Decanol Effect on the Structure of the Hexagonal Phase in a Lyotropic Liquid Crystal

O. Santin Filho

Departamento de Química da Universidade Estadual de Maringá, Av. Colombo 5790, Maringá, Pr, 87020−900, Brazil

R. Itri and L. Q. Amaral*

Instituto de Física da Universidade de São Paulo, Cx. Postal 66318, São Paulo, SP, 05389-970, Brazil

Addition of decanol to the system sodium dodecyl (lauryl) sulfate (SLS)/water leads to the appearance of a nematic domain not present in the binary system. We investigate the structure of the hexagonal phase (H) of the ternary system for a fixed water:SLS molar ratio of 39.4. The decanol:SLS molar ratio was varied in the interval 0.12−0.37, inducing the phase sequence isotropic (I)−H−nematic cylindrical (N_c). Analysis of the obtained hexagonal parameter as a function of (SLS + decanol) volume concentration shows that the H phase in the ternary system shows two dimension swelling, as expected for infinite (or flexible) objects. On the other hand, the H phase in the binary system shows three dimension swelling, as expected for rigid finite objects. The micellar radius, necessary for the above analysis, was determined from electron density maps, obtained from observed diffraction intensities. A "crossover" from the finite rigid model to the infinite model occurs in the ternary system, due to the effect of decanol, which promotes micellar growth, changes the characteristics of the H phase, and induces the entrance on the N_c phase. The possible reasons for the nontrivial I−H−N_c sequence are discussed on basis of existing theories for self-assembly systems of rigid and flexible rods and for the elastic bending energy of mixed micelles.

1. Introduction

The complex polymorphism of systems made up of amphiphile/water/additives (salt and/or alcohol) has been extensively investigated over the past decades.[1,2] Such polymorphism exists because the molecules in solution self-assemble into aggregates of different forms and symmetries. Changes in the micellar shape accompany or trigger the phase transitions as a function of concentration and temperature.

The binary system sodium dodecyl (lauryl) sulfate (SLS)/water presents the phase sequence I (isotropic)−direct H (hexagonal)−L_α (lamellar) upon increase in SLS concentration, with several intermediate phases between H and L_α, all showing long-range positional order.[3] It has been shown[4] that the H phase of the binary system consists of finite rigid rods, with compression in all three dimensions (the functional behavior between the hexagonal unit cell parameter a and the amphiphile volume concentration c_v is characterized by the exponent $-1/3$). A structural study[5] with careful analysis of the electron density maps obtained from diffraction intensities confirmed finite (although long, and therefore rigid) rods in this H phase.

Addition of decanol leads to a nematic (N) domain in ternary system,[6,7] intermediate between the H and the L_α phases. The phase sequence depends on concentration and temperature and may be I−N_c (nematic cylindrical) or I−H−N_c.[8]

The theories of self-assembly predict the sequence I−(N_c)−H, as a function of increased particle volume fraction v_p, for cases of finite hard rods,[9] persistent flexible rods,[10] and wormlike micelles.[11] All of these theories present phase diagrams as a function of v_p with the same topology. There is a triple point that separates I−H and I−N−H phase transitions. In the case of finite rigid objects, the phase diagram[9] is a function of the association free energy, which defines the particle length. In

the case of flexible long rods, the phase diagram[10,11] is a function of the ratio persistent length/micelle diameter (P/D) with the axial ratio (L/D) as parameter. The direct I−H transition is expected in the limits of small rigid objects or very flexible long objects in the I phase. In the former, an increase in micellar length is expected at I−H transition.[9]

The expected theoretical phase sequence I−N_c−H appears in the experimental phase diagram of the ternary system,[8] shown in Figure 1, only for about 4 wt % of decanol and between 24.5 and 27 wt % of SLS. This means that only for those concentrations are the micelles in the correct range of length and rigidity to induce the appearance of the N_c phase with increase in SLS content.

The inverted phase sequence I−H−N_c occurs, however, by increasing decanol content, upon SLS concentration larger than 26 wt %. Such inversion must be due, therefore, to a specific effect of decanol, which possibly affects the growth and flexibility of the mixed micelles in a nontrivial way. The inversion occurs in the context of the complete sequence I−H−N_c−N_d (nematic discotic)−L_α, which appears only with increase in decanol content.[6−8] The N_c−N_d transition has been shown[7,12] to be a function of decanol:SLS molar ratio (M_d) in systems with different amphiphiles.

Aiming to reach a better understanding of the decanol effect on micellar structure and phase transitions, the study of the phase sequence I−H−N_c is made in the present work by investigating the ternary system varying M_d for a fixed value of the water: SLS molar ratio (M_w). It has been recently shown[13] that the inverted sequence appears already for a $M_w = 45.2$ (line A of Figure 1). For such high water content the H domain exists[13,14] only for a very narrow interval, $M_d \sim 0.195$. So, the line A contains, in fact, the H phase in the sequence I−H−N_c and
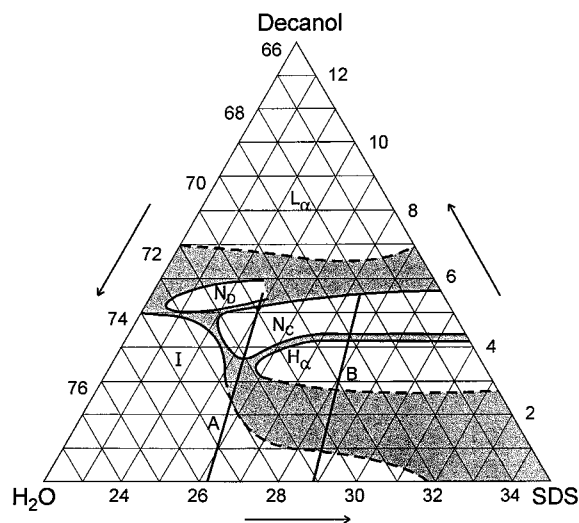
Figure 1. Ternary phase diagram of the system SLS/water/decanol as a function of weight composition from Quist et al.,[8] which includes the nematic domain previously localized by Amaral et al.[6,7] and the limits of the hexagonal phase given by Ekwall,[2] when the N domain was not known. Lines A of a previous work[14] and B of the present work are also represented (see text for details).

occurs in order to decrease the electrostatic interaction between amphiphile polar heads and is responsible for micellar growth with decanol addition.[17] The requirements of the bending energy of the polar/apolar interface in changing the micelle forms[12,18] are also taken into account. It has been shown that a form transformation from prolate spheroids to spherocylinders (SC) occurs as the micellar anisometry increases and it is a prerequisite for the I–H transition,[18] and that N_c–N_d transition correlates[12] with a transformation from SC to planar form, induced by decanol addition.

2. Experimental Section

Commercial Merck SLS (99% purity) 1-decanol from BDH and bi-distilled and deionized water were used. Materials were used as purchased because this gave good reproducibility of phase diagrams, while attempts of further recrystallization did not lead to good reproducibility. Samples were prepared adding controlled amounts of decanol to an aqueous solution with 28.89 wt % of SLS, which corresponds to a water/SLS molar ratio, M_w, of 39.4. The decanol/SLS molar ratio, M_d, was varied in the interval 0.12–0.37. The studied samples are located in line B of the ternary phase diagram of Figure 1. Samples in test tubes were homogenized and equilibrated for at least 1 day. Phases were identified using a polarized optical microscope (Wild, Orthoplanpol). The X-ray diffraction of samples in cylindrical capillaries of 1 mm internal diameter at room temperature (22 °C) was registered with flat photographic films in a Laue transmission geometry, using Cu Kα–Ni filtered radiation (wavelength λ = 1.5418 Å) and sample-to-plate distance of 10 cm. The relative intensities of the diffraction peaks were measured by using a Pharmacya microdensitometer.
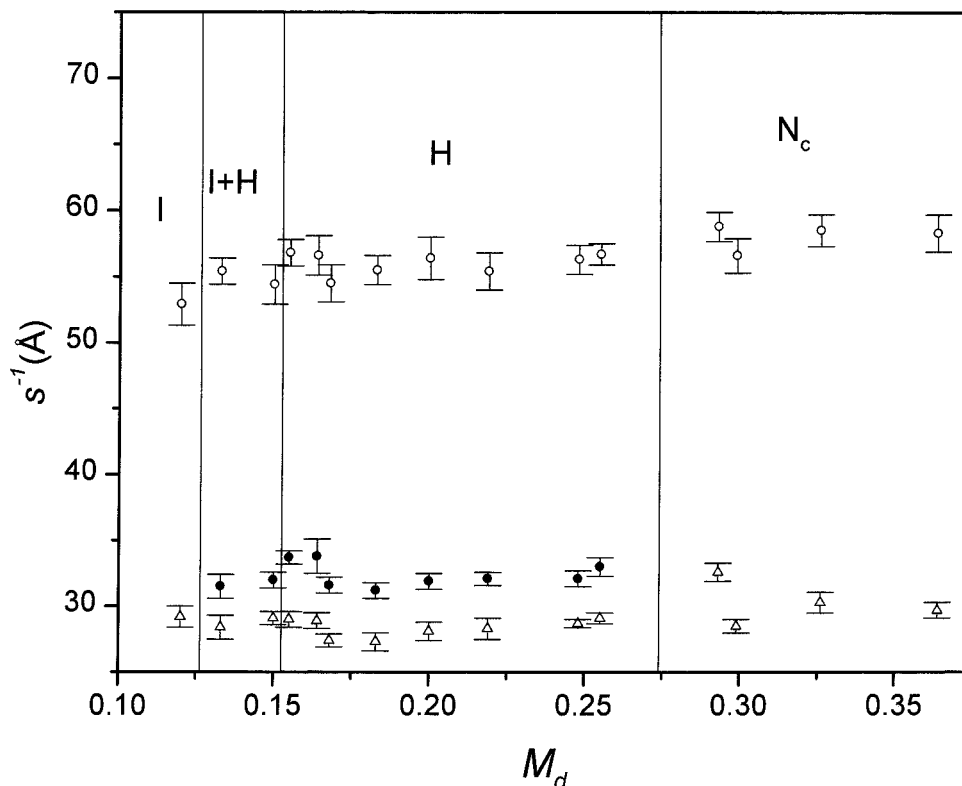
passes very near the triple point. In the present work, we better explore the H phase's features over a larger range of M_d values by investigating samples at M_w = 39.4 (line B of Figure 1), following the sequence I–H–N_c.

The decanol effect in the H phase is here correlated with previous studies of the H phase in this[4,5] and other systems,[15,16] with theories of phase transitions (which are not specific for ternary systems)[9–11] and with previous studies regarding partition of decanol and SLS in mixed micelles. The tendency of decanol to localize in the body of spherocylindrical micelles

Figure 2. s^{-1} values obtained from photographs of samples at room temperature (22 °C) with a fixed water:SLS molar ratio, M_w, of 39.4 and variable decanol:SLS molar ratio, M_d. Open circles, solid circles, and triangles correspond, respectively, to diffraction peak positions in the ratio $1:\sqrt{3}:\sqrt{4}$. These three peaks are observed in the H phases, while only the first and second orders (ratio 1:2) are present in the I and N_c phases.

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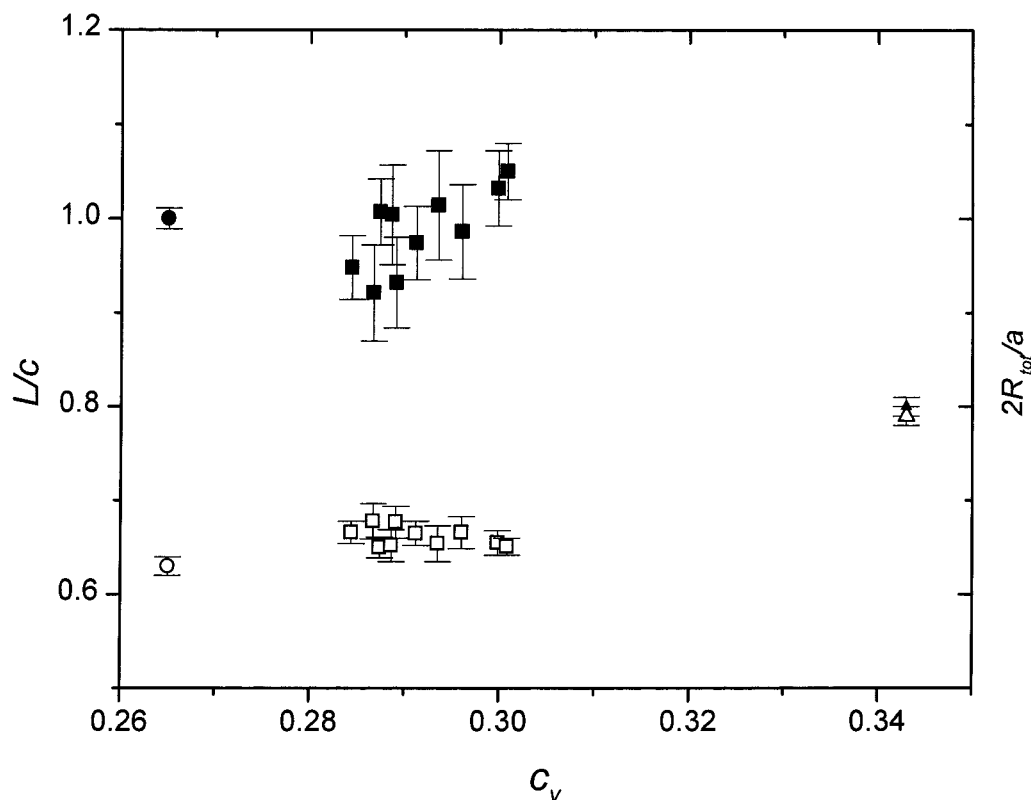
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Figure 3. L/c (solid symbol) and $2R_{tot}/a$ (open symbols) values in the H phases as a function of (SLS + decanol) volume concentration for three data sets, corresponding to three different values of the water:SLS molar ratio. Squares correspond to the results here reported ($M_w = 39.4$), circles to a ternary system with $M_w = 45.2$,[14] and triangles to a binary system with $M_w = 24.0$.[21] L/c values were obtained from eq 1, using c_v and $R_{eff} = 18.4$ Å. R_{tot} and a are, respectively, the total particle radius (see text for details) and the hexagonal cell parameter.

3. Results and Discussion

Figure 2 shows for all studied samples the position of the observed diffraction peaks, s^{-1} ($s = 2\sin\theta/\lambda$, with 2θ the scattering angle) as a function of M_d, with the phase sequence I−H−N$_c$. The nematic discotic phase (N$_d$), which appears [7] for higher M_d values, was not investigated in this work. The higher s^{-1} values correspond to the average intermicellar distance in phases I and N$_c$, and to the interplanar distance in the H phase. Indeed, three diffraction lines in the ratio $1:\sqrt{3}:\sqrt{4}$ characterize the H phase, while I and N$_c$ phases show two broad peaks with ratio 1:2, typical of the SLS system.[6] For the two samples in the coexistence region I + H, the capillary showed phase separation and the X-ray beam was incident on the H phase.

From Figure 2 it is seen that as the system crosses over from I to N$_c$ phase, passing through the H arrangement, due to the influence of increasing decanol molar ratio, the mean intermicellar distance remains practically the same, within the evaluated uncertainties. Let us now explore how decanol affects the micellar structure in the H domain.

As already analyzed in previous papers,[4,5,15,16] for a spherocylinder (SC) of radius R and total length L in an hexagonal cell with parameters a and c, the usual condition of equal density at the microscopic and macroscopic levels implies that the static structure (averaged in time) satisfies the relation

$$(L/c)_{SC} = (2\sqrt{3}/\pi)c_v \, (a/2R)^2 \, (\mu)/(\mu - 1/3) \qquad (1)$$

where $\mu = L/2R$ is the particle anisometry and c_v is the volume fraction of the total amphiphile. Note that in the case of micelles the existence of bound water may make c_v different than the particle volume fraction v_p. For long SC the cylinder (or rod) limit is obtained, and the factor that depends on the

anisometry becomes 1. This limit can be used in order to obtain L/c values in the H phase, since micelles have large μ values.[5]

Furthermore, in the case of micelles, as studied here, care must be taken in the definition of the R and L values in eq 1. They may refer[4,5,15,16] to "effective" radius R_{eff} and length L_{eff}, which represent the "particle without water", related to c_v. To substitute v_p for c_v in eq 1 it would be necessary to use R_{tot} and L_{tot} of the "particle", including bound water. Alternatively, one can consider the paraffinic micelle and the values in eq 1 become R_{par}, L_{par}, and c_{vpar}, where c_{vpar} is referred to as the paraffinic volume fraction. Moreover the following relationship is valid:[5]

$$(R_{eff}/R_{par})^3 = (c_v/c_{vpar})(\mu_{par} - 1/3)/(\mu_{eff} - 1/3) \qquad (2)$$

For long micelles, the differences between L_{eff}, L_{par}, L_{tot} may be neglected, but not the differences between the respective R values.

For systems composed of finite rigid rods, the condition of three dimension expansion leads to $L/c = 2R/a$ and $a \sim c_v^{-1/3}$. Micellar growth in this condition (variable $L/c = 2R/a$) can be detected[15,16] through an exponent smaller than 1/3. For infinite cylinders with end-to-end contact and two dimension expansion one expects $L/c = 1$ and $a \sim c_v^{-1/2}$.

It has been also theoretically shown in statistical mechanics treatment of self-assembled systems[9,10] that these limits (exponents 1/3 and 1/2) hold, respectively, for finite rigid rods and for long flexible rods (with end-to-end contact or with persistent length on the order of c). We shall therefore refer to conditions $L/c = 2R/a$ and $L/c = 1$, related to eq 1, as characteristic of "finite/rigid" and "infinite/flexible" rods, respectively. In the case of flexible objects, eq 1 does not hold in a strict sense, but it is always possible to obtain an "apparent L/c value" which
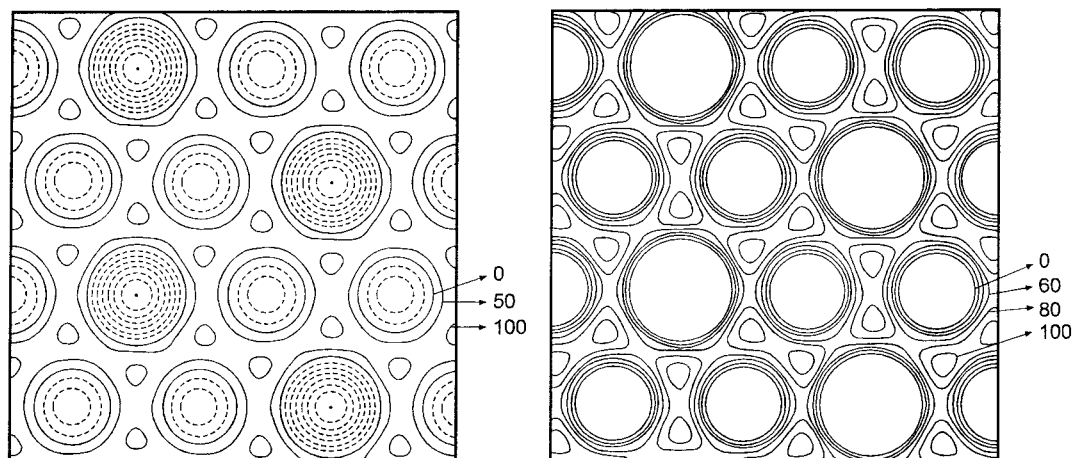
Figure 4. Projection of the electron density distribution in the hexagonal plane of the H phases of the SLS/water/decanol system at room temperature (22 °C) at a fixed water:SLS molar ratio, $M_w = 39.4$, and decanol:SLS molar ratio $M_d = 0.248$. The corresponding ϕ-set is (- - -). The electron density scale is arbitrary, as well as the zero level (see ref 5 for details). On the left side the density levels are equally spaced with an increment of 50, while on the right side only outer regions are represented in more detail, with an increment of 20.

satisfies eq 1 for rods. Values $L/c > 1$ have been obtained[15,16] using eq 1 for H phases near bicontinuous phases, and such result is possibly due to the existence of undulated and flexible surfaces.

In the binary SLS/water system the interval of the explored c_v values, within the H domain, was sufficiently large and allowed to unambiguously define[4] a 1/3 behavior, typical of finite rigid rods. Here the c_v interval is much smaller. However, a characterization can be made by a direct comparison of the L/c value obtained from eq 1, with c_v and $R_{eff} = 18.4$ Å[4,5] and the $2R_{tot}/a$ value ($a = 2/\sqrt{3}\ s^{-1}$), as was also performed[14] with results obtained with $M_w = 45.2$. R_{tot} is the "particle" radius, given by the sum of the extended dodecyl chain, 16.7 Å,[19] and the polar head diameter, 4.6 Å.[20] The two values L/c and $2R_{tot}/a$ give the best definition of the "cylindrical particle" of the H phase in the directions c and a, respectively.

The results are shown in the Figure 3, along with those calculated from two other works,[14,21] as a function of the micellar c_v, which includes both SLS and decanol. The three data sets correspond to different SLS/water molar ratios, two in ternary systems ($M_w = 39.4$ and 45.2) and one in the binary system ($M_w = 24.0$). The first two points for $M_w = 39.4$ correspond to the H phase in coexistence with the I phase.

It is evident from Figure 3 that the condition $L/c = 2R_{tot}/a$ is only attained in the H phase of the studied binary SLS/water system,[21] in agreement with $a \sim c_v^{-1/3}$ behavior.[4] However, L/c values are close to 1 and much larger than $2R_{tot}/a$ in the H phases of the ternary SLS/water/decanol system, for two different values of M_w. It is seen that the addition of decanol deeply changes the characteristics of the H phase, which switches from particle finite/rigid to particle infinite/flexible behavior. The results for $M_w = 39.4$ here reported in Figure 3 show even a tendency for an increase in L/c and a small decrease in $2R_{tot}/a$ with increase in decanol content.

It should be noted, however, that the R_{eff} value used to calculate L/c was obtained in the binary system[4,5] and it is not excluded the possibility of a change in R_{eff} in the ternary system. To further demonstrate this result in the ternary system, it is important to obtain R values from analysis of the electron density maps also in the ternary system. This is now done for four samples with different M_d values within the H domain. The maps were obtained from the X-ray diffracted intensities following the procedures previously reported.[5] The choice of the phase set, the so-called ϕ-set, was based on previous swelling

experiments for the SLS system,[5] which indicated that the two first reflections F(1,0) and F(1,1) have the same sign. The problem remained over the choice of the weak third reflection F(2,0), since it is located near one of the zeros of the cylindrical structure factor[5] and hence close to the region of a phase inversion. Then, both ϕ-set combination (- - -) and (- -+) were considered, which led to similar results.

Figure 4 presents, as an example, the electron density map of the sample with $M_d = 0.248$, with ϕ-set (- - -). The aspect is similar in all studied maps: micelles appear with circular cylinder cross-section in the hexagonal plane. There is a negative inner region (drawn as dashed line) in relation to an average electron density value $\langle \rho \rangle$, which we associate to an arbitrary zero level, and an outer region with positive levels in relation to $\langle \rho \rangle$ (solid line). The inner and outer regions are related, respectively, to the lower-electron density paraffin medium and to the higher electron density polar head in respect to the water. In the right side of the figure, the outer region is represented in more detail, with density levels equally spaced with an increment of 20; some levels are indicated to emphasize the increasing− decreasing electron density level sequence.

The maps of the ternary system look very similar to the maps[5] of the binary system regarding the micellar object. Only the fraction occupied by the micelle in the hexagonal cell changes, according to different c_v and a values of the phases. The ternary system has a hexagonal cell with considerably more water in the hexagonal plane.

A consistent interpretation of the cylindrical structure is obtained[5] by estimating R_{eff} from the electron density maps using as a criterion the largest distance of the continuous contour from the micellar center. Based on that, Table 1 presents the values of R_{eff} evaluated from the maps along with the R_{par} and L/c values calculated according to eq 2 and eq 1, respectively, using the rod limit (independent of anisometry). Results show that, in fact, R_{eff} is slightly smaller in the ternary system. The average value from Table 1 is about 4% smaller than the value obtained in the binary system. The R_{par} values however are within 1% the same as in the binary system. This indicates that the presence of decanol changes only slightly the micellar radius, and that the change in R_{eff} occurs in the polar shell, since decanol decreases its electron density. As far as the L/c values are concerned, they are equal to 1, within the evaluated uncertainties. It means that such ternary H phases are built up of infinite/ flexible cylinders in a hexagonal array.

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TABLE 1: Decanol:SLS Molar Ratio, M_d; (SLS + decanol) Volume Concentration, c_v; and Paraffinic Volume Concentration, c_{vpar}, Related to the H Phases Investigated through Electron Density Maps Obtained from X-ray Scattering Intensities (both phase sets (- - -) and (- -+) are considered (see text for details))

M_d	c_v	c_{vpar}	R_{eff} (Å)^a	R_{par} (Å)^b	L/c^b
0.133	0.2844	0.2466	17.9 ± 0.6 (- - -)	17.0 ± 0.6	1.00 ± 0.08
			17.4 ± 1.1 (- -+)	16.6 ± 1.0	1.06 ± 0.14
0.168	0.2891	0.2512	17.1 ± 0.3 (- - -)	16.3 ± 0.3	1.08 ± 0.07
			17.8 ± 0.8 (- -+)	16.9 ± 0.7	0.99 ± 0.10
0.248	0.2998	0.2614	18.3 ± 1.3 (- - -)	17.4 ± 1.2	1.04 ± 0.15
			17.1 ± 0.8 (- -+)	16.3 ± 0.7	1.19 ± 0.11
0.255	0.3009	0.2624	18.2 ± 1.0 (- - -)	17.3 ± 0.9	1.07 ± 0.12
			18.1 ± 0.6 (- -+)	17.2 ± 0.6	1.09 ± 0.08

^{a} R_{eff} corresponds to an "effective" radius assumed as the largest continuous contour from the micellar center evaluated from the respective map. ^{b} R_{par} and L/c are obtained from eqs 2 and 1, respectively.

4. Concluding Remarks

The results here reported confirm a "crossover" from the finite/rigid model[9] to the infinite/flexible model[10,11] for the H phase with an increase in the decanol content. This effect is probably due essentially to micellar growth with decanol addition. Such growth occurs in a slighter form (anisometries increasing from 2.4 to 3) in the I phase[13,14] but must be greatly enhanced by coupling with orientational and positional order in the H phase.[9–11]

In the binary system micelles are short in the I phase and longer in H phase, growing considerably in the I—H coexistence range.[5,21] From X-ray results[5] the estimated length in phase H gives L/D in the range 6–16. The behavior $a \sim c_v^{-1/3}$ ensures[4] that micelles are in the finite rigid regime, and therefore must have a large persistence length, or $P \sim L$. No nematic phase exists in the binary system, so the system is above the triple point at the I—H transition.

The theories of self-assembly that predict I—(N)—H phase transitions[9–11] are neither specific for ternary systems nor deal with the specific role of decanol. However, the effect of decanol might be deduced through comparison of the experimental phase diagram of Figure 1 with the theoretical predictions. The first point to emphasize is that decanol brings I—H transition to values of SLS concentration much smaller than without decanol. In the binary system I—H direct transition occurs[21] for 40 wt % of SLS, while it can occur for less than 26 wt % for about 3.5 wt % of decanol (see Figure 1). This shows that the particle volume fraction v_p, which defines the transition point, is neither proportional to the SLS nor to the total amphiphile (SLS + decanol) weight concentration.

Let us first compare the experimental phase diagram with the phase diagram for rigid rod.[9] From the position of the triple point we conclude that the decanol content plays the role of the association free energy Φ. A slight decrease in decanol (from 4 to 3.7 wt %) promotes a change from I—N—H to I—H behavior. It shows that an increase in decanol should have the same effect as an increase in the absolute value of Φ (or alternatively a decrease in temperature). This is consistent with the effect of micellar growth with decanol addition mentioned before. From the theoretical phase diagram for rigid rods the H—N line can only be crossed through a decrease in particle volume fraction v_p. The H—N$_c$ transition is experimentally obtained with an increase in c_v and c_{vpar} (since M_d increases), but this does not mean necessarily an increase in v_p. With the constant R_{tot} value used in Figure 2, v_p shows a slight increase with M_d. But if we allow for a small decrease in R_{tot}, as indicated

in the structural analysis that gave a decrease of 4% in R_{eff}, v_p can actually decrease as M_d increases. It is thus possible that, due to a combined effect of marked particle growth and small decrease in polar head size, v_p decreases within the H domain, inducing the H—N$_c$ transition. The particle volume fraction in the hexagonal plane is clearly much smaller in the ternary than in the binary system, while the fraction in the fluid direction increases in the ternary system.

To complete the picture it is necessary to take into account that the nearby nematic N$_c$ phase is made up of small micelles,[22] while micelles are long in the H phase. This can be rationalized only by admitting that micelles must become shorter at the H—N$_c$ transition and, conversely, that a large increase in micellar length must occur at the N$_c$—H transition. Such a fact is qualitatively understandable, since micellar growth is triggered by both orientational and positional order.[9–11] What experimental results show is that, since anisometries are nearly equal in the I phase ($\mu \sim 3$) before the I—H transition[13] and in the N$_c$ phase after the H—N$_c$ transition,[22] growth occurs much more due to positional ordering than due to orientational ordering. Enhancement of growth in the H phase, as compared to the N phase, arises theoretically[11] from details of polydispersity and intermicellar interactions.

The nontrivial I—H—N$_c$ sequence in the SLS ternary system with increase in M_d may be therefore understood on basis of a complex path through the theoretical phase diagram for rigid rods.[9] I—H transition occurs above the triple point, for small lengths and large volume fraction in the I phase, with a large increase in micellar length at I—H coexistence. Along the H phase, an increase in M_d corresponds to further micellar growth, arriving to the "infinite end-to-end" limit. This path goes, therefore, around the triple point (which corresponds to $\mu \sim 3$ for $v_p \sim 0.45$), with an increase in size and decrease in v_p. H—N$_c$ transition occurs below the triple point with a marked decrease in micellar length at the H—N$_c$ coexistence.

Let us now compare the experimental phase diagram with the predictions for flexible rods.[10,11] It has been shown that the existence of the N phase requires a certain rigidity of semi-flexible micelles. Comparison of the triple point of Figure 1 with the theoretical phase diagrams[10,11] shows that increase in decanol content must induce an increase in the P/D ratio of a flexible rod. That means that an increase in decanol should increase rod rigidity, and not promote flexibility. The micelles in the H phase of the binary system are quite rigid, since they have rigid behavior and are long ($L/D \sim 10$). Therefore, they have $P \geq L$. An increase in rigidity can be obtained either by an increase in P/D or a decrease in L/D. Since decanol promotes miceller growth (increase in L/D), it must also promote marked increase in P/D in order to allow the H—N$_c$ transition within the theoretical framework of flexible rods. An increase in rigidity of rodlike micelles with decanol addition can be understood within the framework of the elastic bending energy of mixed micelles.[12] The surfactant parameter of decanol ($p_0 \sim 1$) responsible for its bending energy at the micellar polar/apolar interface is considerably larger than that of SLS ($p_0 \sim 1/3$), and the parameter of the mixed region will be also correspondingly larger.[12] Thus, decanol promotes rigidity in rodlike micelles, even if it may eventually promote flexibility in planar membranes, due to the planar symmetry combined with decrease in charge of polar surfaces.

The direct I—H transition occurs above the triple point (which occurs for $P/D \sim 13$ for long flexible rods[10,11]). An increase in M_d corresponds to a path "turning around the triple point", with an increase in L/D and P/D. The transition line H—N$_c$ is crossed

also with a decrease in v_p, combined with an increase in P/D. It should be remarked that, in one of the theoretical phase diagrams,[10] a slightly re-entrant behavior (for $L/D \sim 25$) is possible, which allows to cross the H−N line at fixed v_p, but with a very large increase in P/D (of about 3 orders of magnitude). However a decrease in v_p seems more plausible.

In conclusion, the experimental facts can be explained within the framework of the theoretical phase diagrams for self-assembled systems. The "infinite/flexible" limiting behavior observed for the H phase of the ternary system should in fact be ascribed more to "infinite" than to "flexible", since decanol promotes growth but not flexibility. There must be therefore a limit on micellar length for the finite rigid behavior (as seen in the binary system), above which the system behaves as "infinite" even if rigid.

It has been shown[17] that it is energetically favored in spherocylindrical mixed micelles that decanol stays in the body of the cylinder, leaving unmixed amphiphile in the hemispherical caps. The shorter micelles in the N_c phase will have a larger decanol mole fraction in the body of the spherocylinder than in the H phase, but still without decanol in the hemispherical caps. Only with a further decanol increase, at the N_c−N_d transition, does the mole fraction of the cylindrical body impose a marked change in micellar form (from spherocylinder to platelet), as extensively studied in ref 12. The N_c−N_d−L_α phase sequence is, however, outside the scope of the present work.

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