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mixtures resembles that of mixtures approaching a tricritical point if one of the field variables is appropriately varied.

Acknowledgment. We are indebted to B. Faulhaber and T. Lieu for their assistance with the experiments and to the German Federal Ministry for Research and Tech-

nology (BMFT) for financial support (Grant No. 0326315 B).

Registry No. C_8E_4 , 19327-39-0; C_8E_3 , 19327-38-9; C_8E_6 , 19327-40-3; C_8E_6 , 4440-54-4; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3; *n*-octadecane, 593-45-3; *n*-hexane, 110-54-3.

Effect of Oil Type on Liquid Crystalline Phase Behavior in Sodium *n*-Dodecanoate-Water-Oil Mixtures[†]

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Received December 2, 1987. In Final Form: February 8, 1988

The liquid crystalline phase behavior of the binary system sodium *n*-dodecanoate (laurate)-water has been studied by 2H and ^{23}Na NMR quadrupole spectroscopy from 55 to 80 °C. Three lyotropic liquid crystal phases were identified: hexagonal and lamellar phases and a single intermediate phase with composition and temperature range falling between the composition and temperature range of the other two phases. Complete high-resolution phase diagrams of the ternary systems sodium laurate-water-*n*-decane and sodium laurate-water-toluene were determined at 60 °C by using optical birefringence and 2H and ^{23}Na NMR quadrupole spectroscopy. The ternary system with *n*-decane is similar to analogous sodium *n*-octanoate-water-nonamphiphilic oil phase diagrams studied by Ekwall and co-workers; little oil is solubilized by isotropic micellar (<3% w/w) and hexagonal (<5%) phases, and a small region of viscous isotropic phase exists at low decane content (ca. 11-13%). The ternary system with toluene is markedly different; toluene is extremely well solubilized by micellar (ca. 13%), hexagonal (29%), and viscous isotropic (25%) phases. Moreover, a large lamellar phase extends from about 3% to 27% toluene at surfactant concentrations of 46-60% and is stable at 60 °C only within the ternary diagram. The differences in *n*-decane versus toluene solubilization are likely attributable to the mode of molecular solubilization: *n*-decane is largely confined to the lipophilic cores of the microstructural subunits while toluene is significantly solubilized in the surfactant interfacial film.

Introduction

The ternary phase equilibria of surfactant-water-oil mixtures are important determinants of their performance in emulsification, lubrication, solubilization, surfactant-mediated separation techniques, and enhanced oil recovery. While the patterns of isotropic phase behavior in these systems are reasonably well understood, the equilibria among liquid crystalline phases have been elucidated for only a small number of model systems. Most of these are cited in the well-known review article by Ekwall,¹ and the majority of these ternary phase equilibrium studies were performed with seven- and eight-carbon surfactants because these compounds form liquid crystalline phases at ambient temperatures and are thus easily studied. For example, more than 20 ternary phase diagrams of sodium *n*-octanoate (caprylate) with water and a variety of oils were determined by Ekwall and co-workers^{1,2} at 20 °C. In an effort to determine how general these patterns of phase behavior are for longer aliphatic tail groups (larger oil solubilization capacity), we describe here a study of the phase behavior of sodium *n*-dodecanoate (laurate) with water and the two prototypical oils: *n*-decane and toluene at 60 °C.

The experimental techniques best suited for a determination of phase number and type in liquid crystal sys-

tems are those which directly probe the anisotropy of the mesophase. Optical birefringence and NMR quadrupole spectroscopy are commonly exploited for this purpose. In the study of lyotropic smectic mesophases, Tiddy, Lindman, and co-workers³⁻⁷ and Khan et al.⁸⁻¹⁰ have made extensive use of both optical polarizing microscopy and 2H and ^{23}Na quadrupole NMR spectroscopy for determining binary surfactant-water and ternary surfactant-water-oil phase equilibria. Persson et al.³ elucidated many of the details of the sodium octanoate-water-*n*-decanol phase diagram by 2H quadrupole NMR spectroscopy, including multiphase coexistence of lamellar, hexagonal, and reversed hexagonal smectic liquid crystals. Lindblom et al.⁴ and Tiddy et al.⁵ demonstrated that ^{23}Na quadrupole splittings can be used for similar ternary liquid crystal phase studies.

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[†] Presented at the symposium on "Fundamental and Applied Aspects of Microemulsions, II", 61st Colloid and Surface Science Symposium, Ann Arbor, MI, June 21-23, 1987; E. Kaler, Chairman.

Khan et al.⁸⁻¹⁰ have recently exploited the quadrupole NMR technique to determine phase equilibria in binary and ternary systems of both single-tail and double-tail surfactants. Beyer¹¹ extensively studied both lyotropic liquid crystal phase equilibria and water mobility and structure by using ²H quadrupole NMR for the Triton X-100-deuterium oxide system.

In the study of lyotropic nematic mesophases, Reeves and co-workers (see Forrest and Reeves, ref 12, for a comprehensive review) and Boden et al.¹³ have made elegant use of ²H and ²³Na quadrupole NMR to determine phase transitions, phase type, and kinetics of phase separation of nematic lyotropic liquid crystals. Lawson and Flautt¹⁴ discovered that nonspherical micellar phases upon concentration can form nematic liquid crystalline phases in which the micellar subunits orient relative to a director axis but possess no long-range positional order. The quadrupole NMR technique is particularly useful for studying these systems because the nematic phase can be oriented from a random, polycrystalline sample to a completely macroscopically ordered sample by the magnetic field of an NMR spectrometer. In this way, both the kinetics of ordering and the sign of the diamagnetic anisotropy of these nematic liquid crystals can be determined.

Quadrupole NMR Spectroscopy

Nuclei with spin quantum numbers I greater than $1/2$, e.g., ²H and ²³Na, possess nuclear quadrupole moments which can interact with gradients in the local electric field to produce an additional contribution to the Hamiltonian of a nuclear spin in a magnetic field.¹⁵⁻¹⁷ For such quadrupolar nuclei in a uniaxial liquid crystal phase, the energy levels of a particular nucleus are given by a superposition of Zeeman and quadrupole terms:

$$E_m = -\gamma h m H_0 + \frac{e^2 q Q}{8} (3 \cos^2 \theta - 1) (3m - 2)^2 \quad (1)$$

where γ is the magnetogyric ratio, H_0 the external applied magnetic field, eq the magnitude of the electric field gradient at the nucleus in question, eQ the quadrupole coupling constant, h Planck's constant, θ the angle between the molecular director axis and the external field, and m the energy level, which takes on values between $-I$ and I (the spin quantum number). With deuterium as the quadrupolar nucleus, the spin quantum number is 1 and the difference between the two transitions $\Delta E_{-1,0}$ and $\Delta E_{0,1}$ is the so-called quadrupole splitting $\Delta\nu$:

$$\Delta\nu = \left(\frac{3eQS_{zz}}{4h} \right) (3 \cos^2 \theta - 1) \quad (2)$$

where S_{zz} is the degree of order of the ²H nucleus with respect to the director of the uniaxial electric field gradient. If the orientational order of the mesophase is macroscopically random (polycrystalline powder pattern), the line shape of the ²H NMR spectrum can be approximated by

$$g(\nu) = \pm \frac{1}{(12)^{1/2} C} \left(1 \pm \frac{2\nu}{C} \right)^{-1/2} \quad (3)$$

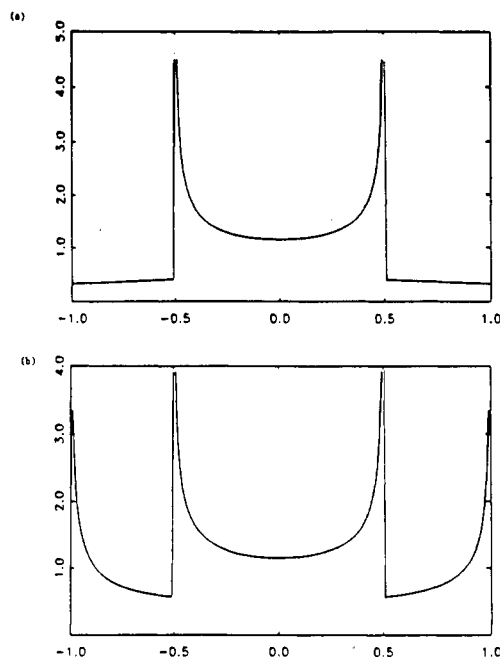


Figure 1. (a) Theoretical NMR line shape for a spin of quantum number 1 (²H, e.g.) given by eq 3 (with $C = 1$) for a random distribution of uniaxial liquid crystallites in three dimensions. Abscissa is units of ν , and ordinate is $g(\nu)$. (b) Theoretical NMR line shape for a spin of quantum number 1 given by eq 4 (with $C = 1$) for a random distribution of uniaxial liquid crystallites in two dimensions. Same units as in Figure 1a.

where $C = \frac{3}{2} eQS_{zz}$, with $-C \leq \nu \leq C/2$ for the negative sign and $-C/2 \leq \nu \leq C$ for the positive sign. The theoretical line shape given by eq 3 for a spin 1 system with random distribution of mesophase directors is shown in Figure 1a.

For a two-dimensional powder pattern, in which the directors of the mesophase domains are randomly distributed in a plane through which the magnetic field passes, the theoretical line shape function has four asymptotes:

$$g(\nu) = \frac{1}{2^{1/2} \pi C} \left(1 \pm \frac{2\nu}{C} \right)^{-1/2} \left(1 + \frac{\nu}{C} \right)^{-1/2} \quad (4)$$

where the “+” sign combination holds for $-C/2 \leq \nu \leq C$ and the “-” combination holds for $-C \leq \nu \leq C/2$. As in eq 3, $C = \frac{3}{2} eQS_{zz}$. A two-dimensional powder spectrum is shown in Figure 1b for $C = 1$.

The line shape and quadrupole spectrum for ²³Na in a polycrystalline liquid crystal phase, which possesses a spin $3/2$ nucleus, are quite similar to ²H spectra with the difference that a central resonance corresponding to the $m = -1/2$ to $m = 1/2$ transition is always observed. With the liquid crystalline phases studied here, only smectic phases were observed, and both ²H and ²³Na spectra were always either three-dimensional powder patterns (eq 3), partially oriented powder patterns (eq 4), or superpositions of these patterns for multiphase samples.

Experimental Section

Materials. Sodium *n*-dodecanoate (laurate) was purchased from Nu Chek Prep, Inc., (Elysian, MN) and had a quoted purity of greater than 99%. It was stored as a finely ground solid in a desiccator over CaSO₄ and used without further purification. *n*-Decane and toluene were Aldrich Gold Label (>99+%) products and were used without further purification. The water was either HPLC grade water from Baker or doubly distilled. Deuterium oxide (99.8 atom % D) was from MSD Isotopes.

Methods. Samples for visual birefringence studies were prepared in 10–20-mL ampules by weighing in dry surfactant, water,

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and the oil, in that order. Before the sample was heated to the equilibration temperature, the ampule was carefully tamped to fully wet the solid surfactant with water and/or oil. With samples made not adhering to this protocol, liquid crystalline phases often formed above, and separated from, the dry crystalline solid, which resulted in very slow equilibration. The ampule was then flame-sealed and placed in a resistively heated flat hexagonal air box which contained a bank of diffuse fluorescent lights in the center surrounded by an opaque glass light diffuser. During observation of a sample, the wooden top of the box was rotated to position a sheet of polarizing film over the diffuser and an analyzer was placed on the outside glass window of the box. During equilibration, the temperature was held constant to ± 0.2 °C. During observation, the temperature was maintained to ± 1 °C.

Samples for NMR measurements were prepared in 5-mm glass NMR tubes (Wilmad Glass Co.) into which the three components were weighed in the same order as above and then flame-sealed. Thermal equilibration was performed either in the air box described above or in a water bath maintained to ± 0.5 °C. NMR spectra were taken on an IBM CX-100 spectrometer operating in the FT mode. The resonance frequencies for ^2H and ^{23}Na were 15.37 and 26.485 MHz, respectively. In a typical ^2H experiment, 500–1000 transients were accumulated in 4–8K data points with an acquisition time of 0.05–0.5 s and no pulse delay. The spectral width was typically 5000 Hz and the pulse width 12 μs . With ^{23}Na , 4000–6000 transients were accumulated in 4–8K data points with an acquisition time of 0.05–0.1 s and no pulse delay. A typical spectral width was 30–50 kHz, and the pulse width was 20 μs . The estimated uncertainties in the reported ^2H and ^{23}Na quadrupole splittings are 5 and 30 Hz, respectively. The temperature was controlled during the NMR experiment by passing nitrogen over a resistive heating coil in the probe and was monitored by a Bruker VT temperature-control unit. The temperature was accurate to ± 0.5 °C. All reported quadrupole splittings were reproduced at least once over several weeks to months to ensure equilibrium.

Results and Discussion

Binary Sodium Laurate–Water Phase Behavior. As a basis upon which to construct ternary phase equilibria with oil, the binary system sodium laurate–water was investigated by using polarized light visual observations and ^2H and ^{23}Na quadrupole NMR spectroscopy. Five different phases in the temperature range 55–80 °C were identified: isotropic micellar (L_1), hexagonal liquid crystalline (H), lamellar liquid crystalline (L_α), crystalline surfactant (X), and a so-called intermediate liquid crystalline phase (I) whose composition and temperature extent fall between those of the H and L_α phases. The isotropic micellar phase was fluid and of visually low viscosity up to the phase transition to a hexagonal liquid crystal phase. The lamellar phase was opaque, birefringent, and sufficiently fluid to flow when tamped slightly. The hexagonal and intermediate liquid crystal phases were extremely viscous and did not flow, even upon vigorous tamping of the sample tubes. Deuterium (D_2O) quadrupole splittings as a function of sodium laurate concentration (on a deuterium-free basis) at 69 °C are shown in Figure 2.

In the region of Figure 2 denoted "hexagonal", a single quadrupole powder pattern was determined for the deuterium nucleus in deuterium oxide. The observed spectra in this region were typically two-dimensional powder spectra as illustrated in Figure 3a for a sample of 53 wt % sodium laurate. The experimental spectrum in Figure 3a compares favorably with a line-broadened version of the theoretical spectrum in Figure 1b. In the two-phase region between hexagonal and intermediate phases in Figure 2, the deuterium NMR spectrum contains two quadrupole spectra: one corresponding to the hexagonal phase and one to the intermediate phase (Figure 3b). Interestingly, when a hexagonal phase is interspersed with the inter-

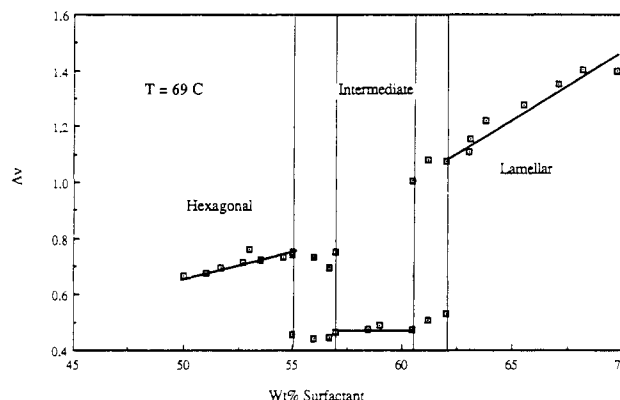


Figure 2. Dependence of deuterium quadrupole splittings in kHz on surfactant composition in binary sodium laurate–deuterium oxide mixtures at 69 °C. Surfactant composition corresponds to the deuterium-free (protonated water) system assuming the sole effect of deuterium is to change the weight percent in the mixture. The straight lines are an aid to the eye illustrating linearity of the data.

mediate phase, the spectrum for the hexagonal phase more closely resembles a line-broadened three-dimensional powder pattern (Figure 1a) than a two-dimensional spectrum. Apparently, the thermal equilibration of a pure hexagonal phase in a small diameter tube (5 mm or less) tends to orient the liquid crystal domains along the tube axis, resulting in a two-dimensional powder spectrum. In the presence of the second phase, however, there is adequate disruption of the hexagonal domains to give rise to a three-dimensional powder spectrum. The pure intermediate phase (Figure 3c) typically gives rise to a three-dimensional powder spectrum, as does the pure lamellar phase (Figure 3e). Two-phase mixtures of intermediate and lamellar phases yield spectra of overlapping three-dimensional powder patterns (Figure 3d).

The magnitudes of the quadrupole splittings are in good agreement with the results of Rendall et al.⁷ reported for sodium laurate–deuterium oxide mixtures at 82 °C: between 500 and 800 Hz for hexagonal phase splittings, between 430 and 500 Hz for the intermediate phase, and greater than 1000 Hz for the lamellar phase. The compositions of the phase transitions between coexisting liquid crystal phases determined here are slightly lower (1–2 wt %) than those measured by Rendall et al.,⁷ while the composition range of the intermediate phase determined here is in good agreement with Madelmont and Perron's¹⁸ I_2 phase. The partial binary phase diagram of sodium laurate–water determined here is shown in Figure 4.

Rendall et al.⁷ interpreted their ^2H and ^{23}Na quadrupole splittings with the two-state water model. This model assumes that the observed quadrupole splitting is the average signal of D_2O in a bound (anisotropic) state and in a free (isotropic) state. Because the exchange between these states is rapid (10^{-5} – 10^{-7} s) compared to the time scale of the NMR experiment (10^{-2} – 10^{-1} s), the observed quadrupole splitting is linearly proportional to the fraction of molecules bound (in a given liquid crystalline phase) to the surfactant composition:

$$\Delta_{\text{obsd}} = k' \frac{C_s}{C_w} \Delta_{\text{bound}} = k\omega_s \Delta_{\text{bound}} \quad (5)$$

where Δ_{obsd} is the observed quadrupole splitting, Δ_{bound} is the quadrupole splitting of bound water molecules, C_s and C_w are surfactant and water concentrations, respectively,

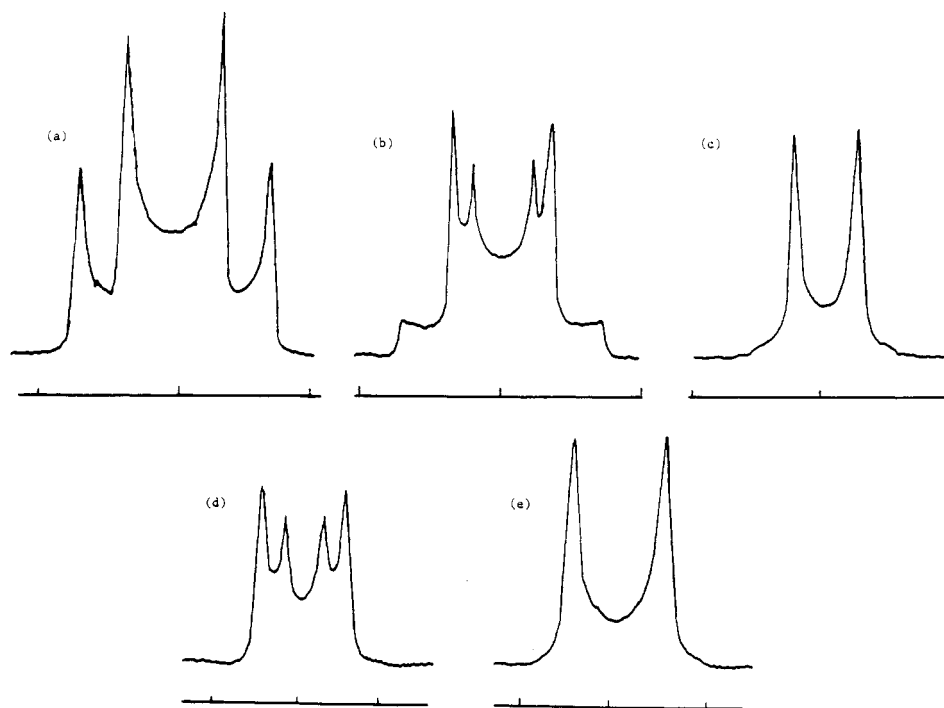


Figure 3. Experimental deuterium NMR spectra of sodium laurate-deuterium oxide samples at 69 °C (sample compositions given on an undeuteriated weight percentage basis): (a) pure hexagonal phase of 52.7 wt % sodium laurate (SL); (b) mixture of hexagonal and intermediate phases, 55.0 % SL; (c) pure intermediate phase, 58.5 % SL; (d) mixture of intermediate and lamellar phases, 60.5 % SL; (e) pure lamellar phase, 63.0 % SL. The tick marks on the horizontal axis are spaced 1000 Hz apart.

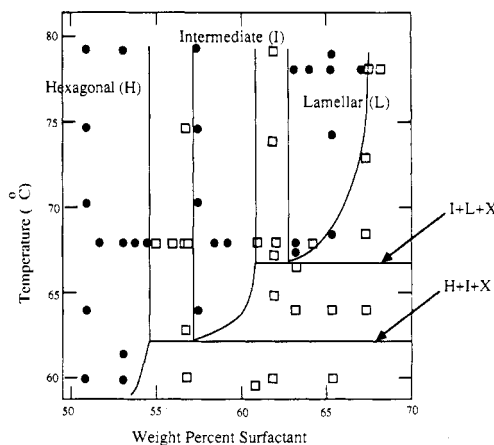


Figure 4. Binary temperature-composition phase diagram of the sodium laurate-water mixture as determined from ^2H and ^{23}Na quadrupole NMR experiments on sodium laurate-deuterium oxide mixtures. Solid circles correspond to one-phase samples and open squares to two-phase samples. Surfactant composition is for the equivalent deuterium-free system.

ω_s is the surfactant weight percentage, and k' and k are constants of proportionality.

The data in Figure 2 are linear with composition in the one-phase regions within experimental uncertainty. Rendall et al.⁷ argue that a small change in structure of the hexagonal phase may occur at compositions just below that of the hexagonal-intermediate phase transition, determined to be 56 wt % sodium laurate in this study. Their basis for this conclusion is the slight deviation of their observed ^2H quadrupole splittings from a linear variation with composition. Their conclusions are further based on a similarity, albeit qualitative, between the ^2H D_2O quadrupole splittings of sodium laurate-water and sodium dodecyl sulfate-water samples. Our D_2O quadrupole splittings vary linearly with surfactant composition from 50 to 55 wt % within experimental uncertainty (± 5 Hz), suggesting no change in structure of the hexagonal

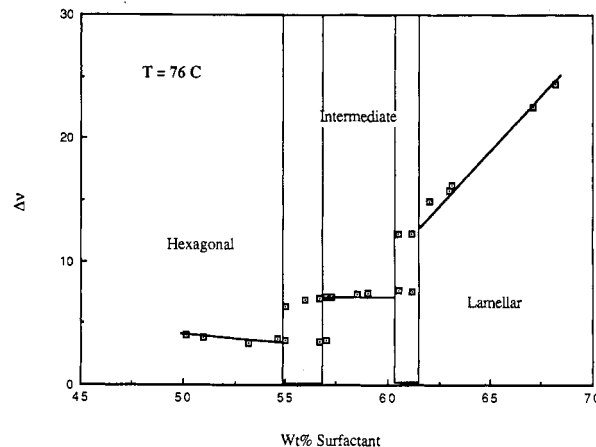


Figure 5. Dependence of sodium quadrupole splittings in kHz on surfactant composition in binary sodium laurate-deuterium oxide mixtures at 76 °C. Surfactant composition is for the equivalent deuterium-free system. The straight lines are added as an aid to the eye.

phase up to the phase transition to an intermediate phase. Moreover, in contrast to Madelmont and Perron's¹⁸ results, we find no evidence of a second intermediate phase at 60–61% surfactant. Instead our results indicate a single intermediate liquid crystalline phase at compositions between 57% and 60.5% sodium laurate by weight at temperatures above 62 °C, the thermal stability limit for this phase. At 60 °C, the temperature at which we report ternary surfactant-oil-water phase equilibria, the hexagonal phase is the only stable liquid crystalline phase along the binary surfactant-water edge of the phase diagram.

^{23}Na quadrupole splittings as a function of surfactant composition in binary sodium laurate-water samples at 69 °C are shown in Figure 5. The phase transitions from hexagonal to intermediate and intermediate to lamellar are in good agreement with our ^2H D_2O results and compare favorably with Rendall et al.'s values.⁷ Again, we detect no evidence of a second intermediate phase.

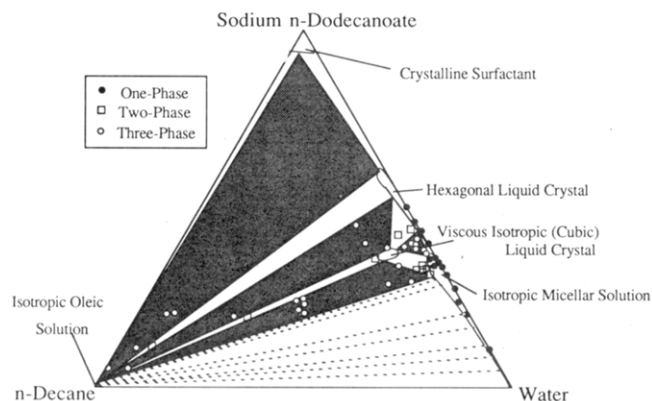


Figure 6. Ternary phase diagram of sodium laurate, *n*-decane, and water at 60 °C. Solid circles correspond to one-phase samples, shaded squares to two-phase samples, and open circles on shaded triangles to three-phase samples. The wavy lines at low surfactant content correspond to experimentally measured tie-lines on two-phase mixtures determined by using Karl Fischer titration for water analysis and gravimetric analysis for surfactant analysis.

Ternary Sodium Laurate-*n*-Decane-Water Phase Behavior. The ternary phase diagram of sodium laurate-*n*-decane-water at 60 °C is shown in Figure 6. The majority of the diagram was determined by polarized light visual observations of samples sealed in glass ampules and equilibrated diffusionally. Five different phases were observed throughout the diagram: isotropic decane-rich (L_2), viscous isotropic liquid crystal (VI), and the L_1 , H, and X phases observed along the binary surfactant-water edge. The VI phase was identified by its optical isotropy at equilibrium (nonbirefringence), high viscosity, cooling-induced birefringence, and local isotropy at equilibrium as deduced by the lack of a deuterium quadrupole splitting in samples for which D_2O was substituted for protonated H_2O on an equimolar basis. The VI phase formed slowly, and samples which contained excess oil (L_2 phase) in contact with VI, L_1 , and H phases were very slow to diffusionally equilibrate, often taking several months.

In order to determine whether any I or L_α phases exist in the ternary system at 60 °C (the thermal stability limit for the lamellar phase in binary sodium laurate-water mixtures is about 67 °C), 2H NMR spectra of samples at high surfactant concentrations (≥ 50 wt %) were determined at various decane contents between 1 and 20 wt %. Neither phase was detected. The H phase always gave a single 2H quadrupole splitting when H_2O was substituted by D_2O with a spectral line shape typical of either a three-dimensional powder pattern or a partially oriented two-dimensional powder pattern (as predicted by eq 3). The value of this quadrupole splitting varied only between 550 and 770 Hz. Similar experiments measuring ^{23}Na NMR quadrupole splittings yielded similar results; no evidence of either the I or L_α phase was found. The alkali metal ion NMR line shapes were typically partially oriented two-dimensional powder spectra with quadrupole splittings of 4.2 to 5.8 kHz, a value consistent with a hexagonal phase structure.

Ternary Sodium Laurate-Toluene-Water Phase Behavior. The ternary phase diagram of sodium laurate-toluene-water at 60 °C is shown in Figure 7. In addition to the L_2 , L_1 , VI, H, and X phases, which are stable in the analogous decane phase diagram, a large region of lamellar liquid crystalline phase (L_α) exists which occurs only on the interior of the diagram. This phase exhibits slightly turbid birefringence in polarized light, has a relatively low viscosity as evidenced by its ability to flow upon tamping, and has both a large (1200–1900 Hz) 2H

Table I. Quadrupole Splittings and Phase Designations for Representative Sodium Laurate-*n*-Decane-Water and Sodium Laurate-Toluene-Water Mixtures at 60 °C^a

sample	composition, wt %	^2H Δ , Hz	^{23}Na Δ , kHz	phase designation
Sodium Laurate- <i>n</i> -Decane-Water				
4	11.6 dec	0	5.45	H + VI + L ₂
	38.4 SL	580		
	50.0 water			
5	10.2 dec	770	4.63	H + L ₂
	49.6 SL			
	40.2 water			
D3	1.0 dec	0		H + L ₁
	40.8 SL	477		
	58.2 water			
Sodium Laurate-Toluene-Water				
A2	5.0 tol	610	3.50	H
	46.9 SL			
	48.1 water			
A3	10.5 tol	580	3.70	H + L _{α}
	47.9 SL	1890	16.55	
	41.6 water			
A4	15.3 tol	630	4.45	H + L _{α}
	44.8 SL	1910	18.20	
	39.9 water			
A5	21.3 tol	620	4.75	H
	41.7 SL			
	37.0 water			
A6	25.8 tol	620	5.05	H
	39.2 SL			
	35.0 water			
A7	30.9 tol	610	5.75	H + L ₂
	36.3 SL			
	32.8 water			
P1	18.8 tol	0		H + VI
	36.6 SL	504		
	44.6 water			
P3	5.7 tol	690	3.33	H + L _{α}
	50.0 SL		15.2	
	43.5 water			
P4	10.5 tol	520	3.45	H + L _{α}
	51.6 SL	1880	19.25	
	38.0 water			
P5	15.7 tol	1920	18.3	L _{α}
	51.2 SL			
	33.1 water			
P6	20.7 tol	530	4.55	H + L _{α}
	45.2 SL	1870	17.37	
	34.1 water			
P7	30.1 tol	1920	17.18	H + L ₂ + X
	45.3 SL			
	24.6 water			
C2	5.1 tol	1170	12.70	L _{α}
	57.5 SL			
	37.4 water			
C3	10.2 tol	1740	18.25	L _{α}
	54.2 SL			
	35.6 water			
C4	15.5 tol	1960	18.675	L _{α}
	52.0 SL			
	32.5 water			
C5	21.1 tol	1910	17.15	L _{α}
	49.7 SL			
	29.2 water			
C6	25.4 tol	640	4.50	H + L _{α}
	46.7 SL	1910	16.95	
	27.9 water			

^aThe various phases present in these ternary mixtures are denoted by H (hexagonal), VI (viscous isotropic), L_1 (aqueous micellar), L_2 (isotropic oleic), X (crystalline), and L_α (lamellar). Phase designations were made by a combination of NMR measurements and visual observations of optical birefringence.

quadrupole splitting when H_2O is substituted by D_2O and a large ^{23}Na quadrupole splitting (15–25 kHz). These quadrupole splittings are similar in magnitude to those

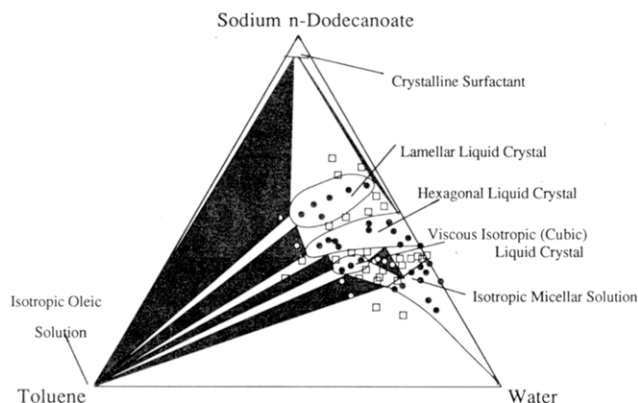


Figure 7. Ternary phase diagram of sodium laurate, toluene, and water at 60 °C. Symbols as in Figure 5.

determined for the lamellar phase that exists in the binary sodium laurate–water system at temperatures above 67 °C. Typical ^2H and ^{23}Na spectra of pure H, pure L_α , and mixed H and L_α phases are shown in Figures 8 and 9.

Over a small range of compositions (ca. 10–15% toluene and 50–55% sodium laurate), ^2H spectra were observed with isotropic peaks constituting 10–15% of the total amount of deuterium in the sample. Ordinarily, ternary surfactant–oil–water samples with deuteriated water at elevated temperatures exhibit small (<5%) isotropic peaks due to evaporation and condensation of water in the air space of the sample NMR tubes. However, in samples of the aforementioned composition, these isotropic signals were larger than might be attributed to this mechanism. It is possible that a small viscous isotropic phase of different structure than the VI phase observed at lower surfactant content exists in this concentration regime. However, the experiments described were unable to resolve

a single-phase viscous isotropic region at these concentrations.

The composition region in which the VI phase of lower surfactant content is stable was largely determined by visual observations of samples in polarized light at equilibrium or slightly perturbed from equilibrium. As with the decane–water–sodium laurate system, the VI phase in the toluene samples was gellike with a high-yield stress, was optically isotropic at equilibrium, exhibited cooling-induced birefringence, and gave an isotropic deuterium signal (when D_2O was substituted for H_2O) that was proportional to the relative amount of VI phase in the sample. Typical values of ^2H and ^{23}Na quadrupole splittings of ternary sodium laurate–oil–water samples at 60 °C, along with phase designations as determined by both NMR and visual observations, are given in Table I.

The sodium laurate–toluene–water system, unlike its decane counterpart, exhibits large amounts of oil solubilization in the L_1 , VI, H, and L_α phases. By way of contrast, a maximum of 13 wt % toluene is solubilized in the aqueous micellar phase as opposed to only 2–3 wt % decane. Similarly, 30% toluene is solubilized by the H phase and only 5% decane. If one converts these numbers to a molar basis, the figures are even more striking as the molecular weight of toluene is about 78 Da as compared to 142 Da for *n*-decane.

Comparison with Other Soap–Oil–Water Phase Diagrams. The sodium laurate–*n*-decane–water phase diagram at 60 °C is very similar to the ternary phase diagrams of sodium *n*-caprylate (*n*-octanoate) with water and the oils octane, *p*-xylene, chlorooctane, and carbon tetrachloride at 20 °C.² The binary system sodium caprylate–water at 20 °C has stable L_1 , H, and X phases. The four nonamphiphilic oils above are poorly solubilized by the L_1 and H phases of sodium caprylate–water, the maximum

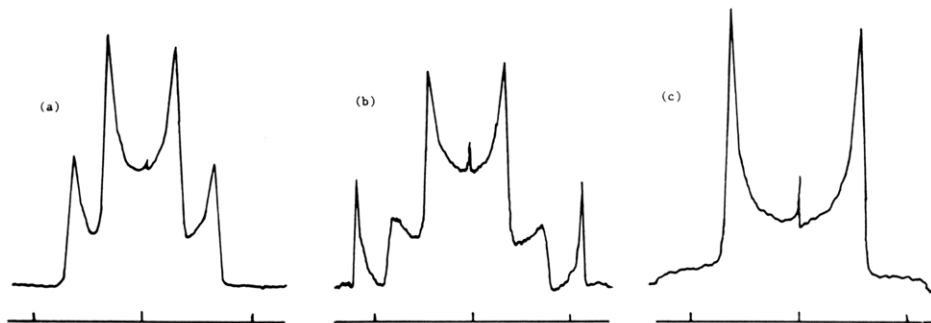


Figure 8. Deuterium NMR spectra of (a) pure hexagonal, (b) a two-phase mixture of hexagonal and lamellar, and (c) pure lamellar samples in ternary sodium laurate, toluene, and deuterium oxide mixtures at 60 °C. Composition of sample a is 5.0 wt % toluene, 46.9% SL, and 48.1% water (on a deuterium-free basis). Sample b is 15.3% toluene, 44.8% SL, and 39.9% water. Sample c is 5.1% toluene, 57.5% SL, and 37.4% water. The tick marks on the horizontal axis are spaced 1000 Hz apart.

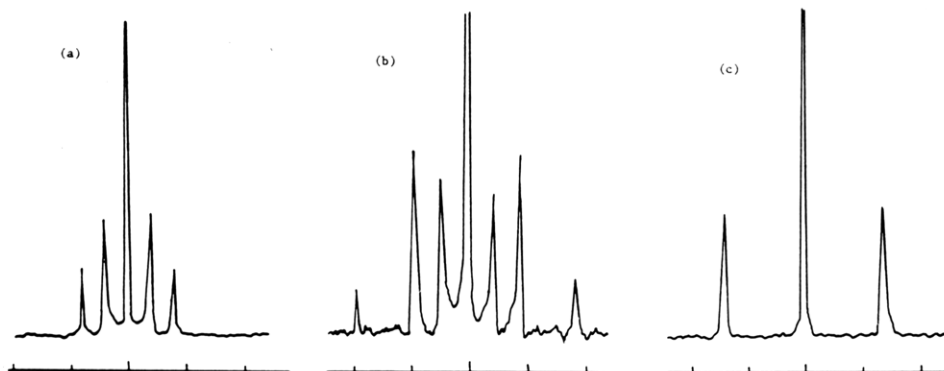


Figure 9. ^{23}Na NMR spectra of (a) pure hexagonal, (b) a two-phase mixture of hexagonal and lamellar, and (c) pure lamellar samples in ternary sodium laurate (SL), toluene, and deuterium oxide mixtures at 60 °C. Sample compositions are as given in Figure 8. The tick marks on the horizontal axis are spaced 10 kHz apart.

amount of oil being about 13% carbon tetrachloride in the ternary sodium caprylate-carbon tetrachloride-water H phase. These four sodium caprylate systems also possess small regions of VI phase which are all internal to the ternary phase diagram and vary in oil content from 5 to 10 wt %.

Several other sodium caprylate-oil-water phase diagrams at 20 °C studied by Ekwall et al.² show large amounts of solubilization of oil by L₁ and H phases but only with amphiphilic oils. For example, methyl octanoate swells the sodium caprylate-water H phase to about 40 wt %. These amphiphilic oils also possess L_α phases completely internal to the phase diagram. However, none exhibit both a VI phase and an L_α phase internal to the phase diagram, such as is found in the sodium laurate-toluene-water system at 60 °C.

The marked differences in the ternary phase diagrams of *n*-decane versus toluene with sodium laurate and water would seem to be a result of the molecular location of solubilization of the two oils. *n*-Decane is poorly solubilized by micellar and hexagonal phases of sodium laurate, and recent experiments in our laboratory probing the anisotropy of the oil by using perdeuterated *n*-decane on the sodium *n*-tetradecanoate (myristate) system¹⁹ suggest that the oil is core-solubilized, that is, located within the lipophilic core of the micellar or hexagonal surfactant subunits and not in the palisade layer of the surfactant. In contrast, toluene seems to be largely palisade-solubilized. This also explains the existence of the lamellar phase in the sodium laurate-water ternary system at temperatures below the stability limit for the lamellar phase in the binary sur-

factant-water mixture. Apparently, at high surfactant concentrations (>40%), solubilization of toluene by sodium laurate hexagonal phase occurs largely in the palisade layer and splay the lipophilic tail groups of the surfactant apart, thereby reducing the curvature of the surfactant interfacial film. A sufficient degree of solubilization can result in a phase transition from hexagonal to lamellar phase. Our evidence from studies on deuterated toluene in hexagonal and lamellar sodium myristate-water-toluene mixtures¹⁹ supports this view.

Conclusions

Lyotropic liquid crystal phase equilibria in the binary sodium laurate-water and ternary sodium laurate-water-*n*-decane and sodium laurate-water-toluene systems have been determined by optical birefringence and quadrupole NMR spectroscopy. In the binary system, the transition from a hexagonal to a lamellar phase is interrupted by the existence of an intermediate phase that is small in compositional extent (57-61 wt %) and is similar in its consistency and appearance to the nearby hexagonal phase. *n*-Decane is poorly solubilized by aqueous micellar (<3%) and hexagonal (<5%) sodium laurate phases. Toluene, on the other hand, is well-solubilized, and its ternary phase diagram exhibits a large lamellar liquid crystal phase at 60 °C which is absent on the binary surfactant-water edge. This seems to be attributable to a large degree of toluene solubilization in the surfactant palisade layer of sodium laurate.

Acknowledgment. This work was supported by grants from the National Science Foundation (CPE-8404599) and from the 3M Company.

Registry No. Sodium *n*-dodecanoate, 629-25-4; *n*-decane, 124-18-5; toluene, 108-88-3.

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A Nonaqueous "Microemulsion" System: Formamide, Sodium Dodecyl Sulfate, Hexanol, and Toluene[†]

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Received November 24, 1987. In Final Form: February 25, 1988

Phase equilibria in the low surfactant concentration part of the system formamide, sodium dodecyl sulfate, hexanol, and toluene were analyzed by determination of solubility regions and tie lines. The colloidal association structures were estimated from light-scattering measurements. The base system formamide-sodium dodecyl sulfate-hexanol showed a continuous solubility region from hexanol to formamide with a critical point on the demixing line at 59 wt % formamide. The continuous solubility region was retained when the hexanol was partially substituted by toluene to a 7/3 toluene/hexanol weight ratio. Higher toluene/hexanol ratios resulted in two separate regions. The solubility regions contained a critical point as shown by phase equilibria and light-scattering measurements. There were no other indications of association structures, and it must be concluded that these "microemulsions" are in fact nonstructured solutions. The tie lines in the four-component system were "vertically" oriented connecting toluene-rich phases with phases with low content of toluene.

Introduction

Surfactant association structures in nonaqueous polar media have been known for some time with early investigations concerned with micellization in polar organic

solvents.¹⁻¹⁰ Sudden changes in properties such as surface tension, electric conductance, etc., were interpreted as signs

[†] Presented at the symposium on "Fundamental and Applied Aspects of Microemulsions, II", 61st Colloid and Surface Science Symposium, Ann Arbor, MI, June 21-23, 1987; E. Kaler, Chairman.

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