The Effect of *n*-Decanol on Solubilization of Water-in-Oil Microemulsions and Stability of Lamellar Liquid Crystals of Alkylphenol Ethoxylates

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ABSTRACT: Addition of n-decanol at appropriate concentrations is beneficial to increasing the solubilization amount of water in a water-in-oil microemulsion in the system of nonylphenol ethoxylate/olive oil/water, but it destabilized the lamellar liquid crystal and reduced the solubilization of olive oil in the lamellar liquid crystal.

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KEY WORDS: Alkylphenol ethoxylate, lamellar liquid crystal, low-angle X-ray diffraction, microemulsion, *n*-decanol, olive oil, phase diagram, solubilization.

Both microemulsions and lyotropic liquid crystals are ordered self-assemblies of amphiphile molecules (1–7). For microemulsions stabilized by an ionic surfactant, a useful cosurfactant is an alcohol with medium chain-length (*n*-butanol to *n*-hexanol). A longer-chain alcohol (*n*-octanol to *n*-decanol) is advantageous to making the phase transition from hexagonal liquid crystals to lamellar crystals (8–11). The effect of a cosurfactant on microemulsions and liquid crystals stabilized by nonionic surfactants has not received corresponding attention, and the number of publications is limited, although the alcohol is beneficial to some nonionic surfactant systems (12,13). For this paper, we studied the phase behavior of the nonionic surfactant system nonylphenol ethoxylate/*n*-decanol/olive oil/water to evaluate the effect of *n*-decanol on solubilization in the (oil in water) microemulsion and on the stability of the lamellar liquid crystal.

Olive oil is a multicomponent system of mainly glycerides and carboxylic acids (oleic acid, palmitic acid, and linoleic acid) and has been used widely in cosmetic (14–18), pharmaceutical (19,20) food (21,22), ink (23,24), and deinking formulations (25). For example, olive oil can inhibit hair penetration by fungi (26) in hair cosmetics and form a lecithin-based blood vessel–regenerating drug in pharmaceutical preparations. Hence, because of its wide importance, olive oil was used as the oil phase to form a water-in-oil (w/o) microemulsion and to be solubilized in a lamellar liquid crystal (LLC) of nonionic surfactant.

EXPERIMENTAL PROCEDURES

Materials. The materials used were nonylphenol ethoxylate (Rhone-Poulenc, Cranbury, NJ), olive oil (Sigma, St. Louis), *n*-decanol (Sigma, 98%). All chemicals were used without further purification. Water was doubly distilled.

Phase regions. The w/o microemulsion region (L_2) of the phase diagrams was determined by titration with water to olive oil solutions of *n*-decanol and nonylphenol ethoxylate. The formation and disappearance of the liquid crystal phase were monitored by microscopic observation of the sample between crossed polarizers and by birefringence of the sample. The borderline of the three-phase region between the L_2 + H_2O two-phase area and the three-phase area with the liquid crystal was also determined by observation of sample birefringence. The other two borderlines were determined by low-angle X-ray diffraction.

The phase boundaries of the liquid crystal phase were verified by the use of small-angle X-ray diffraction (SAXS) measurements. Low-angle X-ray diffraction measurements were obtained by a Keissig low-angle camera from Richard Seifert (Duesseldorf, Germany). Ni-filtered Cu radiation was used, and reflections were determined by a Tennelec positron-sensitive detector system (model PSD-100; Knoxville, TN).

RESULTS AND DISCUSSION

Phase behavior of nonylphenol ethoxylate/*n*-decanol/water is shown in Figure 1. On the left side of the phase diagram there is a narrow two-phase (L_2 + H_2O) region, followed by a large LLC + L_2 + H_2O three-phase region. On the right side there is a large w/o microemulsion phase region L_2 because *n*-decanol and nonylphenol ethoxylate are mutually soluble. At the bottom of the phase diagram there are, in order, an LLC + H_2O two-phase region, an LLC region, an LLC + L_2 two-

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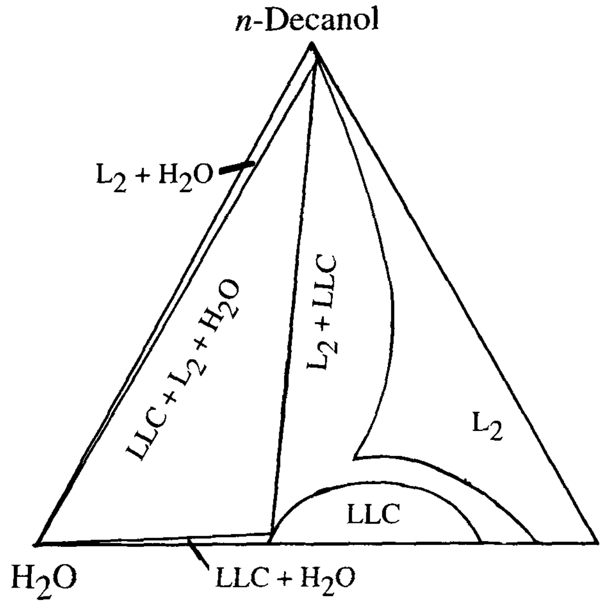

FIG. 1. Phase diagram of system nonylphenol ethoxylate/*n*-decanol/water: LLC = lamellar liquid crystal, L2 = w/o microemulsion.

phase region, and an L_2 isotropic solution region. In the middle part, the huge two-phase (L_2 + LLC) region between the L_2 and LLC one-phase regions should be observed.

Figure 2 (A–F) shows the phase behavior of nonylphenol ethoxylate/*n*-decanol/olive oil/water system with different weight ratios of nonylphenol ethoxylate to *n*-decanol. In parts A–F of Figure 2, in which the weight ratio of nonylphenol ethoxylate to *n*-decanol varies from 100:0 to 85:15, the phase diagram shows similar phase behavior with the nonylphenol ethoxylate/*n*-decanol/H^2O system (Fig. 1). Only the liquid crystal area is reduced with increased content of *n*-decanol. In parts D–F of Figure 2, where the weight ratio of nonylphenol ethoxylate to *n*-decanol ranges from 80:20 to 70:30, the phase diagrams show only an L_2 one-phase region, 2 two-phase regions, (L_2 + LLC) and (L_2 + H_2O), and a three-phase region (LLC + L_2 + H_2O). The three-phase region is only indicated. It is certainly not in the plane of the diagram.

By combining Figures 1 and 2, Figure 3 shows the phase behavior of nonylphenol ethoxylate/*n*-decanol/olive oil/water system in a three-dimensional presentation. The L_2 region fills in the whole back part (Fig. 3A), and the liquid crystal phase exists at the right side of the bottom part (Fig. 3B). There are three different two-phase regions in the nonylphenol ethoxylate/*n*-decanol/olive oil/H_2O system. The LLC + L_2 two-phase region extends from the middle part of the first nonylphenol ethoxylate/H_2O side, between the L_2 one-phase region and the LLC one-phase region, to the *n*-decanol/olive oil side, between the L_2 one-phase region and the L_2 +LLC + H_2O three-phase region (Fig. 3C). The second two-phase region (L_2 + H_2O) is at the left side and grows wider while moving from the H_2O corner to the *n*-decanol/olive oil side. The last two-phase region (H_2O + LLC) is at the left side of the bottom part between the H_2O corner and the LLC phase

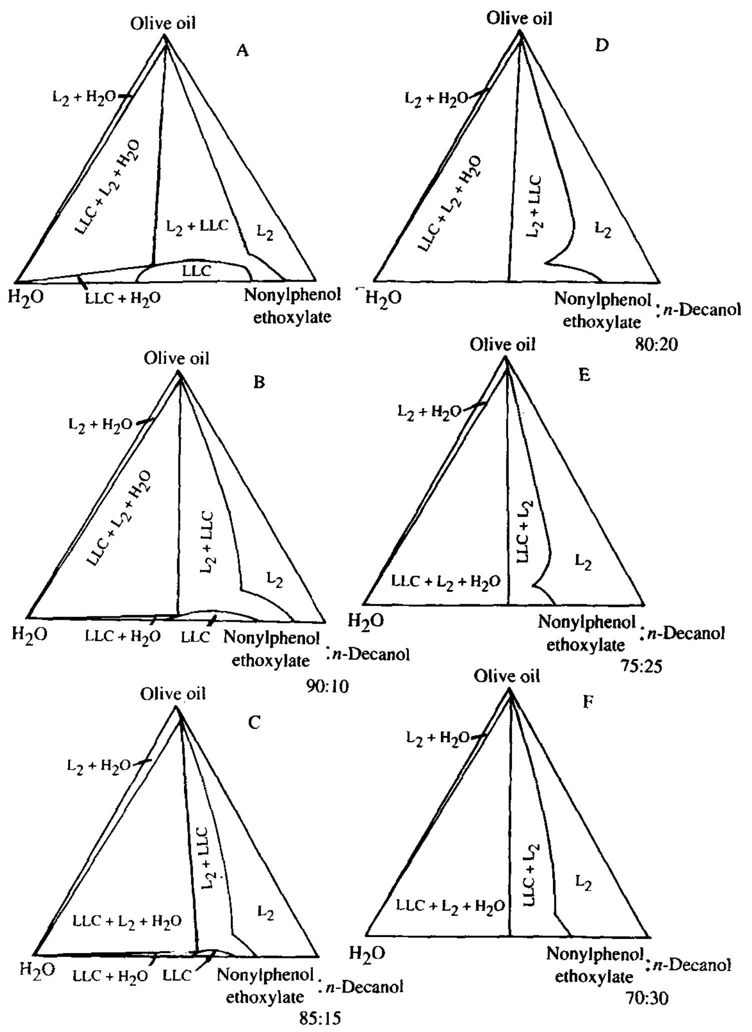

FIG. 2. Phase diagrams of system nonylphenol ethoxylate/*n*-decanol/olive oil/water: nonylphenol ethylate/decanol (w/w): A = 100:0, B = 90:10, C = 85:15, D = 80:20, E = 75:25, F = 70:30.

region (Fig. 3D). The three-phase region (L_2 + LLC + H_2O) is at the right side and extends from the nonylphenol ethoxylate/*n*-decanol/H_2O plane to the nonylphenol ethoxylate/olive oil/H_2O plane (Fig. 3E).

The three-dimensional phase diagram (Fig. 3) provides a clear overview of the results in Figures 1 and 2. For example, the solubility of water in the isotropic solution of nonylphenol ethoxylate and *n*-decanol increases with the weight ratio of nonylphenol ethoxylate to *n*-decanol from 100:0 to 75:25 (Fig. 2A–2E) and then is reduced from 75:25 to 70:30 (Fig. 2E, 2F). Figure 3 relates this result to the L_2 phase region in the nonylphenol ethoxylate/*n*-decanol/H_2O system, which has a maximum H_2O solubility at the weight ratio of nonylphenol ethoxylate to *n*-decanol of 73.6:26.4, as shown at the bottom of Figure 3A (Table 1).

Obviously, the addition of *n*-decanol is favorable for the solubilization of H_2O in the L_2 phase and depends on the weight ratio of nonylphenol ethoxylate/*n*-decanol in nonyl-phenol ethoxylate/*n*-decanol/H_2O system. When the weight ratio of

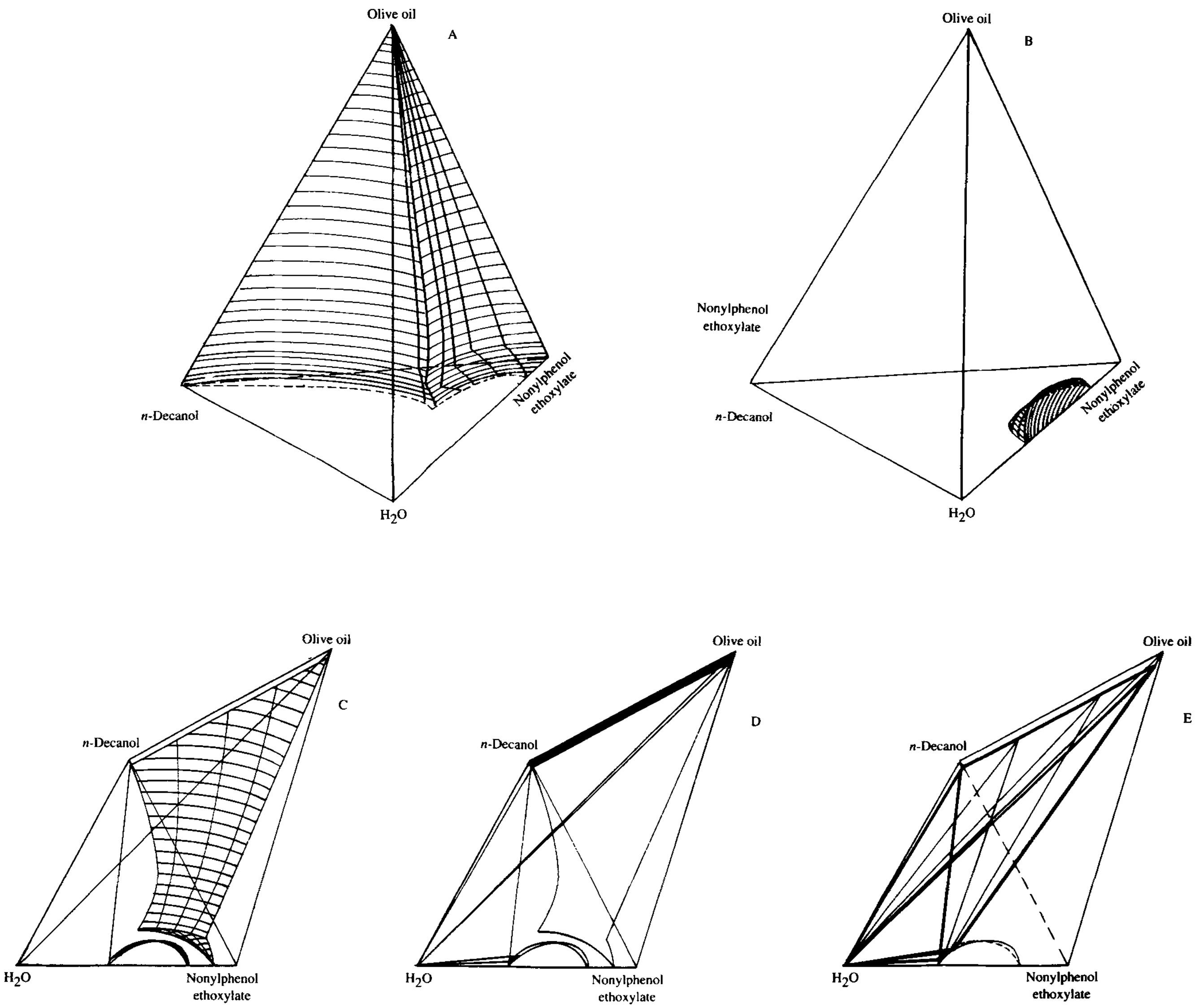

FIG. 3. Three-phase system nonylphenol ethoxylate/*n*-decanol/olive oil/water.

TABLE 1

Composition of Inverse Microemulsions at Maximum Water Content (wt% or w/w)

CO520/ $C_{10}OH$	Water	CO520	$C_{10}OH$	Olive oil	Water/ CO520	Water/ $C_{10}OH$	Water/ olive oil	Olive oil/ CO520	Olive oil/ $C_{10}OH$
100:0	17.5	71.5	—	11.0	0.25	—	1.59	0.15	—
90:10	22.5	58.5	6.5	12.5	0.39	3.46	1.80	0.21	1.92
85:15	25.5	55.7	9.8	9.0	0.46	2.60	2.83	0.17	0.92
80:20	37.0	44.8	11.2	7.0	0.83	3.30	5.29	0.16	0.63
75:25	36.0	42.4	14.1	7.5	0.85	2.55	4.80	0.18	0.53
70:30	28.0	44.1	18.9	9.0	0.64	1.48	3.11	0.20	0.48

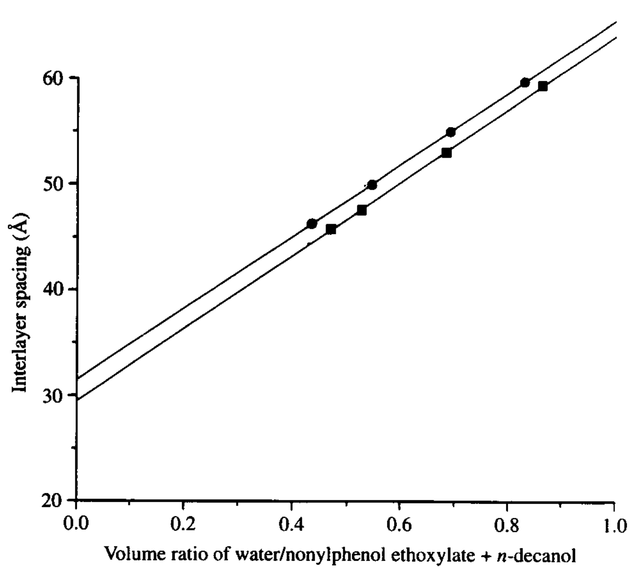

FIG. 4. Interlayer spacing with volume ratio of water/nonylphenol ethoxylate at different weight ratios of *n*-decanol/nonylphenol ethoxylate: ▲, 0:100; ■, 6:94; ●, 10:90.

nonylphenol ethoxylate to *n*-decanol is greater than 73.6:26.4, the solubilization of water in the surfactant nonylphenol ethoxylate increases with an increase of *n*-decanol, so that the addition of *n*-decanol is useful for increasing the solubilization amount of water in the w/o microemulsion phase of olive oil/water. In contrast, when the weight ratio of nonylphenol ethoxylate to *n*-decanol is less than 73.6:26.4, the addition of *n*-decanol causes the solubilization amount of water to decrease in the surfactant nonylphenol ethoxylate, so that the maximum solubilization amount of water in the nonylphenol ethoxylate/olive oil/water system decreases with a decreasing weight ratio of nonylphenol ethoxylate to *n*-decanol.

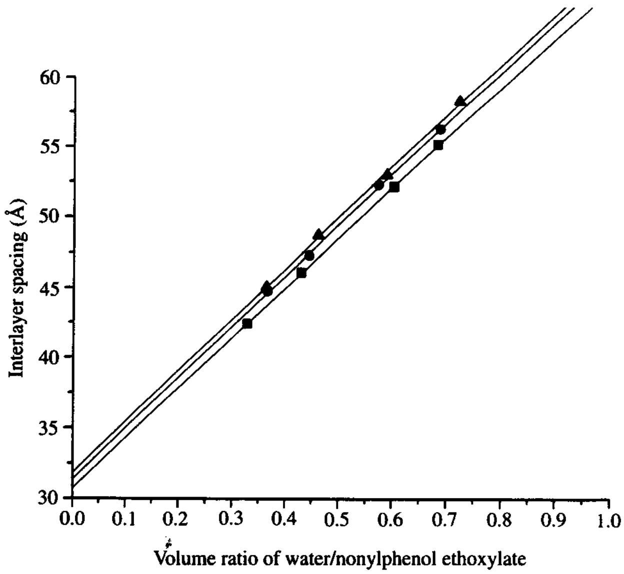

FIG. 5. Interlayer spacing with volume ratio of water/nonylphenol ethoxylate at different weight ratios of olive oil/nonylphenol ethoxylate: ▲, 0:100; ●, 3:97; ■, 8:92.

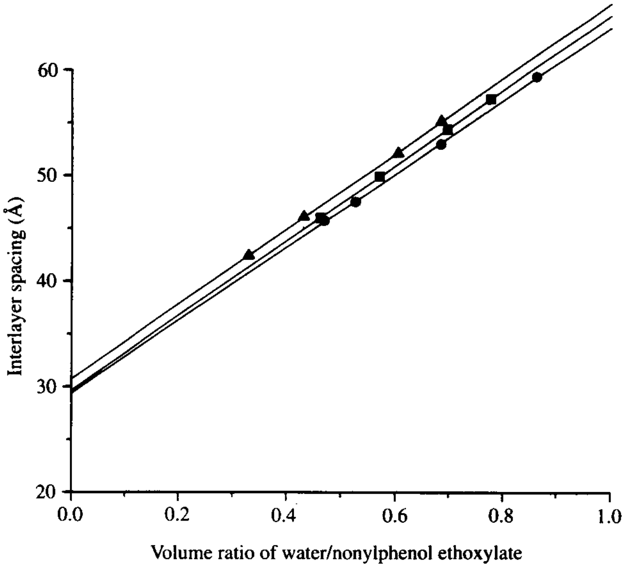

FIG. 6. Interlayer spacing volume ratio of water/(nonylphenol ethoxylate + *n*-decanol) vs. (weight ratio 90:10) for different weight ratios of olive oil/(ethoxylate + decanol) weight ratio: ■, 0:100; ●, 3:97.

Olive oil is the continuous phase in the w/o microemulsion. The variation of olive oil content at the maximum solubilization amount of water in a w/o microemulsion with the weight ratio of nonylphenol ethoxylate to *n*-decanol is opposite to that of the water content, but it is similar to that of the nonylphenol ethoxylate content. The weight ratio of water to olive oil increases first and then decreases, even though the extent of change is smaller, but the weight ratio of olive oil to *n*-nonylphenol ethoxylate decreases first, then it increases. These results mean that the optimal addition of *n*-decanol may reduce the amounts of oil and nonionic surfactant needed to increase the water solubilization in the w/o microemulsion.

Addition of *n*-decanol reduces the LLC region and the solubilization amount of olive oil in the LLC (Figs. 2A–2C). Discussion of the LLC structure, when *n*-decanol is added, is useful. Assuming that there is no change in the conformation or in the tilt of hydrocarbon chains, penetration of H_2O from the solvent layer to the amphiphile bilayer in the LLC structure may be obtained from calculations of the low-angle X-ray diffraction results by employing Equation 1.

TABLE 2
d_0 Values and Penetrations (α) of Solvent in the LLC of CO520/$C_{10}OH$/Olive Oil/H_2O

Solvent weight ratio		d_0 (Å)	α
$C_{10}OH$/CO520	0:100	30.7 ± 0.2	−0.16 ± 0.01
	6:94	29.7 ± 0.1	−0.20 ± 0.01
	10:90	29.4 ± 0.3	−0.18 ± 0.02
Olive oil/CO520	0:100	30.7 ± 0.2	−0.16 ± 0.01
	3:97	31.4 ± 0.3	−0.15 ± 0.02
	8:92	31.8 ± 0.5	−0.14 ± 0.03
CO520/$C_{10}OH$)	90:10	29.4 ± 0.3	−0.18 ± 0.02
Olive oil/(CO520	3:97	31.5 ± 0.1	−0.08 ± 0.01
+ $C_{10}OH$	0:100		

$$d = d_0(1 + R)/(1 + \alpha R) \qquad [1]$$

in which d is the interlayer spacing, d_0 is the interlayer spacing extrapolated to zero solvent content, R is the volume ratio of solvent to amphiphile, and α is the fraction of solvent penetrating the amphiphile bilayer. For R approaching zero, Equation 2 is obtained:

$$d = d_0[1 + (1 - \alpha)R] \qquad [2]$$

$$\delta d/\delta R = d_0(1 - \alpha) \qquad [3]$$

$$\alpha = 1 - (\delta d/\delta R)/d_0 \qquad [4]$$

The results of low-angle X-ray measurement values of d_0 and α for LLC in Figures 1 and 2 are given in Table 2 and in Figures 4–6.

Impurities, coming from the nonionic surfactant nonylphenol ethoxylate, exist between the nonylphenol ethoxylate molecules in the amphiphile bilayer of LLC, but they move to the oil layer when water is added. Calculated penetration of added water from A to B in LLC shows negative values in Table 2. A negative value for the penetration is obtained when the interlayer spacing is increased more than proportionally to the amount of added water. This seemingly contradictory result is explained by the fact that the surfactant is not a single compound but contains homologues with raised degrees of hydrophobicity. Addition of water causes expulsion of the more hydrophobic compounds from the site between the methylene groups to the layer between the methyl groups.

LLC of nonylphenol ethoxylate and water in the bottom lines of Figures 1 and 4 show that d_0 is 30.7 Å. For a molecular weight of 440.63, the area per nonylphenol ethoxylate molecule in LLC is 47.7 $Å^2$ from Equation 5.

Assuming that all the carbon chains in the nonpolar and polar groups in the surfactant are fully extended, the total chain length is (27).

$$L = (1.5 + 1.265n) \qquad [5]$$

where L is chain length and n is the number of methylene groups. For nonylphenol ethoxylate, L = 29.3 (Å), and d_0 should be 58.7 (Å). Comparing with the value of 30.7 (Å), shown in Table 2, the nonylphenol ethoxylate molecule obviously has a highly disordered configuration. For the LLC system of nonylphenol ethoxylate/n-decanol/H_2O, addition of n-decanol causes reduction in d_0 values.

For the nonylphenol ethoxylate/olive oil/water system shown in Figure 5, the olive oil exists in the oil layer of the LLC. Therefore, addition of olive oil increases the d_0 value of the LLC of nonylphenol ethoxylate and water. A similar result is obtained for the addition of decanol.

Figures 2 and 4–6 illustrates that the reduction of the LLC range and the solubilization amount of olive oil in the LLC of nonylphenol ethoxylate and water with increasing weight ratio of nonylphenol ethoxylate to n-decanol is caused by the destabilization of the LLC by n-decanol.

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