Location of solubilized oil in lyotropic surfactant liquid crystalline phases and the resulting effects on phase equilibria

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Location of Solubilized Oil in Lyotropic Surfactant Liquid Crystalline Phases and the Resulting Effects on Phase Equilibria

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The location of solubilized oil in surfactant liquid crystalline aggregates can have a pronounced effect on phase stability and their compositional extent. Detailed experimental ternary phase diagrams of sodium 1-tetradecanoate, water, and four different hydrocarbons—*n*-decane, *n*-hexadecane, toluene, and 1-decanol—are presented. The phase diagrams were constructed through two primary methods: optical birefringence and quadrupole NMR spectroscopy. The results reveal a strong dependence of liquid crystalline phase stability on oil type, through the location of solubilized oil in the surfactant aggregate. *n*-Decane and *n*-hexadecane are shown to be primarily solubilized in the interior or core of the aggregates, toluene is solubilized in both the core and palisade or interfacial layer, and 1-decanol is primarily solubilized in the palisade layer. A simple geometric model of core and palisade solubilization is able to rationalize the shape of the ternary liquid crystalline single phase regions comprised of cylindrical hexagonal phase aggregates. Quadrupole NMR spectroscopy of deuterated toluene confirms its solubilization in both core and palisade regions in lamellar phases.

Introduction

The effect of oil type on solubilization by structured surfactant phases has been the subject of numerous studies involving both liquid crystalline phases[1-6] as well as micellar phases.[6-10] These efforts have revealed a rich structural polymorphism in the type and phase topology of liquid crystalline phases and a variety of solubilization sites in micellar and liquid crystalline phases. With many *n*-alkane oils, solubilization seems to occur primarily in the interior or core regions of surfactant aggregates.[7] With polar and/or aromatic oils, the reported locations of solubilization have varied. Alauddin and Verall,[10] for example, have used partial molar volume studies to probe the location of phenol derivatives in sodium dodecanoate micelles. Depending on the hydrophobicity of the functional groups, these compounds can locate anywhere from the core of the micelle to the micelle–water interface. Kandori et al.[9] have studied the location of phenol and benzene solubilized in dodecyltrimethylammonium bromide micelles. Their studies suggest that benzene resides in the core of the micelles while phenol is solubilized in the outer palisade layer, i.e. the near-head-group region of the surfactant interfacial layer. Nagarajan et al.[8] presented both experimental data as well as a theoretical analysis of benzene and hexane solubilization in sodium dodecyl sulfate, cetylpyridinium chloride, and decylammonium chloride micelles. Their results suggest solubilization of benzene in both the palisade and the core regions, and hexane solubilized in the core only.

In surfactant liquid crystalline phases, there are very few results which aid in elucidating the mode or magnitude of oil solubilization in cylindrical, lamellar, or cubic geometries. Spegt et al.[1] measured hexagonal phase unit cell dimensions and, by mass balance, deduced a rod diameter in sodium 1-tetradecanoate–ethylbenzene mixtures. Their results suggest core solubilization of ethylbenzene at molar ratios of oil to surfactant exceeding about 0.2. For experimental ease, the vast majority of ternary phase studies of surfactant–oil–water liquid crystalline phases have been performed at ambient temperatures. Because many ionic surfactants possess Krafft temperatures (the minimum temperature required for formation of stable surfactant aggregates) above ambient,[4] most studies of liquid crystalline phase behavior in ternary ionic surfactant–water–oil mixtures have been limited to short chain surfactants, such as sodium or potassium 1-octanoate.

In order to clarify the role of interfacial solubilization in determining surfactant–oil–water phase equilibria, we have undertaken a systematic study of liquid crystalline phase behavior in longer chain (1-dodecanoate (DD) and 1-tetradecanoate (TD)) carboxylate soaps with water and oil (refs 5 and 11 and this work). Because the minimum temperature for liquid crystalline phase formation in the sodium 1-dodecanoate–water system is 45–50 °C, our studies of binary phase behavior with water and ternary phase behavior with water and *n*-decane or toluene were limited to temperatures of 60 °C or greater. While *n*-decane was poorly solubilized (<5 wt %) in the NaDD system[5] in both the hexagonal and viscous isotropic phases, similar to comparable sodium 1-octanoate–water–nonamphiphilic oil mixtures at ambient temperatures,[4,6] toluene was exceedingly well-solubilized (30% in hexagonal and 25% in viscous isotropic phases). Moreover, the degree of swelling of the interfacial surfactant layer by toluene was apparently sufficient to induce a phase transition to the lamellar liquid crystalline phase, which is entirely interior to the ternary phase diagram and not observed in sodium octanoate–water–aromatic oil mixtures at room temperature.[4]

In this paper, we report phase equilibra at 68 °C of ternary mixtures of sodium 1-tetradecanoate, water, and the sequence of solubilized oils *n*-decane, *n*-hexadecane,

* Author to whom correspondence should be addressed.

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toluene, and 1-decanol. This sequence spans a range of hydrophobicity from strictly saturated aliphatic to the amphiphilic solubilizate 1-decanol. In addition, we rationalize the shape of the ternary hexagonal liquid crystalline phases by considering a very simple geometric model of either core solubilization of hydrocarbon, in which the oil forms a cylindrical core in the interior of the surfactant rodlike aggregates, or palisade solubilization, in which the hydrocarbon intercalates between the surfactant tail groups in the rodlike aggregates, in addition to solubilizing in the core. Phase equilibria were determined by a combination of visual observations in crossed polarized light to detect anisotropic liquid crystalline phases and quadrupole NMR spectroscopy of either the ^{2}H nucleus in deuterium oxide (as an isotopic substitute) or the ^{23}Na nucleus (virtually 100% naturally abundant). To gain more direct information on the mode of oil solubilization in these liquid crystalline phases, quadrupole NMR experiments were also performed using perdeuterated *n*-decane or toluene substituted for the hydrogenated analogues. A careful study of phase behavior in the binary sodium 1-tetradecanoate–water system was also performed as there is some debate in the literature[12-18] as to the number and sequence of liquid crystal phases in this system.

Experimental Section

Materials. Sodium 1-tetradecanoate (generic name sodium myristate) was obtained from Nu-Chek Prep (Elysian, MN) and had a quoted purity of 99+%. The surfactant was stored in glass bottles over desiccant and removed immediately before sample preparation. The hydrocarbons *n*-decane, *n*-hexadecane, toluene, and 1-decanol were all Gold Label grade (99+%) from Aldrich. Undeuterated water was doubly distilled and filtered through a Millipore filtration system. Deuterated water was 99.9% isotopically pure from either MSD Isotopes or from Wilmad. Perdeuterated *n*-decane-d_{22} and toluene-d_8 were the purest grades available (~99%) from MSD Isotopes.

Methods. Sample Preparation. The sample preparation and equilibration have been recently described,[5,11] and only a brief account will be given here. Both NMR samples and samples for visual observation were prepared in glass ampules or tubes and flame-sealed to prevent compositional changes during prolonged equilibration at high temperatures (50–100 °C). NMR samples were periodically centrifuged to effect mixing and promote mass transfer. Only samples which exhibited time-stable and thermodynamically consistent phase behavior are included in equilibrium phase diagrams. Samples for visual observation were equilibrated isothermally in 10–30-mL ampules. The number, amount, and birefringence of phases in these samples were determined by observing the samples in crossed polarized light in an environmental chamber which has been described previously.[5]

Quadrupole NMR Spectroscopy. Deuterium (^{2}H) and sodium (^{23}Na) quadrupole NMR experiments were performed with an IBM CX-100 superconducting spectrometer operating in the FT mode. Typical spectral conditions have been described previously.[5,11] The uncertainty in temperature for both NMR and visual experiments is about ±0.5 °C.

Phase Diagram Determination. Phase diagrams were determined using NMR spectra in conjunction with the Gibbs phase rule. Quadrupole NMR has been widely used for the de-

termination of phase transitions and the construction of phase diagrams in liquid crystalline systems.[5,11,18-24] Single-phase samples were identified from the NMR lineshape.[5,11] Multiphase samples exhibit a lineshape which is the sum of the individual phase lineshapes.[19,23] After the number and identity of liquid crystalline phases were determined for each sample in the composition space of the phase diagram, single-phase regions were drawn and were connected according to the requirements of the phase rule. Three-phase samples lie within a tie-triangle in which the composition of each contributing phase is dictated by the apex of the triangle at the single-phase boundary. Between the three-phase regions are two-phase areas which consist of tie lines connecting single-phase regions. By preparing a sufficient number of samples in single-, two-, and three-phase regions, it is possible to construct accurate phase features (tie-triangles, tie-lines, and one-phase regions).

Results and Discussion

Binary Sodium 1-Tetradecanoate (NaTD)–Water Phase Equilibria. In order to establish the sequence of liquid crystalline phases in the binary sodium 1-tetradecanoate (NaTD)–water system, both ^{2}H and ^{23}Na NMR experiments were performed at surfactant compositions between 45 and 75 wt % and at temperatures between 55 and 80 °C. Single-phase hexagonal and lamellar phases give ^{2}H lineshapes typical of uniaxial powder spectra. At NaTD compositions of 55–58 wt %, which are intermediate between hexagonal (H$_\alpha$) and lamellar (L$_\alpha$) phases and at temperatures above 66 °C, a third liquid crystalline phase is observed. The ^{2}H lineshapes of samples in this region are uniaxial, and the quadrupole splitting is smaller than that of samples which are either hexagonal or lamellar in structure. A plot of ^{2}H and ^{23}Na quadrupole splittings at 74 °C over the range of compositions at which these three liquid crystalline phases are observed is given in Figure 1. The ^{2}H quadrupole splittings increase monotonically with increasing surfactant composition in the H$_\alpha$ and L$_\alpha$ phases but are smaller ($\Delta\nu_Q = 0.45$ kHz) and are virtually independent of composition in the intermediate (Int) phase. This is very similar to the ^{2}H D$_2$O quadrupole splittings previously reported in sodium 1-dodecanoate–D$_2$O mixtures.[5] The ^{23}Na quadrupole splittings also increase monotonically with surfactant composition, but the ^{23}Na splittings of Int phase samples are intermediate in magnitude ($\Delta\nu_Q = 4.3$ kHz) between the hexagonal and lamellar phase values. Rendall et al.[18] offered an explanation for these trends in quadrupole splittings of the intermediate phase in the comparable sodium 1-dodecanoate–water system based on a presumed lamellar structure for this phase. However, the precise geometry and ordering of anisotropic subunits in this phase remain unresolved. Kekicheff et al.[24] observed similar quadrupole splittings of D$_2$O for a phase intermediate between H$_\alpha$ and L$_\alpha$ phases in the sodium dodecyl sulfate–water system at 320 K. The structure of this intermediate phase, assigned primarily from neutron scattering data, is of short interconnected rods on a two-dimensional rhombohedral lattice.[20] This structure is consistent with reduced quadrupole splitting (as compared to the hexagonal phase) as bound D$_2$O molecules can exchange between the interconnected rods and thus reduce the observed anistropy by averaging the three orientations relative to the external magnetic field available to bound molecules in this structure.

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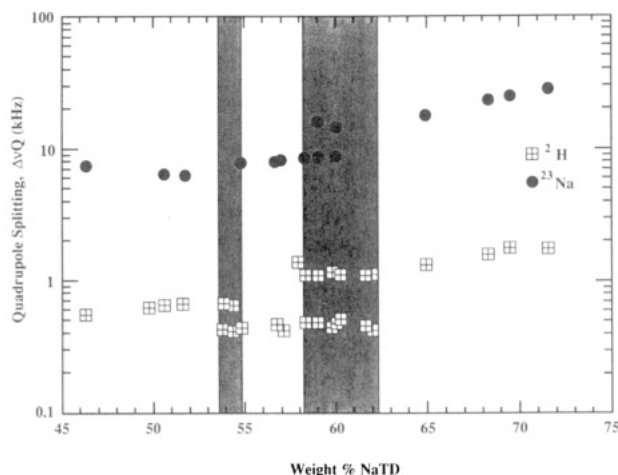
Figure 1. Variation of deuterium (^{2}H) and sodium (^{23}Na) quadrupole splitting values with composition in the sodium 1-tetradecanoate–water system at 74 °C. The squares denote ^{2}H quadrupole splitting data and the circles denote ^{23}Na quadrupole splitting data. Biphasic regions are shaded.
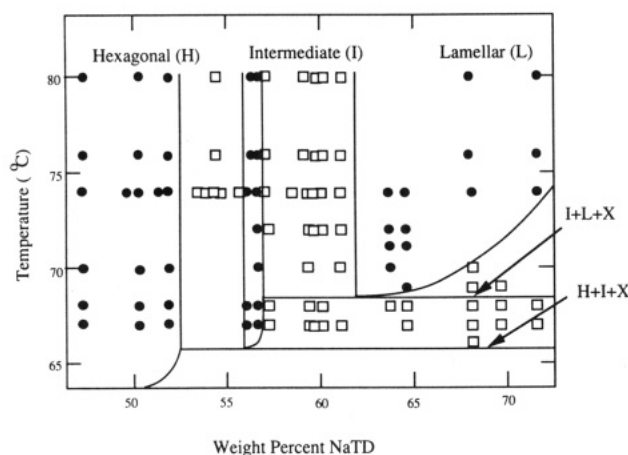

Figure 2. Liquid crystalline phase diagram for the sodium 1-tetradecanoate–water system. Circles denote singe phase samples and squares denote biphasic samples. Three liquid crystalline phases are observed: hexagonal, intermediate, and lamellar. The hydrated crystal phase (X) is observed to coexist in high composition samples at temperatures below 75 °C.

The compositional extent of the three liquid crystalline phases is clearly delineated by the plot of quadrupole splittings provided in Figure 1. Two-phase regions separate each one-phase region from those of adjacent composition. In the two-phase regions, the ^{2}H and ^{23}Na NMR spectra are superpositions of the uniaxial lineshapes for each individual phase with the relative amount of D$_2$O or Na in each phase given by the integrated area of the lineshape corresponding to each phase. From these data, a portion of the binary temperature–composition phase diagram was constructed and is shown in Figure 2. The one-phase liquid crystalline samples were identified by their ^{2}H and ^{23}Na NMR spectra and by visual observations in crossed polarized light. Multiphase samples in which one of the equilibrium phases is crystalline surfactant were identified both by the dependence of the NMR spectra on small variations in temperature and by direct observation of turbid solid or crystals in the NMR tube. As can be seen from the phase diagram (Figure 2), the compositions of liquid crystalline phases in equilibrium with crystalline surfactant change markedly with temperature. As a consequence, the quadrupole splitting of a liquid crystalline phase in equilibrium with surfactant crystals is also a strong function of temperature.

In contrast to earlier work by Luzzati et al.,[12-16] Madelmont and Perron,[17] and Rendall et al.,[18] we find evidence of only one distinct liquid crystalline phase in the NaTD water system at surfactant compositions between the hexagonal and lamellar phases. It is conceivable that a second intermediate phase exists of extremely small compositional extent and was unresolved by our experiments. The one intermediate (Int) phase which we observe is brightly birefringent in crossed polarized light, is of comparable viscosity to the hexagonal H$_\alpha$ phase, possesses uniaxial liquid crystalline subunits, and has a ^{2}H D$_2$O NMR quadrupole splitting smaller than that of hexagonal and lamellar phases of comparable composition. The liquid crystal domains of this intermediate phase do not align with the NMR tube axis over prolonged periods. Two structures consistent with all of these observations are (i) short, interconnected rods on a rhombohedral lattice, as proposed for the SDS–water system[20,25] or (ii) short, interconnected rods on a square lattice (so-called T phase), determined for a similar intermediate phase in lithium perfluorooctanoate–water systems by Kekicheff and Tiddy.[26]

The dependence of quadrupole splitting ($\Delta\nu_Q$) on surfactant composition is consistent with the simple two-site model.[21,27,28] In this model, the experimentally measured value for $\Delta\nu_Q$ is a weighted average of the quadrupole splitting for water molecules bound by electromagnetic forces to the surface of the subunits (Δ_b) and the splitting of water which is isotropically tumbling between subunits (Δ_f)

$$\Delta_{exp} = X^f_{H_2O}\Delta_f + X^b_{H_2O}\Delta_b \approx X^b_{H_2O}\Delta_b \quad (1)$$

The free water does not contribute because the splitting vanishes for isotropically tumbling water. The mole fraction of bound water is proportional to the mole fraction of surfactant

$$X^b_{H_2O} = rX_s = n_b\frac{\dfrac{\omega_s}{M_s}}{\dfrac{\omega_s}{M_s}+\dfrac{\omega_w}{M_w}} = n_b\frac{M_w\omega_s}{M_w\omega_s + M_s\omega_w} \approx$$

$$n_b\frac{M_w\omega_s}{M_s\omega_w} \quad (2)$$

where ω_i is the mass fraction of component i, n_b is the number of bound water molecules per surfactant head group, and M_i is the molecular mass of component i. The experimentally observed quadrupole splittings for hexagonal and lamellar phases in Figure 1 conform well to

$$\Delta_{obs} = n_b\Delta_b\left(\frac{\omega_s}{\omega_w}\frac{M_w}{M_s}\right) \quad (3)$$

with $n_b\Delta_b$ equal to 9500 Hz. By forming the ratio of $n_b\Delta_b$ and $\Delta_{D_2O,static}$,[29] the static quadrupolar coupling constant, one obtains a measure of the time-averaged order parameter for water bound to liquid crystalline subunits. The value obtained is 0.058 and is smaller than that of the C–D bonds of deuterated surfactant molecules in the liquid crystallites near the subunit surface ($S \approx 0.2$).[30-32] It is of the order of magnitude of the order parameter of C–D

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bonds near the tail ends in such liquid crystallites, indicative of significant motional disorder.

Information about macroscopic ordering of the liquid crystallites in a polycrystalline sample is obtained by analysis of the ^{2}H NMR spectral lineshapes. A random distribution of liquid crystallite director axes gives rise to a powder, or Pake, pattern.[33] Alignment of these directors along a preferred macroscopic direction, such as the tube axis in an NMR sample tube, sharpens the Pake pattern at the wings at the expense of intensity in the primary peaks.[19] Experimentally, Pake patterns are observed with lamellar and intermediate phases in the NaTD–water system. Hexagonal phases, however, exhibit a slow orientation of liquid crystallite domains along the NMR tube axis. At short times after preparation of a hexagonal sample (2–4 weeks), the spectral lineshape is a typical three-dimensional powder spectrum. After several months, the spectrum becomes increasingly sharp in the wings. With cesium *n*-tetradecanoate hexagonal phases, the original peaks which are separated by $\Delta\nu_Q$ disappear altogether and the lineshape approaches that of a completely macroscopically oriented sample. Interestingly, two-phase samples of hexagonal phase with a small amount of dispersed intermediate phase yield ^{2}H NMR spectra of superimposed powder patterns with no evidence of macroscopic alignment after months of equilibration. The mechanism of domain alignment in pure hexagonal phases is still unclear but it is apparently disrupted by dispersion of a modest amount (10–20%) of the viscous intermediate liquid crystal phase.

Ternary NaTD–*n*-Decane–Water Phase Behavior at 66 °C. With a detailed knowledge of liquid crystalline phase behavior in the binary NaTD–water system, it is possible to determine isothermal ternary surfactant–water–oil phase diagrams with guidance from the Gibbs phase rule as to the possible juxtaposition of one-, two-, and three-phase regions. In order to compare with analogous studies of solubilization in mixtures of sodium 1-octanoate and sodium 1-dodecanoate combined with water and oil, a temperature was selected which exceeds the minimum temperature needed for formation of hexagonal phase (54 °C)[17] and is below the temperatures required for formation of intermediate (66 °C) and lamellar (69 °C) phases. In the literature studies of liquid crystal solubilization by the shorter chained alkali metal carboxylates[4]—sodium and potassium 1-octanoate—the analogous temperature corresponding to stable binary hexagonal phase, and below the thermal stability limit of the lamellar phase, is about 20 °C.

The ternary phase diagram of NaTD, 1-decane, and water at 65 °C is shown in Figure 3. At this temperature, five phases are observed to be stable: isotropic micellar solution (L$_1$) at low surfactant and *n*-decane concentrations, hexagonal (H$_\alpha$) phase, crystalline (X) surfactant, viscous isotropic (VI) liquid crystal, and an isotropic oleic (L$_2$) phase comprised of nearly pure *n*-decane. Most of the phase diagram was determined by visual observation of equilibrated samples through cross polarized light. The VI phase is optically isotropic at equilibrium, is extremely viscous, and exhibits birefringence when perturbed from equilibrium by rapid cooling. There was no evidence, along the binary edge or with small amounts of added *n*-decane, of either of lamellar (L$_\alpha$) phase or the intermediate (Int) phase at this temperature. Deuterium NMR spectroscopy was used to check for the existence of I and L$_\alpha$ phases interior to the diagram, but neither phase was detected.

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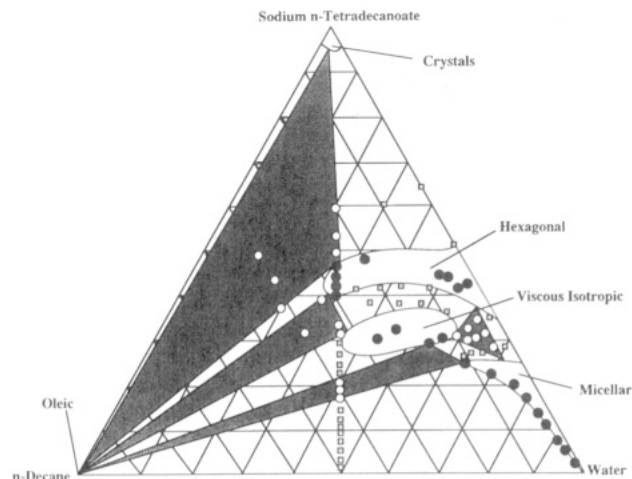(33) Pake, G. E. *J. Chem. Phys.* **1948**, *16*, 327.

Figure 3. Ternary phase diagram for the sodium 1-tetradecanoate–*n*-decane–water system at 65 °C. Black circles denote single-phase samples, gray squares denote biphasic samples, and open circles denote three-phase samples. Single phase regions are white and three-phase regions are shaded.

All three microstructured surfactant phases in this ternary system are noteworthy for the large amount of *n*-decane which they solubilize. Neither the soaps of octanoic acid[4] nor those of dodecanoic acid[5] are capable of solubilizing more than 10–15% by weight *n*-alkane in L$_1$, H$_\alpha$, or VI phases. By contrast, the NaTD–water micellar L$_1$ phase solubilizes 13% by weight *n*-decane, the VI phase is stable with 34% solubilized *n*-decane, and the H$_\alpha$ phase solubilizes about 30% *n*-decane at its maximum. The marked increase in *n*-decane solubilization by the hexagonal phase of NaTD as compared to the hexagonal phases of the shorter chained carboxylate homologues suggests that the mode of solubilization may be qualitatively different.

Geometric Model of Hexagonal Phase Solubilization. A simple model of *n*-decane solubilization seems to be consistent with the experimentally observed values of surfactant and *n*-decane concentration in the hexagonal phase. The partial specific volumes v_i of surfactant, water, and *n*-decane are assumed to be constant, independent of concentration, and equal to 1.03, 1.0, and 1.37 cm^3/g, respectively.[15,34] Further, it is assumed that *n*-decane swells the cylindrical surfactant aggregates in the hexagonal phase only in the core of the aggregates. Figure 4 is a schematic drawing of the hexagonal phase depicting oil, water, and surfactant locations in this model of core solubilization. The width of the surfactant annulus in Figure 4 ($r_2 - r_1$) is assumed to be constant and equal to half of the diameter of the surfactant rods in the binary surfactant–water hexagonal phase (16.2 Å). Luzzati et al.[13] measured a rod diameter of 32.4 Å for the NaTD–water hexagonal phase and demonstrated that this rod diameter is constant throughout the compositional extent of the hexagonal phase. Finally, it is assumed that the hexagonal phase swells with *n*-decane such that the distance between rods varies over the same range of values as in the binary surfactant–water hexagonal phases from 35 to 52 wt % surfactant.

For a given value of r_1, the radius of the *n*-decane cylindrical core in the swollen hexagonal phase, the volume fractions of oil, surfactant, and water are easily calculated from geometry

(34) *Handbook of Chemistry and Physics*, 63rd ed.; Chemical Rubber Co.: Cleveland, OH, 1982.
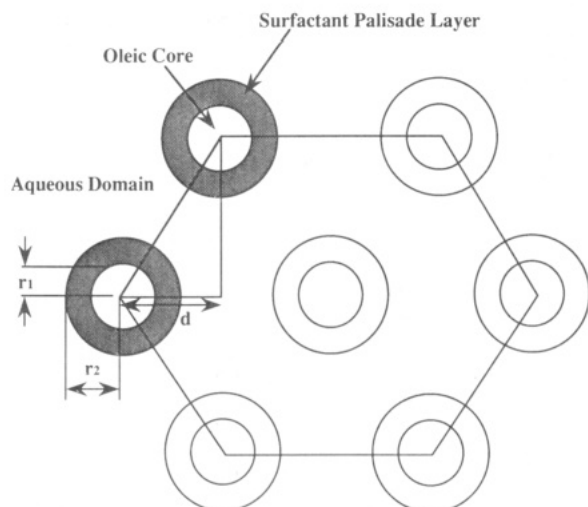
Figure 4. Schematic diagram of the hexagonal liquid crystalline phase with core solubilized oil. The gray area is the surfactant layer with a white core of solubilized oil.

$$\phi_o = \frac{\pi}{2\sqrt{3}}\left(\frac{r_1}{l}\right)^2$$

$$\phi_s = \frac{\pi}{2\sqrt{3}}\left(\frac{r_2^2 - r_1^2}{l^2}\right) \quad (4)$$

$$\phi_w = 1 - \frac{\pi}{2\sqrt{3}}\left(\frac{r_2}{l}\right)^2$$

Volume fractions are converted to mass fractions with the assumed constant values of partial specific volumes for the three components

$$\omega_i = \frac{\phi_i/\nu_i}{\sum_i \phi_i/\nu_i} \quad (5)$$

Once r_1 is selected, the radius of the swollen surfactant aggregate r_2 is taken to be $r_1 + 16.2$ (Å); i.e. the surfactant layer thickness is assumed constant. The hexagonal cell dimension l is calculated along the binary edge from $\omega_s = 0.35$–0.52 by solving for l using eqs 4 and 5 and with a value of r_1 of zero (no oil swelling). The values obtained are from 25.8 to 21.2 Å, respectively, which fall in the appropriate range of values determined experimentally by Luzzati et al.[13] and confirmed by Gallot and Skoulios.[35] The prediction of this simple model of one-dimensional core swelling of the hexagonal phase by n-decane for binary surfactant–water hexagonal phases containing 35–52 wt % surfactant is shown in Figure 5a. The model is in semiquantitative agreement with the compositional extent of the ternary NaTD–water–n-decane hexagonal phase at 69 °C, although it does underpredict the surfactant composition required at high 1-decane solubilization. A comparison of the hexagonal phase cell dimensions predicted by the model with experimental X-ray diffraction measurements would constitute a rigorous test of the model.

Additional information about the molecular environment of n-decane solubilized in the hexagonal phase of NaTD–water is obtained from deuterium NMR spectra of deuterated n-decane. At low decane concentration in the hexagonal phase (5–10 wt % decane), the deuterium spectrum exhibits what appears to be powder spectra superimposed on each other with isotropic resonances. From the width in frequency units of the base of these
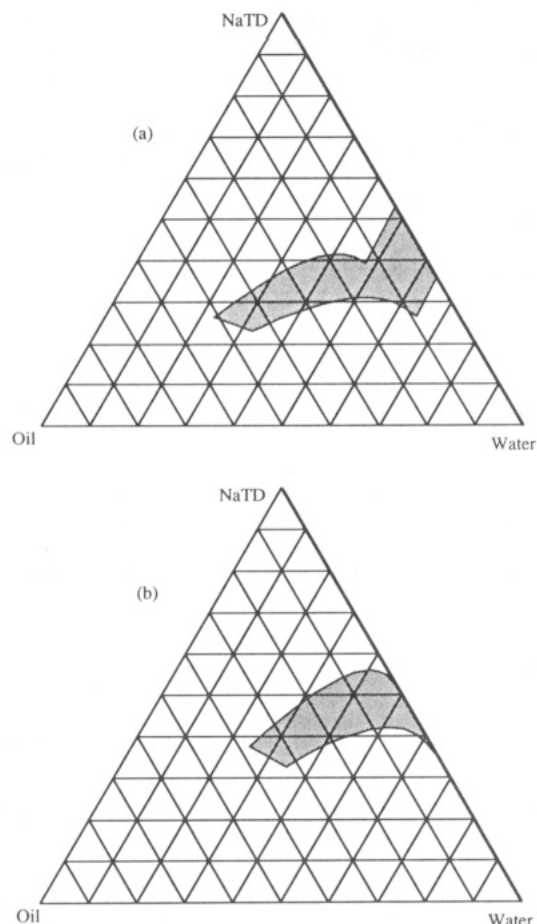
(35) Gallot, B.; Skoulios, A. *Kolloid Z. Z. Polym.* **1968**, *208*, 37–43.

Figure 5. Model results for the solubilization of oil into the hexagonal phase of the sodium 1-tetradecanoate–water system: (a) result for only core solubilization of oil; (b) result for both palisade ($f_{max} = 0.27$) and core solubilization contributions. The shaded area represents the calculated extent of the hexagonal phase into the phase diagram.

spectra, it appears that the maximum quadrupole splitting in these samples is on the order of 200–300 Hz. Taking the static quadrupolar coupling constant of n-alkane deuterons to be 175 kHz,[22] such a low quadrupole splitting corresponds to an order parameter of approximately 0.001. n-Decane solubilized in the core of the hexagonal surfactant cylinders would likely yield isotropic deuterium spectra due to isotropic tumbling of n-decane. Conversely, n-decane solubilized in the palisade layer would likely yield anistropic deuterium spectra with an order parameter typical of surfactant chains in a hexagonal liquid crystalline environment.[31] The deuterium NMR spectra thus seem to support the model of predominantly core solubilization of n-decane in ternary NaTD–water–n-decane hexagonal liquid crystals.

Ternary NaTD–n-Hexadecane–Water Phase Behavior at 66 °C. In order to test the specificity with which NaTD–water hexagonal phases solubilize n-alkanes of varying chain length, the ternary phase diagram of NaTD, water, and n-hexadecane was determined at 65 °C. A schematic of the phase diagram is shown in Figure 6 and it is qualitatively similar to the ternary phase diagram of NaTD, water, and n-decane. n-Hexadecane, like n-decane, is solubilized well in L₁, VI, and H$_\alpha$ phases, only slightly less effectively on a weight percent basis than n-decane. The VI phase in the NaTD–water–n-hexadecane system appears to be smaller than that in the comparable n-decane system and all phase boundaries in the ternary n-hexadecane system appear to be shifted to higher surfactant concentrations (by a few weight percent) and to a lower n-alkane concentration. For the most part,
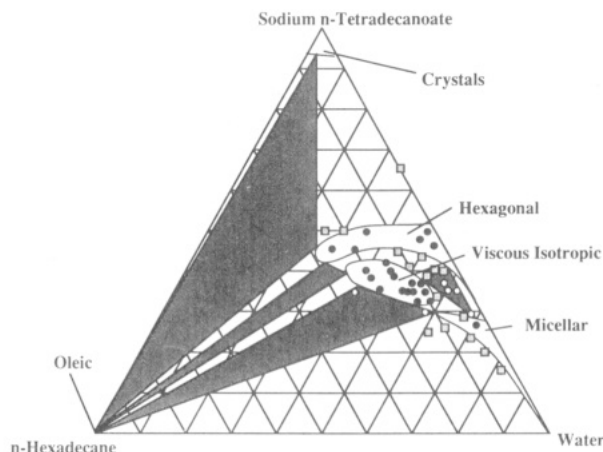
Figure 6. Ternary phase diagram for the sodium 1-tetradecanoate–*n*-hexadecane–water system at 65 °C. Black circles denote single-phase samples, gray squares denote biphasic samples, and open circles denote three-phase samples. Single-phase regions are white and three-phase regions are shaded.
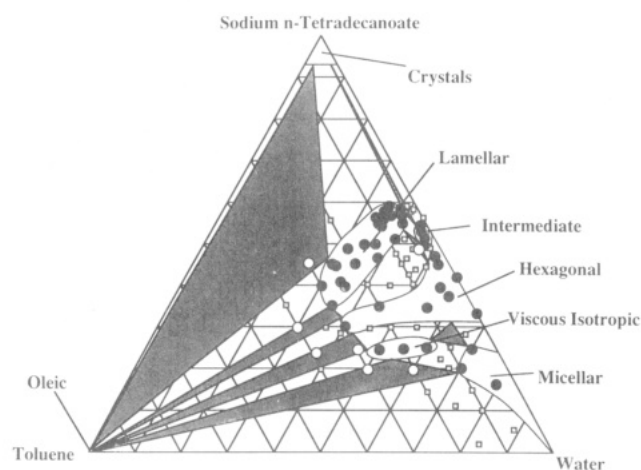

Figure 7. Ternary phase diagram for the sodium 1-tetradecanoate–toluene–water system at 68 °C. Black circles denote single-phase samples, gray squares denote biphasic samples, and open circles denote three-phase samples. Single-phase regions are white and three-phase regions are shaded.

however, the two-phase diagrams are nearly identical. One would conclude that there is no significant effect of alkane chain length on liquid crystalline phase behavior in NaTD–water–*n*-alkane systems at a temperature of 65 °C. The significant parameter seems to be the tail length of the carboxylate group, as the solubilization of *n*-decane by the NaDD–water system was substantially less[5] than in the NaTD system. For a range of *n*-alkane lengths (C_{10} and C_{16}), the solubilization properties of NaTD are approximately uniform. Moreover, the core model of solubilization of oil in the hexagonal phase appears to be equally valid for *n*-hexadecane as for *n*-decane.

Ternary NaTD–Water–Toluene Phase Behavior at 68 °C. The solubilization of toluene by liquid crystalline phases of NaTD–water at 68 °C is markedly different than the comparable solubilization of *n*-alkanes. A detailed ternary phase diagram for the NaTD–toluene–water system at 68 °C is shown in Figure 7. While 68 °C is beneath the thermal stability limit of the lamellar (L_α) phase along the binary NaTD–water edge, it is above the stability limit for the intermediate (Int) phase. The L_α phase occupies a large region of phase stability from about 3–4 wt % toluene and 55–60 wt % NaTD to about 30 wt % toluene and 36–40 wt % NaTD. The Int phase occupies a small compositional extent, solubilizing approximately 2–3 wt % toluene at surfactant compositions of 49–54 wt % NaTD. Apparently toluene solubilization favors the

formation of the low curvature lamellar phase and at a decreased surfactant concentration with increased hydrocarbon solubilization. The location of the L_1–L_2 phase boundary (maximum solubilization of toluene in the L_1 micellar phase) and of the VI phase are also shifted to lower values of NaTD concentration than in the *n*-alkane systems. The L_2 phase is the oleic isotropic phase which solubilizes very little surfactant and water. The shape of the hexagonal phase is also altered considerably and the concentration of surfactant required to solubilize a given amount of toluene in the hexagonal phase is reduced significantly below that required in the comparable *n*-decane and *n*-hexadecane systems.

The model of core solubilization used above to describe the swelling of the NaTD–water hexagonal phase with *n*-decane and *n*-hexadecane does not adequately describe the shape of the ternary NaTD–water–toluene hexagonal phase nor does it adequately model the concentrations of surfactant in hexagonal phase with increasing toluene solubilization. However, a model in which toluene first swells the palisade layer of the surfactant in the hexagonal phase cylinders and then swells the core does seem to be consistent with the hexagonal phase region in Figure 7. Just as in the model of core solubilization described above, the partial specific volumes of toluene, water, and NaTD are assumed independent of composition and equal to 1.15, 1.0, and 1.03 cm³/g, respectively.[15,34] In addition, the distance between surfactant head groups in the swollen aggregates $2(l - r_2)$ (see Figure 4) is assumed to range over the same values as along the binary edge. Now, however, the volume fractions of oil and surfactant are related not only to the rod and cell dimensions—r_1, r_2, and l—but also to the volume fraction f of palisade layer of thickness (16.2 Å) which is occupied by toluene. The equations for the volume fractions thus become

$$\phi_o = \frac{\pi}{2\sqrt{3}}\left(\frac{r_1}{l}\right)^2 + f\frac{\pi}{2\sqrt{3}}\left(\frac{r_2^2 - r_1^2}{l^2}\right)$$

$$\phi_s = (1 - f)\frac{\pi}{2\sqrt{3}}\left(\frac{r_2^2 - r_1^2}{l^2}\right) \qquad (6)$$

$$\phi_w = 1 - \frac{\pi}{2\sqrt{3}}\left(\frac{r_2}{l}\right)^2$$

In calculation of the volume and weight fractions of the three components in the swelling of a binary NaTD–water hexagonal phase, it is first assumed that toluene swells the palisade layer with no core swelling, i.e. f varies from 0 to f_{max} with $r_1 = 0$. Then, once f has achieved its maximum value, core solubilization occurs and r_1 varies from 0 to $r_{1,max}$. A number of values of f were examined and best agreement with the shape of the hexagonal phase in the NaTD–toluene–water phase diagram was achieved with an f_{max} value of about 0.27. Taking the extent of the hexagonal phase of the binary NaTD–water edge as 35–52 wt % NaTD, the ternary toluene-solubilized hexagonal phase depicted in Figure 5b was calculated. The agreement between the shape of the calculated and experimentally measured hexagonal phase region is remarkable. Moreover, the shape of this region is markedly different than that in the NaTD–*n*-decane–water system, in which solubilization of oil into the hexagonal phase clearly leads to an increase in the surfactant concentration requirement in this phase.

Quadrupole NMR Studies of Deuterated Toluene in NaTD–Toluene-d_8–Water Mixtures. In order to gain additional insight into the molecular mechanism of toluene solubilization in NaTD–water liquid crystalline phases, quadrupole NMR experiments were performed with per-
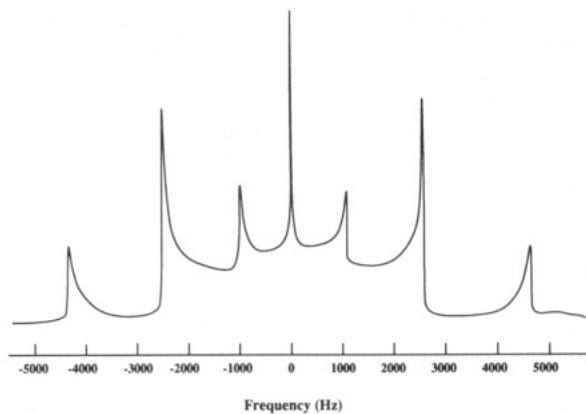
Figure 8. Sample deuterium (^{2}H) quadrupole NMR spectrum for perdeuterated toluene.
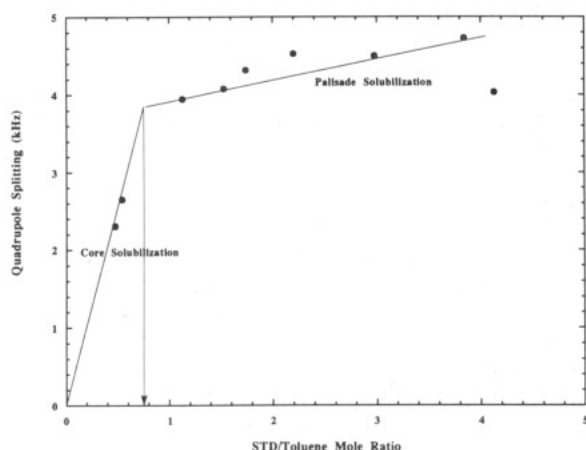

Figure 9. Variation of deuterium quadrupole splitting values in the lamellar phase as a function of surfactant to toluene mole ratio. The break in the linear fits is the mole ratio (0.75) at which solubilization changes from core to palisade solubilization.

deuterated toluene-d_8. A representative deuterium NMR spectrum of perdeuterated toluene in an L_α phase is shown in Figure 8. The largest peaks in the spectrum (other than the isotropic spike at 0 Hz) correspond to the quadrupole splitting of the four nearly equivalent aromatic deuterons in toluene (CD-2, CD-3, CD-5, and CD-6). This quadrupole splitting represents a useful measure of the time-averaged order parameter of the toluene molecule in an anisotropic environment. The dependence of this quadrupole splitting on the NaTD to toluene mole ratio in the *lamellar* phase is shown in Figure 9. At high surfactant to toluene ratio, the quadrupole splitting is nearly independent of composition and equal to 4.3 kHz. This corresponds to a low toluene concentration (<10 wt %), where one might expect toluene solubilization to be of the palisade mode. As toluene concentration increases and the surfactant-to-toluene mole ratio decreases, a point is reached whereupon the quadrupole splitting begins to decrease sharply. The characteristic quadrupole splitting for the toluene in the palisade layer is ca. 4.3 kHz while that for the core solubilized toluene is substantially smaller. When there is a combination of the two solubilization locations occupied within the aggregate, the observed quadrupole splitting is a weighted average of the two locations similar to the description of the two-state model previously discussed.

As shown in Figure 9, this transition occurs at a surfactant–toluene mole ratio of about 0.75 (corresponding to a volume fraction of toluene in the surfactant–toluene palisade layer of 0.275). This result suggests that a transition from palisade to core solubilization occurs in the lamellar phase much like the shape of the hexagonal
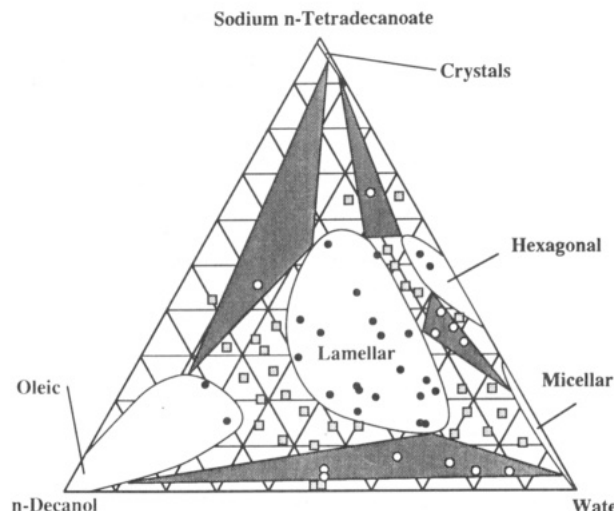

Figure 10. Ternary phase diagram for the sodium 1-tetradecanoate–1-decanol–water system at 65 °C. Black circles denote single-phase samples, gray squares denote biphasic samples, and open circles denote three-phase samples. Single-phase regions are white and three-phase regions are shaded.

phase region suggests a similar transition. Both transitions seem to occur at volume fractions of toluene of about 0.25–0.3 in the palisade layer. This is comparable in magnitude to the volume fraction of ethylbenzene in NaTD–water–ethylbenzene hexagonal phases at which the apparent rod diameter begins to increase sharply,[1] suggesting a transition from palisade to core swelling.

Ternary NaTD–1-Decanol–Water Phase Behavior at 66 °C. The ternary phase diagram of the NaTD–1-decanol–water system at 65 °C is shown in Figure 10. It differs qualitatively from the corresponding n-decane, n-hexadecane, and toluene ternary systems in a number of respects. First, the viscous isotropic phase has disappeared altogether. Second, the ability of the micellar and hexagonal phases to solubilize 1-decanol is limited to about 6 wt % 1-decanol. The lamellar phase occupies a very large compositional region extending from 15 to 55 wt % NaTD and 15 to 42 wt % 1-decanol. Finally, the L_2 region (isotropic oleic phase) is quite large and contains appreciable amounts of both water (<25 wt %) and surfactant (<25 wt %). The increase of the L_2 region is likely a result of the change in additive from a strictly oleic component to an amphiphilic oil. There is apparently cooperative aggregation of surfactant with decanol in the oil-rich portion of the phase diagram. The large region of lamellar phase existence suggests either that the mode of solubilization of decanol is through both palisade and core regions in which the palisade layer is predominantly surfactant or solubilization is strictly by palisade incorporation in which equimolar amounts of surfactant and decanol reside in the interfacial layer at maximum oil content.

Comparison of Ternary Phase Topology: Field Variable Representation. The trend in ternary phase topology of NaTD–oil–water liquid crystalline phases, upon varying oil type by increasing amphiphilic or polar character, can be succinctly described by representing the phase diagrams in field variable coordinates.[36,37] Such a representation makes use of the chemical potential of each of the three components as the independent variables in the phase diagram. Regions of two-phase coexistence reduce to one-dimensional curves and regions of three-phase coexistence are represented as points. The resulting

(36) Griffiths, R. B.; Wheeler, J. C. *J. Phys. Chem.* **1970**, *42*, 1427.
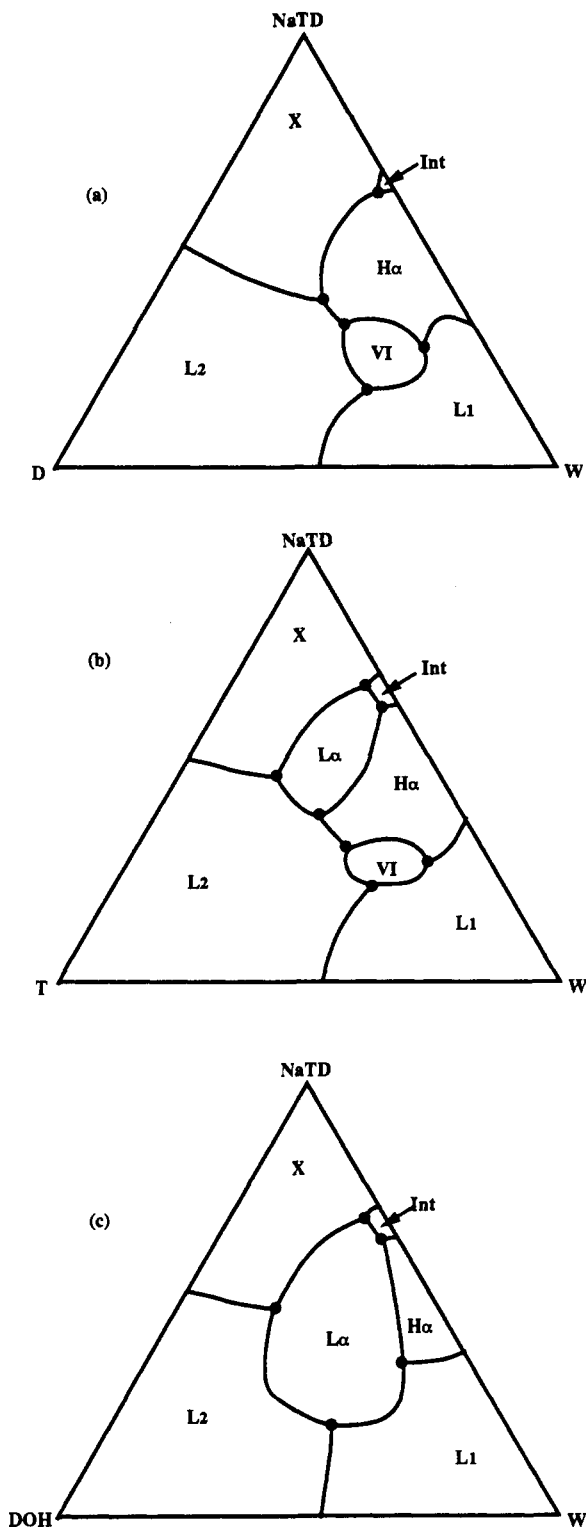(37) Guerin, G.; Bellocq, A. M. *J. Phys. Chem.* **1988**, *92*, 2550.

Figure 11. Field variable representation of the ternary liquid crystalline phase diagrams for sodium 1-tetradecanoate–water at 68 °C with solubilized (a) *n*-decane, (b) toluene, and (c) 1-decanol.

field variable depictions of the ternary phase diagrams at 70 °C are shown in Figure 11. The sequence of phase diagrams illustrated in Figure 11 provides a compact description of the effects of varying oil type on the liquid crystalline phase structure and resulting phase topology of NaTD–water mixtures. The NaTD–water–*n*-decane system is a prototypical example of a nonpolar paraffinic oil which is completely core-solubilized. The resulting phase structures are highly curved due to surfactant head group electrostatic repulsion. The conversion of the hexagonal and micellar phases into viscous isotropic phase

upon solubilization of *n*-decane is not yet understood mechanistically, but it is clear that the VI phase possesses a high degree of interfacial film curvature.

The substitution of *n*-decane with toluene results in two noteworthy changes in the phase topology. First, a large region of lamellar phase coexistence is induced interior to the diagram. As discussed above, this is likely due to the palisade solubilization of toluene at low toluene contents which reduces the interfacial film curvature by effectively increasing the surfactant tail volume. The palisade solubilization of toluene in the hexagonal phase, followed by core solubilization, also results in a dramatic change in the shape of the hexagonal phase region. Finally, the substitution of 1-decanol for toluene results in the elimination of the viscous isotropic region and the domination of the phase diagram by the lamellar phase. In contrast to toluene, 1-decanol partitions into the palisade layer and reduces electrostatic repulsion between head groups at all concentration levels. This suggests that the viscous isotropic phase relies for its stability on a certain amount of head group interaction resulting in interfacial film curvature. The solubilization of an aromatic non-amphiphilic oil, such as toluene, in the palisade layer is insufficient to destabilize the VI phase. However, the partitioning of 1-decanol into the palisade layer produces a sufficient reduction in charge density that the VI phase is destabilized.

Conclusions

The trends in ternary liquid crystalline phase behavior of NaTD–water mixtures with four different oils have been explored: *n*-decane, *n*-hexadecane, toluene, and 1-decanol. The phase diagrams of these ternary systems at 65 °C have been determined using a combination of polarized light visual observations and ^{2}H and ^{23}Na quadrupole NMR spectroscopy. These techniques enable the assignment of phase type and number of phases for one-, two-, and three-phase samples containing either isotropic fluid phases, viscous isotropic liquid crystalline phases, anisotropic liquid crystalline phases, and crystal phases. On the basis of the shapes of the liquid crystalline regions in the phase diagram, *n*-decane and *n*-hexadecane appear to be solubilized strictly in the core of the hexagonal phase in the ternary diagram. A simple geometric model of this core solubilization predicts a hexagonal phase region qualitatively consistent with the shape of the region observed experimentally. Conversely, toluene appears to be initially solubilized in the interfacial surfactant or so-called palisade layer and core-solubilized only after saturating the interfacial layer. Again, a simple geometric model is consistent with the shape of the ternary hexagonal phase. Quadrupole NMR spectroscopic measurements on perdeuterated toluene support the solubilization of toluene in both palisade and core regions in the ternary lamellar phase. The large extent of lamellar phase in both the ternary NaTD–water–toluene and NaTD–water–1-decanol systems is also consistent with a reduction in curvature of the interfacial layer due to solubilization in the palisade layer of the oil. A simplified topological picture of the sequence of phase changes with oil type is provided by casting the phase diagrams in field variable coordinates.