phase transition.

The mesomorphic behavior of dioctyl sodium sulfosuccinate-dodecane systems (Fig. 1) is typical of that of the other dioctyl sodium sulfosuccinate-*n*-aliphatic hydrocarbon solvent systems studied. In Fig. 1, anisotropic-to-isotropic phase transition temperatures are plotted as functions of the weight/weight percentage of dioctyl sodium sulfosuccinate in dodecane. The transition temperature increased as the dioctyl sodium sulfosuccinate concentration increased, consistent with the work of others (7). The lyotropic mesomorphic phase existed at higher temperatures with each increase in dioctyl sodium sulfosuccinate concentration. Below 40°, the data are nonlinear, an apparent result of the instability of the microscope hot stage at temperatures close to ambient. For this reason, the linear portion of the curve was extrapolated to the concentration axis to determine the dioctyl sodium sulfosuccinate concentration at the anisotropic-to-isotropic transition at 30°. Concentrations above 94% weight/weight were not included due to difficulty encountered in achieving adequate homogeneity of the fused binary mixtures. Due to the small amount of solvent present, it was not possible to ensure uniform solvent distribution.

The data for the five *n*-aliphatic hydrocarbon solvents are summarized in Fig. 2. As the *n*-aliphatic solvent chain length increased from octane to dodecane, the anisotropic-to-isotropic transition curves migrated to higher dioctyl sodium sulfosuccinate concentrations at a given constant temperature. For tetradecane and hexadecane, however, this trend was reversed, and at a constant temperature the transition occurred at a lower dioctyl sodium sulfosuccinate concentration with each increment in solvent chain length. Solvent chain length appears to have a significant effect on the formation of the lyotropic liquid crystalline phases in these binary surfactant-solvent mixtures.

When the anisotropic-to-isotropic transition temperature is plotted as a function of increasing *n*-aliphatic hydrocarbon sol-

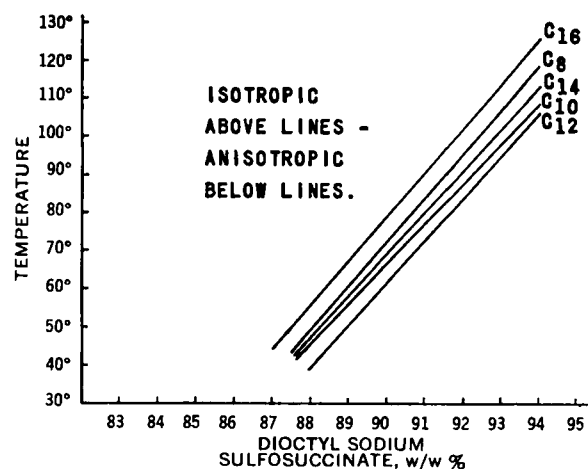


Figure 2—Anisotropic- (liquid crystalline) to-isotropic transition temperatures for dioctyl sodium sulfosuccinate-*n*-aliphatic hydrocarbon solvent systems.

vent chain length at constant dioctyl sodium sulfosuccinate concentration (Fig. 3), the transition temperature reaches an apparent minimum at dodecane and then rises as the solvent chain length is increased to hexadecane. At constant dioctyl sodium sulfosuccinate concentration, the transition temperature for tetradecane and for hexadecane was higher than that for decane and octane, respectively. This behavior was observed for all of the surfactant concentrations studied. An alternative method of presenting these data is to plot isotherms of dioctyl sodium sulfosuccinate concentration as a function of *n*-aliphatic hydrocarbon chain length (Fig. 4). In interpreting the data in Fig. 4, it is important to remember that the systems are anisotropic above the curves and isotropic below. This is the reverse situation from that in Fig. 3. As shown in Fig. 4, at a constant temperature the dioctyl sodium sulfosuccinate concentration required to give an anisotropic liquid crystalline system increases as the solvent chain length is increased to dodecane and then decreases to hexadecane. The anisotropic system occurs at a lower dioctyl sodium sulfosuccinate concentration in hexadecane than in octane and similarly in tetradecane as compared to decane.

Balmbra *et al.* (7) determined that molecules of dioctyl sodium sulfosuccinate in the absence of solvent exist in hexagonally arranged elongated cylindrical structures. The two-dimensional hexagonal array of cylindrical structural units were generally similar to the inverse middle phase (M_2) proposed by Winsor (13) and the hexagonal II phase of Luzzati and Husson (4). The cylinders resembled elongated micelles, with the surfactant molecules oriented to give a polar core and a hydrocarbon exterior.

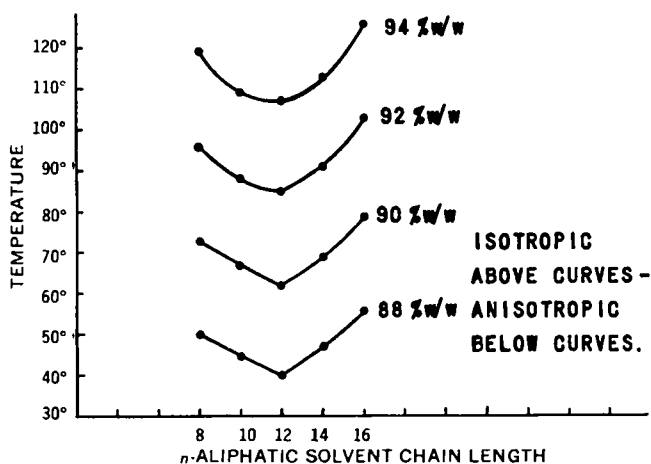


Figure 3—Anisotropic- (liquid crystalline) to-isotropic transition temperatures for dioctyl sodium sulfosuccinate-*n*-aliphatic hydrocarbon solvent systems at constant dioctyl sodium sulfosuccinate concentration.

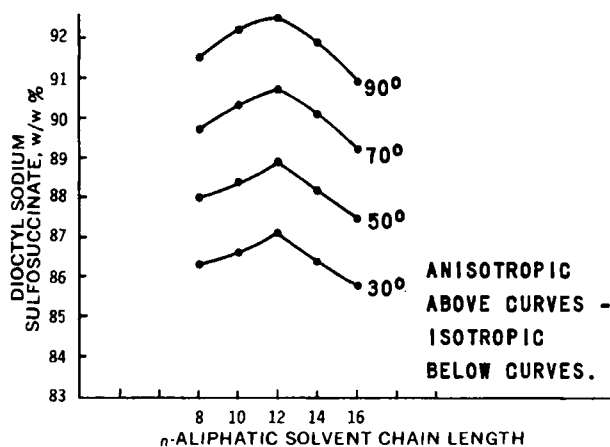


Figure 4—Isothermal effect of dioctyl sodium sulfosuccinate concentration on the anisotropic- (liquid crystalline) to-isotropic phase transition of dioctyl sodium sulfosuccinate-*n*-aliphatic hydrocarbon solvent systems.

Additional fine structure was found (7), suggesting a structural unit consisting of linear chains of aggregated spherical micelles arranged in an hexagonal array. Regardless of the model selected for the structure of the elongated units, it appears that upon addition of solvent the structural arrangement is loosened by solvent orientation at the interface between the structural units (4, 5, 13). Such solvent orientation would, in effect, separate the structural units, decreasing the short-range order but maintaining a degree of long-range ordering dependent on the distance of separation of the units. If the units are composed of linearly aggregated micelles, such solvent penetration would be expected to occur between the micelles and, perhaps to a greater extent, between the linear aggregates themselves. Either of these effects, or both, would produce a weakening of the structural order of the liquid crystalline phase.

At solvent concentrations below the critical amount at a given temperature, deaggregation may be produced by elevating the temperature to the anisotropic-to-isotropic phase transition for the particular system.

Comparison of the octane and hexadecane systems indicates that the anisotropic-to-isotropic phase transition occurs at a higher temperature in hexadecane than in octane (Fig. 3). The lack of significant solvation of dioctyl sodium sulfosuccinate micelles in the longer chain *n*-aliphatic hydrocarbon solvents along with the higher cohesive energy of these solvents resulted in an increase in the micelle weight as the chain length of the solvent was increased (14). It is, therefore, reasonable to expect the dioctyl sodium sulfosuccinate micellar structural units to be more strongly bound in the longer chain *n*-aliphatic hydrocarbon solvents; hence, deaggregation occurs at a higher temperature in hexadecane than in octane. This explanation, however, does not account for the behavior of the dioctyl sodium sulfosuccinate systems in decane, dodecane, and tetradecane. As indicated earlier, the anisotropic-to-isotropic phase transition temperature decreased from octane to dodecane and then increased to hexadecane (Fig. 3). The decrease in thermal stability of the mesomorphic phase, resulting in the minimum at dodecane, indicates that the dioctyl sodium sulfosuccinate structural units are more loosely bound in this solvent than in the other solvents studied.

The "transitional" behavior of dodecane has been reported in studies of the micelle weight of dioctyl sodium sulfosuccinate in the same *n*-aliphatic hydrocarbon solvents. It was found that the micelle weight of anhydrous and hydrous dioctyl sodium sulfosuccinate-dodecane systems was larger than that expected by extrapolation of the corresponding micellar weights in the other solvents (14). In addition, studies of the solubilization of water by solutions of dioctyl sodium sulfosuccinate in the *n*-aliphatic hydrocarbon solvents also indicated the transitional behavior of dodecane systems (15). The relatively low water solubilization and phase properties resembled that of the longer chain solvents, whereas the temperature dependency of the phase transitions was similar to that of the shorter chain solvents. It is not clear at this point what interrelation may exist between these studies; however, it appears that the dioctyl sodium sulfosuccinate-dodecane systems are extremely interesting and worthy of additional study. Work is in progress to elucidate the mechanism of the transitional behavior of dodecane.

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