Nonuniversal Critical Behavior at the Uniaxial-Biaxial Nematic Phase Transition in a Lyotropic Mixture

L. T. Thieghi, S. M. Shibli, A. M. Figueiredo Neto, V. P. Dmitriev,* and P. Tolédano[†]

Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315-970, São Paulo, SP, Brazil
(Received 4 August 1997)

Measurements of the order-parameter critical exponent β at the uniaxial-biaxial nematic phase transition in a lyotropic mixture are reported. They reveal a strong dependence of β on the concentration of the mixture compounds with two distinct intervals of values separated by a discontinuity. This nonuniversal behavior is interpreted as the result of three different contributions, which express the micellar biaxiality and the distribution of the micellar population with respect to biaxiality and volume. [S0031-9007(98)05806-2]

In the spirit of the renormalization group theory of critical points [1] it is generally believed that the asymptotic critical behavior of any non-ionic fluid binary mixture should belong to the same universality class as ferromagnets and pure fluids, irrespective of the self-association properties of the molecular aggregates forming the solute, or of the specific solute-solvent interactions. In contrast to this view, Corti, Degiorgio and co-workers [2] reported measurements in binary lyotropic mixtures of water and non-ionic surfactants, showing continuously variable critical exponents γ (susceptibility) and ν (correlation length), depending partly on the size of the micelles, and more essentially on the solvent-micelles interactions. Experimental evidence of nonuniversal values for γ and ν was also obtained by Bellocq *et al.* [3] for a four-component microemulsion. The measurements of Corti *et al.* [2] on $C_{12}E_8$ (dodecyloctaoxyethilene glycol monoether) in H_2O and D_2O, were repeated by Dietler and Cannell [4] who found 3D Ising exponent values, consistent with current theory and universality. Further works [5] generally concluded that universality was not violated in non-ionic micellar fluids, but corrections to scaling could be necessary.

In this Letter we report experimental results of the order-parameter critical exponent β at the uniaxial-biaxial nematic phase transition in a lyotropic mixture, which bring support to the idea of nonuniversality for the critical behavior of micellar liquid crystals of non-ionic surfactants. However, at variance with the conclusion of Corti *et al.* [2], our results show a strong dependence of β on the *form* and *volume* of the micelles. Furthermore, while the preceding authors, as well as Bellocq *et al.* [3], found critical values of γ and ν *below* the mean-field behavior, we find that β takes values *below or above* the mean-field prediction depending on the location of the critical point on the transition line. This crossover is explained in the framework of a phenomenological model recently proposed for describing the phase diagram of lyotropic nematics [6,7].

In 1980 Yu and Saupe [8] reported the first experimental phase diagram of a lyotropic liquid crystal which

presents three nematic phases. The mixture investigated was potassium laurate, decanol, and water (D_2O). Three distinct nematic phases are stabilized: two uniaxial (denoted N_D and N_c) and one biaxial (N_B), which merge at a four-phase "Landau" point with the high-temperature isotropic phase (ISO 1). Another reentrant isotropic phase (ISO 2) takes place at lower temperature. From x-ray and neutron diffraction measurements the N_D and N_c uniaxial nematic phases have been first analyzed [9] to be made, respectively, of oblate and prolate micellar aggregates dispersed in water. Further measurements [10] revealed a more subtle scheme.

(i) In the three nematic phases it was shown that within a large interval of temperature and concentration, the micelles mainly preserve their biaxial symmetry, and have on average the form of curved platelets of dimensions $1 \times 2 \times 3$ (e.g., $26 \times 55 \times 85$ Å in $KL/DeOH/D_2O$). Therefore, the differentiation between the phases was shown to be the macroscopic consequence of different orientational spatial fluctuations of the platelets.

(ii) One has a continuous decrease of the micellar shape anisotropy and orientational order when the temperature is lowered from approximately the middle of the nematic region to the ISO 2 phase. This decrease also occurs on the left- and right-hand limits of the nematic region. The change in shape of the micelles from curved platelets to flattened spheres is clearly apparent when approaching the ISO 2 phase or close to the stability limits of the biaxial phase.

A theoretical model of the phase diagram of lyotropic liquid crystals in which the three nematic phases are present was proposed [6,7], relating the observed modification of the micellar shape to the onset of the low-temperature ISO 2 phase, and to the typical dependence on concentration and temperature of the N_D-N_B and N_B-N_c second-order transition lines. In this model, the ordering and deformation process of the micelles are taken into account using two coupled order parameters [7]: (i) a symmetry-breaking order parameter with two effective components (r, θ), where r and θ have, respectively,

the meaning of the deviation of the micellar form from a sphere ($r = 0$) and from a revolution ellipsoid ($\theta = 0$), and (ii) a nonsymmetry-breaking scalar order parameter τ which represents the distribution of the micellar shape at each temperature and concentration. τ also expresses the change in volume of the micelles is what contributes to the specific shape of the boundaries of the biaxial phase. The effect of τ is to produce a restructuring (a "topological metamorphosis" [6,7]) of the phase diagram consisting in a symmetric folding of the phases and of the singularities.

Using the notations of Ref. [7] [Eq. (10)] one can write the thermodynamic potential associated with the phase diagrams of the lyotropic mixtures which present the three nematic phases as

$$F(r, \theta, \tau) = \tilde{\alpha}\tau + \tilde{\beta}\tau^2 + \tilde{\gamma}r^2 + \tilde{\delta}r^3 \cos 3\theta$$
$$+ \tilde{\mu}r^4 + \tilde{\nu}r^6 \cos^2 3\theta$$
$$+ \tilde{\lambda}r^2\tau + \ldots \tag{1}$$

where $\tilde{\alpha}$, $\tilde{\beta}$, $\tilde{\gamma}$, $\tilde{\delta}$, $\tilde{\mu}$, $\tilde{\nu}$, and $\tilde{\lambda}$ are phenomenological coefficients depending on the number n_0 of micelles per unit volume [7]. Minimization of F with respect to r, θ, and τ give the equations of state of the system. Introducing the condition $\cos \theta = \pm 1$ which defines the boundaries of the biaxial phase, one gets the equations of the N_D-N_B and N_c-N_B second-order transition lines:

$$\tilde{\alpha} + 2\tilde{\beta}\tau + \tilde{\lambda}r^2 = 0 \tag{2}$$

and

$$2\tilde{\gamma} \pm 3\tilde{\delta}r + 4\tilde{\mu}r^2 + 6\tilde{\nu}r^4 + 2\tilde{\lambda}\tau = 0. \tag{3}$$

One can calculate from Eqs. (2) and (3) the critical behavior of the order parameters τ, r, and (r, θ) across, let us say, the N_D-N_B transition in the three directions $\tilde{\alpha}(\tilde{\gamma} = \tilde{\delta} = 0)$, $\tilde{\gamma}(\tilde{\alpha} = \tilde{\delta} = 0)$, and $\tilde{\delta}(\tilde{\alpha} = \tilde{\gamma} = 0)$. Assuming the usual linear dependence of these coefficients on $(T - T_c)$, where T_c is the critical temperature at the preceding transition, one finds

$$\tau \simeq -\frac{\tilde{\alpha}}{2\tilde{\beta}} = \tau_0(T_c - T),$$

$$r \simeq \left(\frac{-\tilde{\gamma}}{2\tilde{\mu}}\right)^{1/2} = a_0(T_c - T)^{1/2},$$

and $r_\theta \simeq \left(\frac{-\tilde{\delta}}{2\tilde{\nu}}\right)^{1/3} = b_0(T_c - T)^{1/3}, \tag{4}$

where τ_0, a_0, and b_0 are positive constants.

Accordingly, the value of the β exponent across the N_D-N_B transition is governed by the values of *three* different exponents: $\beta_{r,\theta} = \frac{1}{3}$, $\beta_r = \frac{1}{2}$, and $\beta_\tau = 1$, which represent three extreme tendencies associated with the respective influence of the three components of the (reducible) order parameter (r, θ, τ). For a given thermodynamic path corresponding to a curve on the N_D-N_B transition line, the actual critical value of the β expo-

nent will reflect the mixed influence of the r, θ, and τ variables, and will therefore take intermediate values between the preceding three numbers. At the experimental level the β exponent of the physical order parameter of lyotropics, obtained from birefringence measurements in a temperature-concentration phase diagram, *will also vary between these numbers as a function of the molecular concentrations of the mixture*.

In order to verify this theoretical scheme, we have undertaken interferometric measurements of the β exponent along the N_D-N_B second-order transition line in a mixture of potassium laurate/1-decanol/water (KL/DeOH/H$_2$O) with a fixed content in DeOH (7.10 wt %). Figure 1(a) shows the experimental phase diagram with the ten measured samples corresponding to an increase of water content from 64.50 (in wt %) to 65.31%; i.e., they extend from a region close to the lower-temperature Landau point, to the region where the transition lines limiting the biaxial phase inverse their curvature. A small quantity (less then 1 μg per mℓ of liquid crystal) of a water base ferrofluid has been added to the samples in order to help their orientation in the presence of a weak magnetic field ($B \sim 200$ G). After the mixture achieved a homogeneous state, it is left at rest (at $T \sim 22°$C) for about four days, before the measurements of β are performed.

The samples were encapsulated inside microslides of 0.1 mm thickness, placed in a INSTEC HS1-i hot stage system, and positioned in a Leitz orthoplan-pol microscope. The smallest temperature steps used were 0.01 °C and the temperature was kept constant to about 0.005 °C. The samples were aligned by the combination of a small magnetic field and the walls of the microslide. With this procedure a homogeneous pseudoisotropic texture was obtained in the N_D phase, with the director parallel to the light propagation direction. After the transition to the N_B phase, a homogeneous planar texture was achieved.

The birefringence was measured with a Berek tilt compensator. The experimental setup is presented in detail in Ref. [11]. The magnetic field B is at 45° from the polarizer and the analyzer, in the plane perpendicular to the light propagation direction. Special care was taken to reach an equilibrium state before each measurement. After temperature being changed between each point there was a waiting period of about 20 mn. Four measurements of the birefringence Δn were made at each temperature and a mean value of Δn, adjusted by least-squares statistics, was obtained. Figure 1(b) gives the typical $\log(\Delta n) = f\{\log(T - T_c)/T_c\}$ curves, for three concentrations of water. The experimental results of Δn obtained range from about 0.01 °C to about 0.1 °C from T_c. The errors in Δn present in Fig. 1(b) were calculated from the usual propagation procedure and took into account the reproducibility of the experiment.

From logarithmic plots of the birefringence data as a function of reduced temperature for samples with variable water quantities, we have determined the exponent β
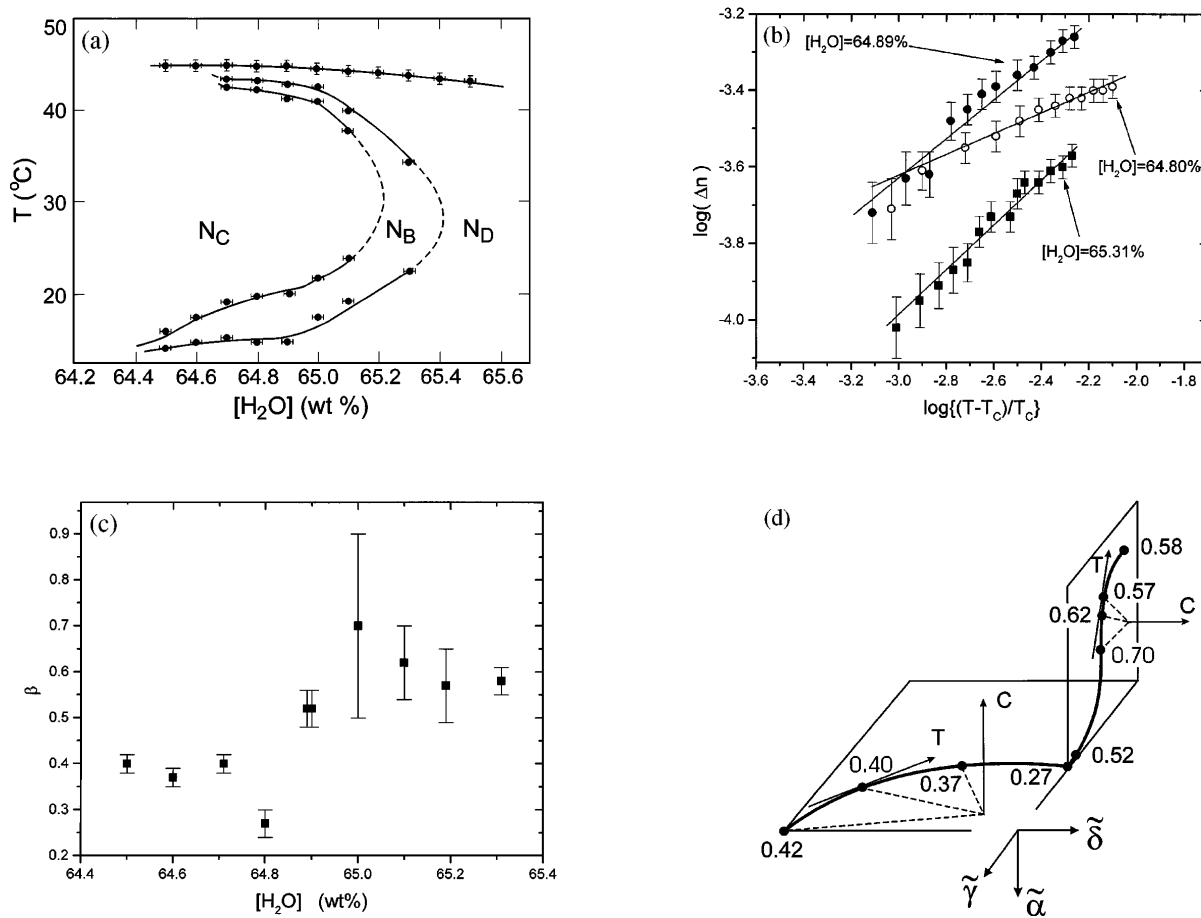
FIG. 1. (a) Experimental phase diagram with the critical points on the N_D-N_B transition line at which the β exponent has been measured. [H_2O] represents the concentration of water in the mixture (KL/DeOH/H_2O) with [DeOH] = 7.10%. The solid and dashed lines are only guides for the eyes. (b) Typical dependence of $\log(\Delta n)$ on $\log\{(T - T_c)/T_c\}$ for three concentrations listed in Table I (first column). The solid lines are the best fits obtained with a least-squares statistics. (c) Variation of β as a function of [H_2O]. (d) Theoretical curve showing the thermodynamic path followed in the experiment in the $(\tilde{\alpha}, \tilde{\gamma}, \tilde{\delta})$ space. The measured values of β are indicated on the curve (here, $c = $ [H_2O]).

and T_c, by means of a least-squares statistics, for each sample. Table I and Fig. 1(c) summarize the values obtained for β. The errors in β present in Table I were obtained taking into account the fit quality *and* the reproducibility of the experiment. The third column of Table I presents the fit quality, defined here as the squared sum of the differences between the experimental value and the calculated value (from the fitting), divided by the number of experimental points used. These values suggest the following comments and interpretation.

(i) Two distinct intervals of values of β can be distinguished: Values between 0.27 and 0.40 (region I) are measured for the lower concentrations of water and correspond to a narrow width of stability in temperature for the N_B phase. Values comprised between 0.52 and 0.7 (region II) are obtained for the larger concentrations of water where the biaxial region is enlarged. A discontinuity appears between the two regions.

(ii) In the framework of our approach the influence of the order parameter τ seems to be negligible in region I,

where the measured β exponents take values below 0.40, and are thus principally determined by the (r, θ) order parameter. In contrast, in region II the influence of τ becomes predominant, with values of β above 0.52. In our interpretation it expresses the fact that the population of micelles having a strong biaxiality is in minority in region I, whereas it dominates in region II. This is consistent with the large increase in the width in temperature of the N_B phase in region II, shown in the temperature-concentration phase diagram of Fig. 1(a). The influence of the volumetric change of the micelles can be less easily distinguished in the two regions. The discontinuity observed in the measured values of β for water concentrations between 64.8% and 64.9% reflects a sharp crossover between the two regimes.

Figure 1(d) shows the thermodynamic path followed in the experiment, in the $(\tilde{\alpha}, \tilde{\gamma}, \tilde{\delta})$ space. In region I the thermodynamic path almost remains in the $(\tilde{\gamma}, \tilde{\delta})$ plane. Between 64.5% and 64.8% of water content β decreases continuously deviating from the bisector of

TABLE I.   Measured values of β (second column) for ten different concentrations of water (in weight percent) (first column) at the uniaxial(N_D)-biaxial(N_B) nematic phase transition. The third column present the fit quality defined in the text.

[H_2O] (wt %)	β	Fit quality
64.5	0.40 ± 0.02	1.4×10^{-4}
64.6	0.37 ± 0.02	0.7×10^{-4}
64.71	0.40 ± 0.02	2.8×10^{-4}
64.80	0.27 ± 0.03	3.3×10^{-4}
64.89	0.52 ± 0.04	7.4×10^{-4}
64.90	0.52 ± 0.04	10×10^{-4}
65.00	0.7 ± 0.2	70×10^{-4}
65.10	0.62 ± 0.08	24×10^{-4}
65.19	0.57 ± 0.08	25×10^{-4}
65.31	0.58 ± 0.03	4.7×10^{-4}

this plane versus the $\tilde{\delta}$ axis, and goes *below* the limit theoretical value $\beta_{r,\theta} = \frac{1}{3}$. Above 64.9% one has a drastic reorientation of the concentration axis with respect to the fixed theoretical axes. The maximal experimental value $\beta = 0.7$ is reached for a water concentration of 65%, then β decreases to 0.58 close to the $\tilde{\gamma}$ axis, when the limit of stability of the N_B phase is approached. In Fig. 1 the thermodynamic path is constructed as to be always tangent to the temperature axis.

(iii) Previous measurements of the β exponent at the N_D-N_B transition [12] found values comprised between 0.35 and 0.38. This was interpreted as a confirmation of the 3D-XY model, close to the theoretical number $\beta = 0.346$ predicted by the renormalization group approach [13]. Following our results such values of β can be found in a narrow region of the N_D-N_B transition line, between 64.6% and 64.7% water content. When exploring a larger portion of the N_D-N_B line in a mixture of KL/DeOH/water, doped with a few percent of the poly-ethylene-glycol polymer, values of β comprised between 0.38 and 0.53 were found [14].

In summary, we have reported measurements of the β exponent along the uniaxial-biaxial lyotropic nematic transition, which reveal a strong dependence of β on the concentrations of the molecules of the mixture, and two distinct intervals of values separated by a discontinuity. These measurements have been interpreted in the framework of a phenomenological model describing the phase diagram of lyotropic nematics [6,7]. This model allows us to relate the measured values of β to three different contributions expressing the biaxiality of the micelles and the evolution of the distribution of the micellar population with respect to biaxiality and volume.

The nonuniversal behavior reflected by our experimental data does not contradict the previous measurements confirming a 3D-XY regime [12], but exploring only a narrow region of the N_D-N_B transition line. The possibility that our measurements should correspond to a noncritical regime is not excluded although the same precision

($\sim$0.01 K close to the critical line) as in the previous experiments was realized. Furthermore, the strong deviations below *and* above mean-field values, which have been found with a very good reproducibility, would remain to be explained. The fact that β reaches values ($\beta = 0.27$) which are *below* the lowest theoretical limit ($\beta_{r\theta} = \frac{1}{3}$) shows that corrections to the numbers deduced from our model are necessary. A more surprising result is the *increase* of β when getting closer to the Landau point, in contrast to the *decrease* usually expected when approaching this point.

Various measurements are required to confirm our results and their interpretation. Measurement of the β exponent along the *upper N_D-N_B* transition line should, *a priori,* provide analogous results, since the model of Refs. [6] and [7] predicts a symmetric situation for the upper and lower parts of the phase diagram. Measurements of the critical exponents γ and ν should also give values depending on the micellar concentration, and varying between limits which can be calculated from the model.

*On leave from the University of Rostov on the Don, Rostov on Don, Russia.

†On leave from the University of Amiens, Amiens, France.

[1] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University, London, 1971).

[2] M. Corti and V. Degiorgio, Phys. Rev. Lett. **55**, 2005 (1985).

[3] A. M. Bellocq, P. Honorat, and D. Roux, J. Phys. (Paris) **46**, 743 (1985).

[4] G. Dietler and D. S. Cannell, Phys. Rev. Lett. **60**, 1852 (1988).

[5] G. Martínez-Mekler *et al.,* in *Phase Transitions in Soft Condensed Matter,* edited by T. Riste and D. Sherrington (Plenum, New York, 1989), p. 211, and references therein.

[6] P. Tolédano and A. M. Figueiredo Neto, Phys. Rev. Lett. **73**, 2216 (1994).

[7] P. Tolédano *et al.,* Phys. Rev. E **52**, 5040 (1995).

[8] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).

[9] J. Charvolin, A. M. Levelut, and E. Samulski, J. Phys. (Paris), Lett. **40**, L587 (1979).

[10] Y. Galerne, A. M. Figueiredo Neto, and L. Liebert, J. Chem. Phys. **87**, 1851 (1987); A. M. Figueiredo Neto *et al.,* J. Phys. (Paris), Lett. **46**, L499 (1985).

[11] Z. A. de Sant'Ana and A. M. Figueiredo Neto, Phys. Rev. A **46**, 7630 (1992).

[12] P. Boonbrahn and A. Saupe, J. Chem. Phys. **81**, 2076 (1984); G. Melnik, P. J. Photinos, and A. Saupe, J. Chem. Phys. **88**, 4046 (1988); Ref. [11].

[13] E. Brézin and J. Zinn-Justin, Phys. Rev. Lett. **36**, 691 (1976).

[14] S. M. Shibli and A. M. Figueiredo Neto, Mol. Cryst. Liq. Cryst. **260**, 623 (1995).