

# Improper orientational ordering regime and tricritical behavior in a lyotropic liquid crystal

V. P. Dmitriev\* and G. R. Ouriques

*Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil*

(Received 30 November 1998)

Optical microscopy, deuteron quadrupolar NMR, x-ray diffraction, and electrical conductivity techniques have been used to map the phase diagram and to measure the nematic order parameter variation ( $S$ ) in ternary mixtures of pentadecafluorooctanoate acid ammonium salt (APFO), heavy water ( $D_2O$ ), and ammonium chloride ( $NH_4Cl$ ). A phenomenological model with an isotropic parent phase and a single primary segregation order parameter is elaborated on to describe in consistent terms the linear dependence of  $S(T)$  through the whole nematic stability region as well as the existence of a tricritical point at the nematic-to-lamellar phase transition line. [S1063-651X(99)06708-2]

PACS number(s): 61.30.Gd, 05.70.Fh, 64.60.Kw, 64.70.Md

## I. INTRODUCTION

During the three last decades, phase transitions between isotropic, nematic, and smectic phases in thermotropic liquid crystals have been the subject of intense and successful studies, both theoretical and experimental. Because of the normally weak or even vanishing discontinuity of such transformations, the corresponding molecular statistical and phenomenological theories have been able to avoid mathematical difficulties and thus not only have observed phase transitions been correctly described, but many interesting properties have been predicted as well. One interesting point worth studying in detail was the existence of two possible regimes for the nematic-to-smectic phase transition (second and first order) predicted by Kobayashi [1] and McMillan [2] on the basis of mean field calculations, for which there have been a number of experimental confirmations [3,4]. Phenomenological consideration within the framework of the Landau-de Gennes approach has also predicted the same possibility of a second- to first-order crossover for the nematic-to-smectic transformation [5]. In both molecular statistical and phenomenological theories, tricritical behavior is due to the coupling between a positional primary order parameter, which is approximated by its first Fourier component, and a secondary one, which is either a higher order Fourier component [6] or an orientational order parameter [2].

To consider positionally and orientationally ordered phases in the lyotropic system, it is tempting to make a direct analogy with smectic and nematic phases of thermotropic liquid crystals, replacing the individual molecules with micelles as elements of structure. However, the aggregative activity of amphiphilic molecules in lyotropic solutions can serve as the mechanism of change for phase transition.

In this paper we consider the existence of two regimes and the occurrence of a tricritical point on the nematic-to-lamellar phase transition line. Experimentally such a source of tricritical behavior is shown to take place in APFO/ $D_2O$ / $NH_4Cl$  lyotropic systems.

## II. EXPERIMENTAL PHASE DIAGRAM

### A. Methods

The pentadecafluorooctanoate acid ammonium salt (APFO) was purchased from Fluka, Switzerland (purity better than 98%) and was purified by recrystallization twice from butanol. High purity (>99.9%) deuterium oxide and ammonium chloride salt (purity >99.5%) were used.

The phase diagram was mapped using mainly optical microscopy and high resolution NMR. All the optical observations were carried out under a polarizing microscope in transmitted white light. Other techniques, such as x-ray and electrical conductivity, were also employed in order to confirm the optical and NMR measurements and to determine the temperature dependence of the order parameter.

Deuteron quadrupolar spectra of APFO/ $D_2O$ / $NH_4Cl$  ternary system were recorded on a Bruker MSL 300 spectrometer operating at a frequency of 41.6 MHz. The temperature of the sample was controlled and measured to within 5 mK.

X-ray diffraction experiments were carried out using a Philips generator with a nickel-filtered  $Cu K_\alpha$  radiation of wavelength  $\lambda = 1.5418 \text{ \AA}$ . The alignment of the samples was provided by a small electromagnet (0.5 T) and the x-ray capillary (Linderman, 0.5 mm i.d., W. G.) was positioned in the heating block such that the magnetic field was perpendicular to both the long capillary axis and the x-ray beam.

The electrical conductivity measurements in the frequency range 5 Hz–13 MHz were made using a HP 4192a LF impedance analyzer and an immersion conductivity cell with  $5 \times 5$  mm platinum electrodes. The accuracy and stability errors in the temperature experiment were  $\pm 0.01$  K and  $\pm 0.003$  K, respectively.

### B. Phase diagram and nematic order parameter variation

The phase diagram of the binary APFO/ $D_2O$  system was published earlier by Boden *et al.* [7]. The part of this diagram containing isotropic ( $I$ ), nematic ( $N$ ), and lamellar ( $L$ ) discotic phases is presented schematically in Fig. 1(a). The tricritical point at which the nematic-to-lamellar transition crosses over from second- to first-order behavior has been fixed at an amphiphile concentration of  $w_A = 0.495$  with a corresponding temperature of  $T_{tr} = 304$  K. In order to study

\*On leave from the University of Rostov-on-Don, Russia. Electronic address: dmitriev@fsc.ufsc.br

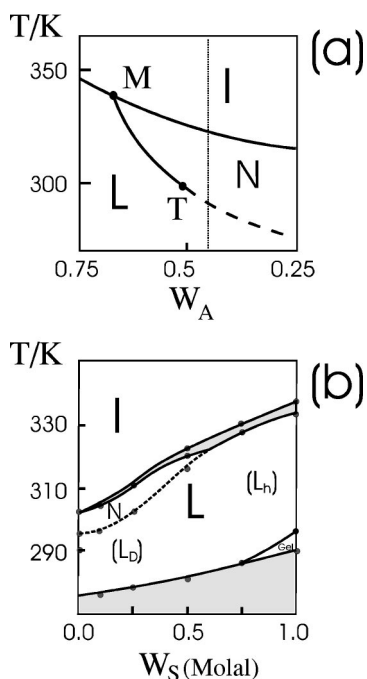


FIG. 1. (a) Schematic phase diagram of the APFO/D<sub>2</sub>O binary system. The section devoted to the variation of salt concentration is shown by the dotted line. Solid and dashed lines are first-order and second-order transition lines, respectively.  $T$  is the tricritical point and  $M$  is the three-phase point. (b) The evolution of the phase regions with temperature and salinity  $w_s$  of the ternary system APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl. Shaded areas are two-phase regions.

the temperature variation of the nematic order parameter, we prepared a set of ternary compounds that added ammonium chloride salt to the APFO/D<sub>2</sub>O mixture. Aqueous solutions of salt at different salinities  $w_s$  were mixed with a surfactant in such a proportion that the amount of surfactant present in the solution was kept constant at 45 wt% APFO. A region of the binary phase diagram was chosen so as to maintain different regimes for phase transitions (first order for  $I$  to  $N$  and second order for  $N$  to  $L$ ) and to ensure a universal temperature behavior of the nematic order parameter. The evolution of the phase regions with added salt is shown in Fig. 1(b). As a consequence of the increase in the salt concentration, several features were observed: the phase transition temperatures rose, the micellar nematic phase  $N$  was suppressed, and the lamellar  $L_D$  changed to a defective lamellar structure  $L_h$  with holes within the layers instead of the disk-shaped structure formed in the  $L_D$  phase. This latter effect will be published in detail elsewhere. The triple  $I/N/L$  point identical to the one found in the APFO/D<sub>2</sub>O binary system was fixed at  $w_s = 0.63$  molal and  $T = 322$  K. The transitions on cooling from the isotropic to the nematic phase are made through a narrow two-phase region,  $I+N$ , which becomes wider at the end of the nematic region on the high salt concentration side (i.e., 0.63 molal). On crossing from isotropic to lamellar phases  $L_D$  or  $L_h$ , the phase transition is through a wide two-phase region,  $I+L_D$  or  $I+L_h$ . These phase coexistence regions are indicative of a first-order phase transition.

Small-angle x-ray scattering patterns from a magnetically aligned ternary sample of APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl were found to be typical for the isotropic and lamellar phases. On cooling from the isotropic into the nematic phase, just after  $I-N$

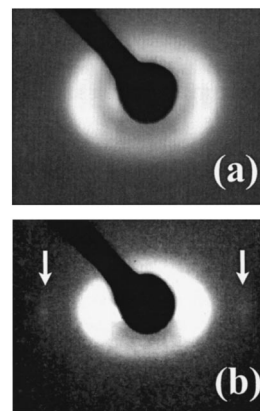


FIG. 2. Small-angle x-ray patterns of APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl taken from a  $w_s = 0.1$  molal sample ( $T_{IN} = 304$  K,  $T_{NL} = 295$  K) in the nematic phase just below  $T_{IN}$  (a) and in the middle of the phase stability region ( $T = 300$  K) (b). Arrows show second-order reflections.

transformation, the pattern is elliptical in shape [Fig. 2(a)], characteristic of the classical pattern for a nematic phase of disk micelles [8]. However, the pattern evolves with decreasing temperature. The first-order reflections, the strongest ones (Bragg peaks), seen in Fig. 2(b), are characteristically more diffuse than the Bragg peaks observed in the micellar lamellar phase but sharper than those observed for the high temperature limit of the nematic phase. In addition, the second-order reflections appear. Both of these features are indicative of the onset in the nematic phase of long range positional order. It should be noted that the same long range pseudolamellar type order in the nematic phase was observed earlier in APFO/D<sub>2</sub>O [7] and CsPFO/D<sub>2</sub>O [9] lyotropic systems.

The micellar orientational order parameter  $S$  calculations were made using the NMR quadrupolar splittings measurements in labeled water combined with x-ray data and electrical conductivity. The variation of  $S$  for different salt concentrations has been calculated and the results plotted in Fig. 3 as a function of the relative temperature  $T/T_c$ , where  $T_c$  is the high temperature stability limit of the nematic phase

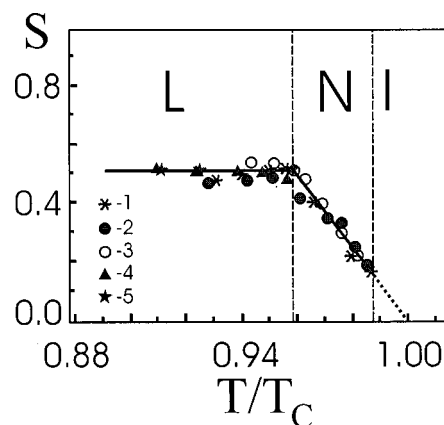


FIG. 3. Temperature dependence of the orientational micellar order parameter  $S$ . Straight lines are least-squares fits to the data points. Salt concentrations  $w_s$  (in molal) in the samples are 1-0.0, 2-0.5, 3-1.0, 4-2.0, 5-2.5.

found as an extrapolation of  $S(T)$  line. Three interesting points to note here and to discuss later concern the temperature behavior of the orientational order parameter  $S$ : (i) the dependence of  $S(T)$  in the whole nematic phase region is *linear*, (ii) in the lamellar phase the function  $S(T)$  is temperature *independent*, i.e.,  $S(T) = S_0 = \text{const}$ , and (iii) the *saturation value* of  $S_0$  in the lamellar phase is not related to the predictions of existing theories for a layer (smectic) state.

In order to consistently explain different experimental results obtained for binary APFO/D<sub>2</sub>O and ternary APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl systems, let us consider phase transition from an isotropic to a layered state within the framework of a phenomenological approach.

### III. PHENOMENOLOGICAL THEORY OF ONE-DIMENSIONAL SEGREGATION

#### A. Stable anisotropic states

As a starting point, let us derive some general conclusions independent of model approximations concerning an ordered lyotropic system. The corresponding phenomenological approach describing the formation of segregated lyotropic mesophases from the isotropic solution has recently been proposed [10]. It allows us to work out the phase diagrams associated with transformations from the isotropic to segregated states and also to consider variations of related physical parameters.

The symmetry group of the isotropic solution is the extended Euclidean group  $\tilde{E}_3$ , which is a semidirect product of continuous three-dimensional (3D) translational group  $R_3$ , and the orthogonal group  $O(3)$  consisting of all continuous proper and improper rotations in the 3D space [11]. We consider the segregation-type transformation that appears as initial density distribution  $\rho_0(\mathbf{r}) = \text{const}$  to be modulated periodically with undulation function  $\delta\rho(\mathbf{r}) = \rho_d(r) - \rho_0(r)$ . This periodic deviation of density  $\delta\rho$  can be expanded using  $\Phi_{k_j}^m(\mathbf{r})$  basis functions of a relevant irreducible representation (IR) of the  $\tilde{E}_3$  group:

$$\delta\rho(\mathbf{r}) = \sum_{k_j, m} \eta_{k_j}^m \Phi_{k_j}^m(r), \quad (1)$$

where  $\eta_{k_j}^m$  are the *order parameter* (OP) components and  $\mathbf{k}_j$  are the reciprocal space vectors. The functions  $\Phi_{k_j}^m(\mathbf{r})$  span infinite-dimensional irreducible representations (IRs) of the  $\tilde{E}_3$  group; these IRs will hereafter be denoted  $D^{m, k_j}$ . In order to construct IRs  $D^{m, k_j}$ , a method of induced representation can be used in which irreducible representations (small representations) of the invariant point group  $G_{k_j} = C_{\infty v}$  of the  $\mathbf{k}_j$  vector that is isomorphous to the  $SO(2)$  group induce IRs in the  $\tilde{E}_3$  space group [11].

The order parameter components for the transition from an isotropic state to a 1D periodic state transform in the same way as basis functions of  $D^{0, k_j}$ . This results from the fact that the ‘‘unit cell’’ of the parent isotropic state is reduced to a *single subunit* (molecular or micellar center of mass) which is invariant under all symmetry operations of the  $\tilde{E}_3$  group. Since the ordering process can be fully specified by the *sca-*

*lar* parameter, which is a probability density variation, and due to the invariance of the structure just mentioned, the  $\{\eta^{m, k_j}\}$  necessarily transforms into the IR denoted  $D^{0, k_j}$ .

In order to determine the stable anisotropic phases, one needs to minimize the variational free energy (Landau potential)  $F(T, p, \eta_{k_j}^m)$  with respect to the OP components:

$$\frac{\partial F(T, p, \eta_{k_j}^m)}{\partial \eta_{k_j}^m} = 0. \quad (2)$$

Despite the infinite number of equations in (2), the problem can be solved geometrically in the order-parameter space  $\varepsilon$  for which the set of OP components  $\{\eta_{k_j}^m\}$  forms the basis [12]. The  $\delta\rho$  variation of probability density associated with a phase transition can be considered as a vector in the  $\varepsilon$  space, and the components of the  $\{\eta^{m, k_j}\}$  vector are the values of the OP that minimize the thermodynamic potential. Minimization conditions (2) determine in  $\varepsilon$  space  $\{\eta_{k_j}^{e, q}\}$  *stationary vectors* that are invariant with respect to different subgroups of the OP symmetry group, formed by the matrices of the relevant IR.

Matrices of the relevant  $D^{0, k_j}$  IR corresponding to the rotation subgroup of the  $\tilde{E}_3$  group are unity matrices permuting the arms of the  $\{\mathbf{k}_j\}$  vector star. Matrices corresponding to the elements of the translation subgroup are diagonal; the elements of these matrices are exponentials  $\exp(i\mathbf{k}_j \mathbf{a}_j)$ . One can see that for the 1D-periodic anisotropic phase with the critical  $\mathbf{k}_j$  vector and periodicity  $|\mathbf{a}_j| = |\mathbf{k}_j|^{-1}$ , the stationary vector in OP space has only two nonzero components,  $\eta_{k_j}$  and  $\eta_{-k_j}$ , since only for these OP components are the corresponding exponential multipliers equal to unity ( $\exp\{i\mathbf{k}_j \mathbf{a}_j\} = 1$ ). Among the matrices associated with rotation elements only those belonging to the group of the  $\mathbf{k}_j^0$  vector, by definition, have such vector invariance. Finally, the symmetry group of this phase is  $G_d = D_{\infty h}$  as with the lamellar and smectic phases. Space inversion permutes  $\mathbf{k}_j$  and  $-\mathbf{k}_j$  vectors, which results in the equality  $\eta_{k_j} = \eta_{-k_j}$  for OP components.

It has been shown for the segregation process that a variational free-energy  $F(T, p, \eta_{k_j}^0)$  expansion in the  $\{\eta_{k_j}^0\}$  components contains invariant polynomials of all degrees, excluding the linear one [10]. In particular, the cubic invariant is present and in a segregating system a second-order phase transition is possible only at an *isolated point* of the phase diagram (Landau point).

#### B. Effective order parameter and phase diagram

The thermodynamic model with single-component effective OP can be formulated for the 1D-periodic positional ordering process, taking into account the equilibrium conditions  $\eta^{0, k_z} = \eta^{0, -k_z} \neq 0$ ,  $\eta^{0, k_j} = 0$  ( $j \neq z$ ) found in the preceding section. However, it should be pointed out that the ordinary phenomenological scheme does not include the stable fully segregated state, which is characterized by unit probability that molecules will be inside periodically arranged aggregates and zero probability in interaggregate space. The corresponding variational free energy  $F(T, p, \eta)$

has no minima for a state with OP, independent of the thermodynamical parameters. Thus, the Landau-type theory in its classical form is applicable to the *initial stages* of a segregation process, where OP varies from zero to unity but does not reach the latter ( $0 \leq \eta < 1$ ). The probability that amphiphilic molecules will be in the interlayer space is still nonzero, i.e., this theory is sufficient to consider only transformation from the isotropic state to a periodic *bicontinuous* one.

In order to include the full segregation regime corresponding to the limit situation  $\eta = 1$ , a nonlinear form for the OP must be used [10,12]. Thus,

$$\eta = \eta_0 \sin \frac{\pi}{2} \xi, \quad (3)$$

where  $\eta$  is a phenomenological OP, that is, a *deviation of averaged probability* that molecules will occupy periodically distributed volumes, and  $\xi$  is a normalized *variation of population* by molecules of the same volume.

Due to the existence of a tricritical point on the nematic-to-lamellar phase transition line, found experimentally [Fig. 1(a)], one needs to use at least a sixth degree effective order-parameter expansion:

$$F_1(T, p, \eta) = a_1 \eta^2 + a_2 \eta^3 + a_3 \eta^4 + a_4 \eta^5 + a_5 \eta^6. \quad (4)$$

Here the effective OP has the form of Eq. (3) and the temperature dependence is assumed to be  $a_1 = a_{10}(T - T_c)$  ( $a_{10} > 0$ ). The minimization of  $F_1$  with respect to the actual variational parameter  $\xi$  is expressed by  $\partial F_1 / \partial \xi = (\partial F_1 / \partial \eta)(\partial \eta / \partial \xi)$ , which yields the equation of state

$$\eta \eta' \{2a_1 + 3a_2 \eta + 4a_3 \eta^2 + 5a_4 \eta^3 + 6a_5 \eta^4\} = 0. \quad (5)$$

In addition to the isotropic solution  $\langle I \rangle$  ( $\eta = 0$ ), Eq. (5) allows two types of low symmetry stable states: (i) the Landau state  $\langle N \rangle$ , corresponding to the standard minimization of  $F_1$  with respect to the OP  $\eta$ , which has values between 0 and 1 (a partially segregated state), and (ii) the limit state  $\langle L \rangle$ , given by  $\eta' = 0$ , corresponding to the fixed values  $\xi = \pm 1$  and  $\eta = \pm 1$ . This one coincides with a fully segregated lamellar state.

Figure 4 shows equilibrium phase diagrams of the model (4) for different signs of coefficient  $a_3$  in the plane of thermodynamic parameters ( $a_1, a_2$ ). Since the Landau potential (4) contains odd-degree invariants, the corresponding phase diagrams are symmetric with respect to  $a_2$  or, equivalently, with respect to the change in the sign of  $\eta$ , and only the half plane is displayed. The second-order topological phase transition line

$$2a_1 + 3a_2 + 4a_3 + 5a_4 + 6a_5 = 0 \quad (6)$$

separates the Landau phase and limit phase stability regions. For  $a_3 < 0$  [Fig. 4(b)] this line crosses over the first-order transition line

$$\begin{aligned} a_1 - a_2 + a_3 \eta - a_4 \eta^2 + a_5 \eta^3 &= 0, \\ 2a_1 + 3a_2 \eta + 4a_3 \eta^2 + 5a_4 \eta^3 + 6a_5 \eta^4 &= 0 \end{aligned} \quad (7)$$

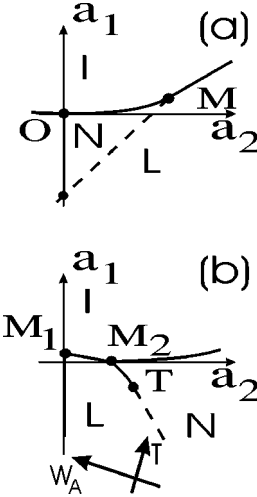


FIG. 4. Phase diagrams of the model Eq. (4) for  $a_3 > 0$  (a) and  $a_3 < 0$  (b). Full and dashed lines represent first-order and second-order transition lines.  $M$ ,  $M_1$ , and  $M_2$  are three-phase points.  $N$  is the triple point.  $T$  is the tricritical point. The orientation of the temperature-amphiphile concentration axes as compared with Fig. 1(a) is shown schematically.

at the *tricritical point*  $T(a_1^T = 7a_3 + 9a_5; a_2^T = 6a_3 - a_4 + 8a_5)$ . The first-order transition line between the  $\langle I \rangle$  and  $\langle N \rangle$  phases

$$\begin{aligned} a_1 + a_2 \eta + a_3 \eta^2 + a_4 \eta^3 + a_5 \eta^4 &= 0 \\ 2a_1 + 3a_2 \eta + 4a_3 \eta^2 + 5a_4 \eta^3 + 6a_5 \eta^4 &= 0 \end{aligned} \quad (8)$$

meets, in the three-phase point  $M(M_2)$ , the line of direct first-order transformation from the isotropic to the limit state:

$$a_1 \pm a_2 + a_3 \pm a_4 + a_5 = 0. \quad (9)$$

The diagram for  $a_3 > 0$  [Fig. 4(a)] has no topological difference from the diagram of the fourth-degree model (see, for example, [12]), but the negative sign of  $a_3$  results in an essential change in the topology. Besides the change in the location of the stability regions, which one can see in Figs. 4(a) and 4(b), both first- and second-order regimes separated by the *tricritical point* exist for the Landau-to-limit-state phase transition. One can see obvious similarity between the theoretical phase diagram of Fig. 4(b) and the experimentally elaborated diagram shown in Fig. 1(a) when comparing the Landau phase to the one experimentally assigned as nematic and considering the non-Landau limit state as the lamellar phase. Moreover, the preceding information enables one to estimate *quantitatively* the high order Landau coefficients for the model potential (4). To reach this goal, one can use special point coordinates in the phase diagram. Precise determination of parameters for a model potential would require a self-consistent procedure that employs, in addition, experimentally established equations of transition lines. This is not possible for all systems. For example, it cannot be done for APFO/D<sub>2</sub>O because instead of clear first-order transition *lines* two-phase *bands* are mapped in the phase diagram (see Fig. 1 and [7]). The location of the phase coexistence region is indicative of first-order transition, but precise information about the transition temperature is missing. However, one can estimate order of magnitude for Landau expansion coef-



ficients by comparing experimentally determined positions of special points and the same positions predicted by theory. The expressions for coordinates of the tricritical  $T$  point have been calculated above. The three-phase  $M_2$  point is an intersection point of the  $I$ - $L$  first-order transition line and  $a_2$  axis, and one can find its coordinates from Eq. (9): ( $a_1^{M_2}=0, a_2^{M_2} = -a_3 - a_4 - a_5$ ). Making use of standard linear relations between thermodynamic variables (temperature and concentration) and lower-order Landau coefficients  $a_i = a_{i0}(T - T_c) + b_{i0}w_A$ , one can derive, for the temperature projections of the coefficients, the following values:  $a_3 \approx -2.5$  K,  $a_4 \approx -330$  K,  $a_5 \approx -1.5$  K. Completely in accordance with the above-made assumption, the  $a_3$  coefficient derived from the experimental data is negative. Since the type of phase diagram was shown above to depend critically on the sign of  $a_3$ , such a correlation of results supports the model we are considering. It is also interesting to note the negativity of the highest order  $a_5$  coefficient. In the framework of the traditional Landau approach to phase transitions, the positivity of the coefficient of the highest degree invariant, in the thermodynamic potential, insures the global stability of phases and the convexity of the potential for large values of the order parameter. However, in the model under consideration, Eq. (3) shows that the magnitude of the order parameter cannot be arbitrarily large, and it raises the possibility of global stable phase diagrams even for negative values of the highest-degree term coefficients [12].

### C. Secondary order parameters

In the preceding section, we worked out the phase diagram that is entirely determined by the *symmetry characteristics* of the *primary* (critical) transition mechanism, that is, segregation of amphiphilic molecules and solvent. However, in a real system, coupling between critical and *noncritical* degrees of freedom also exists. These are termed *secondary order parameters* [12,13]. *Improper* coupling between primary and secondary OPs *does not change* the symmetry characteristics of the transitions, but induces specific anomalies in the physical properties, which can be used to identify and distinguish primary and secondary transition mechanisms.

Let us consider improper coupling between the primary segregation OP and a secondary macroscopic one. The lowest degree coupling invariant has the form  $\eta_i^2 X_j$  and the symmetry of induced (secondary) OPs  $\{X_j\}$  can be found by decomposing the symmetrized second power of IR spanned by the primary OP components  $\{\eta_j\}$  [12,13]. For the relevant IR,  $D_+^{0,k_j}$ , we have

$$[D_+^{0,k_j}]^2 = D_+^0 + D_+^1 + D_+^2 + D_+^3 + \dots + \{D_+^{m,(k_j+k_j')} + \dots\}, \quad (10)$$

where  $D_+^l$  are the IRs of the  $O(3)$  point group, and the IRs in parentheses are related to the second harmonics of undulation function  $\delta\rho$ . The mechanism corresponding to the totally symmetric IR,  $D_+^0$ , is responsible for the micelle volume variation (the associated function is the trace of a symmetrical second-rank tensor).  $D_+^1$  is a pseudovectorial IR and the corresponding mechanism results in ferromagnetic-type ordering that has meaning only for amphiphilic mol-

ecules possessing diamagnetic properties. The components of a symmetrical second-rank tensor form the basis for the  $D_+^2$  IR and at least two mechanisms are related to this IR in lyotropic liquid crystals: (i) the *homogeneous deformation changing the micellar shape* from spherical to uniaxial, or to biaxial; (ii) long-range *orientational nematic-type ordering* [13,14]. Higher rank symmetric tensors spanning IRs  $D_+^3, D_+^4, \dots$ , etc. describe more complex tensorial ordering mechanisms.

Despite the fact that in the following we will treat only nematic-type secondary OPs, general conclusions are applicable to any of the above mechanisms due to similarities in the lowest degree invariants for the relevant IR of the  $O(3)$  group and the correlation of its coupling type with the primary OP.

The full variational free energy  $F(T, p, \eta, S)$ ,

$$F(T, p, \eta, S) = F_1(T, p, \eta) + F_2(S) + F_3(\eta, S), \quad (11)$$

in addition to the primary OP expansion  $F_1(T, p, \eta)$  [see Eq. (4)], contains  $F_2(S)$ , which is a secondary OP noncritical contribution and coupling energy  $F_3(\eta, S)$ . For  $F_2(S)$  we will consider only uniaxial nematic ordering, i.e., a single-component effective nematic OP  $S$ , and restrict, as usual [13], the OP expansion to the second-degree term  $b_1 S^2$ , which allows only isotropic interactions between the nearest micelles in a micellar solution. The lowest degree coupling  $F_3 = c_1 \eta^2 S$  satisfying the symmetry conditions is included in  $F$ . The minimization of  $F$  with respect to  $S$  ( $\partial F / \partial S = 2b_1 S + c_1 \eta^2 = 0$ ) yields, for the nematic OP,

$$S = -\frac{c_1}{2b_1} \eta^2 \propto S_0(T - T_c). \quad (12)$$

Although in the above equation the usual linear approximation for the OP  $\eta^2 \propto a_{10}(T - T_c)$  could be justified *a priori* by a standard argument concerning the smallness of OP, only in a restricted range close to  $T_c$  does this approximation receive *posteriorly* experimental support for the whole range of its variation (see Fig. 3).

For the primary OP expansion, improper contributions modify phenomenological coefficient  $\tilde{a}_2 = 3a_2 + 2c_1 S$  in  $F_1$ , but keep the functional form of Eq. (4). Following the topology of the phase diagrams in Fig. 4, two types of temperature behavior for the secondary nematic OP are possible, depending on the thermodynamic path (position of the  $T$  axis) in the phenomenological phase diagram. For the second-order  $N$ - $L$  phase transition, i.e., for  $a_3 > 0$  [Fig. 4(a)], or for  $a_3 < 0$  but after tricritical point  $T$  [Fig. 4(b)], only a discontinuity in the  $I$ - $N$  transition occurs [Fig. 5(a)]. For  $a_3 < 0$  there are two possible first-order phase transitions,  $I$ - $N$  and  $N$ - $L$ , which result in two jumps of the secondary OP [Fig. 5(b)]. Nevertheless, despite a possible variation in the singularity type for  $I$ - $N$  and  $N$ - $L$  transitions, the predicted temperature dependence of  $S$  within the region of stability of the Landau phase  $N$ , following Eq. (12), is linear.

## IV. TRANSFORMATION MECHANISMS AND PHASE STRUCTURES IN THE APFO/D<sub>2</sub>O LYOTROPIC SYSTEM

The preceding considerations (Sec. III) are based on pure symmetry principles; no data about the mesoscopic structure

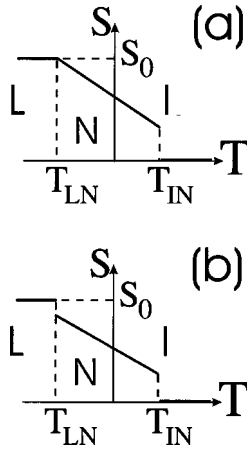


FIG. 5. Temperature dependence of the orientational order parameter  $S$  in the model Eq. (11). (a) Second-order  $N$ - $L$  transition; (b) first-order  $N$ - $L$  transition.

of phases were used. We will now consider the already discussed mechanisms in the APFO/D<sub>2</sub>O system, analyzing the structural aspects of the problem using experimental data previously published or presented in Sec. II. Typically for amphiphilic molecular systems, when a critical micellar concentration (cmc) is achieved the amphiphilic molecules self-assemble into micelles [7]. Such an aggregation process is controlled by chemical factors and does not change the symmetry of the system. Since the isotropic state bordering the anisotropic ones has been found experimentally to be an *isotropic micellar* solution (Fig. 1 and [7]), one can refer to the latter as the parent phase  $\langle I \rangle$ . A partial segregation regime controlled by the primary segregation OP induces, in the Landau state  $\langle N \rangle$ , 1D-periodic undulation of the amphiphilic molecule density. In the system of aggregated molecules, such undulations appear as the *pseudolamellar micellar* structure, a phenomena that has been previously observed in nematic phases of APFO/D<sub>2</sub>O [7] and CsPFO/D<sub>2</sub>O [9] lyotropic systems. This is also confirmed by our SAXS studies to exist in the ternary APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl (Sec. II B). It should be pointed out here that the onset of the pseudolamellar structure in the nematic phase of APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl is reminiscent of the behavior in some thermotropic liquid crystals where *short-range* lamellarlike correlations (so-called cybotactic clusters [15]) were observed. However, the origins of these effects are not correlated. Simultaneously, secondary mechanisms begin to develop. In the case where initial aggregation at cmc has produced micelles of spherical shape, the secondary deformation OP,  $D_+^2$ , reduces its symmetry from isotropic to uniaxial and, thus, discotic or calamitic (depending on the sign of secondary OP) micelles with variable anisometry do exist in the  $\langle N \rangle$  phase. Since the orientational ordering mechanism has the same  $D_+^2$  symmetry (see Sec. III C), simultaneous nematic ordering of uniaxial micelles can be observed in the segregating system. The property indicative of such an orientational ordering process was shown in the preceding section to be the linear temperature dependence of nematic OP (Fig. 5). It should be stressed that the range of variation of  $S$  and the saturation value  $S_0$  for the orientational nematic OP, because of its improper nature, following Eq. (12), is completely determined by the phenomenological parameters  $b_1$  and  $c_1$ . This means that as opposed

to the classical nematic phase,  $S_0$  cannot be predicted to have a special value (see, for example, [2]), but it should be possible to find it experimentally.

The limit segregation regime in the  $\langle L \rangle$  state localizes aggregated amphiphilic molecules inside separated lamellae. In the dilute amphiphilic region of the phase diagram, where the concentration of amphiphilic molecules is not high enough to form classical continuous lamellae, micellar or perforated lamellar structures do exist. Increasing concentration, in combination with chemical factors and surface energy minimization, induces transitions from such a “defective” lamellar structure to the normal continuous one, a process that is not included in the symmetry-based consideration.

## V. CONCLUSIONS

The analogy between the principal mesoscopic structures of thermotropic and lyotropic liquid crystals clearly does not contradict the symmetry fundamentals of phenomenological theory, since the principal predictions of such a theory result from the data about symmetry change and they are independent of the concrete molecular structural organization of the system. However, our results highlight the points that need to be clarified in such analogies. First, chemical factors, important for lyotropic systems, promote aggregation (and segregation) of amphiphilic molecules and *fully segregated* states are realized in these systems. A convenient definition of the lamellar phase as a periodic stacking of molecular bilayers *separated by solvent interlayers* identifies the fully segregated state. The existence of such a state in thermotropic liquid crystals is questionable both from the theoretical point of view, taking into account Landau-Peierls instability [16], and from an experimental point of view due to the fact that the form of density undulation function in the smectic phase is not rectangular but very well described by sinusoidal undulation and higher harmonics contribution is on the order of  $10^{-3}$ – $10^{-4}$  [17]. Apparently, this is predetermined by the condition that it is impossible for thermotropic molecular layers not to keep contact and therefore to be truly spatially separated. The thermotropic smectic- $A$  phase, which should be considered in this case to be *diffusively layered*, corresponds to the intermediate (Landau) partially segregated phase but not to the lyotropic lamellar fully segregated phase. If we identify a mesoscopic phase type on the basis of the transition mechanism, i.e., consider the nematic phase to be induced by purely orientational OP and the smectic phase to be induced by segregation OP, both Landau  $N$  and limit  $L$  phases should be considered as *smectic* phases realized by different segregation regimes. Second, the high aggregative and segregative activity of lyotropic systems can result, as in APFO/D<sub>2</sub>O, in the segregation mechanism becoming dominant and truly primary, controlling the symmetrical and thermodynamical properties of all anisotropic phases. In this case, special attention should be paid to the peculiarities of the orientationally ordered structure, the segregated nature of which can be overlooked, and the lyotropic analog of the classical smectic phase can be mistakenly identified as a pure nematic phase. The nature of the OP temperature variation and the appearance of 1D density modulation are sufficient to identify with certainty the phase type.

In summary, we have reported measurements of the phase diagram and orientational order parameter variation in the ternary APFO/D<sub>2</sub>O/NH<sub>4</sub>Cl lyotropic system. Our data and previously published experimental data have been shown to be consistent with a phenomenological model with an isotropic parent phase, considering the segregation mechanism as primary and inducing orientational ordering of micelles. In particular, the occurrence of a tricritical point on the Landau-

to-limit-phase transition line is associated in our model with a single order parameter.

#### ACKNOWLEDGMENT

We would like to thank T. Taylor for a critical reading of the manuscript.

- 
- [1] K. K. Kobayashi, *Phys. Rev. Lett.* **31**, 125 (1970).  
[2] W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971); **6**, 933 (1972).  
[3] J. Doane, R. S. Parker, B. Cvikl, D. L. Jonhson, and D. L. Fishel, *Phys. Rev. Lett.* **28**, 1694 (1972).  
[4] M. Delaye, R. Ribotta, and G. Durand, *Phys. Rev. Lett.* **31**, 443 (1973).  
[5] P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **21**, 49 (1973).  
[6] R. B. Meyer and T. G. Lubensky, *Phys. Rev. A* **14**, 2307 (1976).  
[7] N. Boden *et al.*, *J. Chem. Phys.* **93**, 9096 (1990).  
[8] J. Charvolin, A. M. Levelut, and E. T. Samulski, *J. Phys. (France) Lett.* **40**, L587 (1979).  
[9] M. C. Holmes, M. C. Leaver, and A. M. Smith, *Langmuir* **11**, 356 (1995).  
[10] V. Dmitriev, P. Tolédano, A. M. Figueiredo Neto, and I. V. Lebedyuk, *Phys. Rev. E* **59**, 771 (1999).  
[11] Wu-Ki Tung, *Group Theory in Physics* (World Scientific, Singapore, 1985).  
[12] P. Tolédano and V. Dmitriev, *Reconstructive Phase Transitions in Crystals and Quasicrystals* (World Scientific, Singapore, 1996).  
[13] J.-C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).  
[14] P.-G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).  
[15] A. de Vries, *Mol. Cryst. Liq. Cryst.* **10**, 31 (1970); **10**, 219 (1970); **11**, 361 (1970).  
[16] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980), Vol. 1.  
[17] J. Als-Nielsen *et al.*, *Phys. Rev. Lett.* **39**, 1668 (1977).