Interpretation of density and conductivity measurements in the liquid-crystal phases of the cesium pentadecafluorooctanoate-water system and its implication for the structure of the lamellar phase

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It has recently been argued [P. Photinos and A. Saupe, Phys. Rev. A 41, 954 (1990)], on the basis of density measurements (as measured by a vibrating densitometer) and the observation of long relaxation times in both these and electrical conductivity measurements, that the nematic-to-lamellar transition in the cesium pentadecafluorooctanoate(CsPFO)-water system involves a significant change in the aggregate structure, probably a transformation from discotic (disk-shaped) micelles to continuous lamellae. With a view to distingushing between these conclusions and previous ones, by the present authors [N. Boden et al., J. Phys. (Paris) 47, 2135 (1986)], which suggested the transition solely involves the onset of translational order without significant changes in micellar structure, we have made a comparison of the densities of a CsPFO- 2 H₂O (w = 0.406) sample as measured by both a vibrating densitometer and a classical dilatometer. The densitometer measurements exhibit discontinuities at both the isotropic-tonematic and the nematic-to-lamellar transitions: at the isotropic-to-nematic transition, the specific volume increases by 7×10^{-5} cm³ g⁻¹ of solution, a result at variance with a predicted decrease of 1×10^{-7} cm³ g⁻¹ as calculated from the previously reported pressure dependence of the isotropic-tonematic transition temperature [M. R. Fisch, S. Kumar, and J. D. Litster, Phys. Rev. Lett. 57, 2830 (1986)]; a large increase in specific volume is also observed at the nematic-to-lamellar transition. No such changes are, however, detectable in the dilatometer experiments. This has led us to conclude that the excess specific volumes characterizing the nematic and lamellar phases in the densitometer experiments must be associated with some nonequilibrium state of the sample, induced by the vibration of the sample container. These effects are specific to the liquid-crystal phases, not to the isotropic solution phase, and must therefore arise because of the long-range structural organization of the former. It appears that the vibrating densitometer cannot be used to measure densities of amphiphilic liquid-crystal phases. Hysteresis and long relaxation times observed in electrical conductivity measurements in the lamellar phase are associated with partial focal conic textures; they do not arise from changes in aggregate structure.

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I. INTRODUCTION

At low concentrations, water-soluble surfactants undergo reversible self-assembly into typically small spherical micelles whose structure and properties have been studied for over 70 years. Attention is now shifting to studies at higher concentrations, where micelles may become nonspherical and intermicellar forces become important. For nonspherical micelles, transitions to uniaxial and, in some cases, biaxial nematic states are observed when the volume fraction of surfactant $\phi \approx a/b$, a and b being, respectively, the lengths of the minor and major axes of the micelle [1]. These micellar liquid crystals are of fundamental interest because of the new opportunities they offer to study the factors which govern-at high concentrations—the size and shapes of micelles and the nature of the forces between them, and the coupling between local self-assembly and larger scale organization. This coupling is little understood, but it could, for example, drastically affect the nature of phase transitions as compared to those encountered in thermotropic liquid crystals. For example, Gelbart and co-workers have described theoretical models [2] which predict that coupling between the size and long-range orientational ordering of the micelles in nematic phases leads to their explosive growth and this drives the transition from N_C nematic phases (canonic micelles) into conjugate hexagonal phases, or from N_D nematic phases (discotic micelles) into conjugate smectic-lamellar phases.

However, x-ray diffraction measurements suggest that for the cesium pentadecafluorooctanoate (CsPFO)-water [3], ammonium pentadecafluorooctanoate (APFO)-water [4], and tetramethylammonium heptadeca-(TMAHFN)-water [5] fluorononanoate systems, the transition from the nematic to the conjugate lamellar phase solely involves the propagation of long-range translational ordering of the discotic micelles along the nematic director, that is, the lamellar phase which is formed is a discotic lamellar phase L_D . These observations are seemingly supported by recent work by Taylor and Herzfeld [6] who have used a hard-particle model to calculate the phase diagram for a system of rodlike surfactants (CsPFO) which self-assemble into polydispersed disk-shaped micelles; this phase diagram is qualitatively similar to those observed for the CsPFO-water [7] and APFO-water [4] systems.

Photinos and Saupe [8], however, have recently argued for a classical bilayer structure for the lamellar phase of the CsPFO-water system. Their argument is based on the observation of hysteresis and associated long (hours to days) relaxation times in density and electrical conductivity measurements in the vicinity of the second-order lamellar-to-nematic transition of a CsPFO-H₂O sample with weight fraction w of CsPFO of 0.41. In contrast, no hysteresis was observed at the nematic-to-isotropic transition. Such long relaxation times are not consistent with a simple rearrangement of micelles into layers at a second-order transition. To explain their observations Photinos and Saupe have, therefore, suggested that significant changes in micellar structure take place at the nematic-to-lamellar transition. In particular, they have suggested that the lamellar phase consists of continuous bilayers and that the long relaxation times reflect the slow approach to an equilibrium distribution of defects following the formation of the phase. Central to the interpretation of the density measurements is the assertion that the packing density of the PFO⁻ anion in a micelle (aggregate) increases with the surface curvature; that is, the packing density is greater in the curved "rim" than in the flat "cap" of the micelle. This notion was invoked to interpret density measurements made with a vibratingtube densitometer: the density versus temperature "curve" reveals decreases in density at the I-to- N_D and N_D -to- L_D transitions. The apparent decrease in density on passing from the isotropic into the nematic phase would be consistent with an increase in the diameter of the micelle as revealed by x-ray diffraction [3,4]. The apparent decrease in density at the nematic-to-lamellar transition has been interpreted as being suggestive of a divergence in the aggregation number, that is, a transition to continuous lamellae. The observed slow approach to the smaller equilibrium density following rapid cooling from the nematic to the lamellar phase would then be in keeping with a slow evolution towards classical bilayers. The interpretation of hysteresis in electrical-conductivity measurements [8] in the vicinity of the lamellar-tonematic transition is more complex due to the formation of focal domains in the lamellar phase; nonetheless, the associated long relaxation times have been attributed to the evolution of the structure of the lamellae.

A signal to the need for an alternative explanation of the density measurements comes from the observation of Fisch, Kumar, and Litster [9] that the isotropic-tonematic transition temperature T_{IN} increases with increasing pressure. (Values of T_{IN} were determined, at fixed pressure, from the break in slope of the lightscattering intensity versus temperature curves as measured on cooling the isotropic phase.) Now, the relation between changes in pressure and T_{IN} is [10]

$$\left[\frac{\partial p}{\partial T_{IN}}\right]_{x_{I}} = \frac{x_{N}(H_{S}^{N} - H_{S}^{I}) + (1 - x_{N})(H_{W}^{N} - H_{W}^{I})}{T\{x_{N}(V_{S}^{N} - V_{S}^{I}) + (1 - x_{N})(V_{W}^{N} - V_{W}^{I})\}},$$
(1)

where the H_i and V_i (with i = S for surfactant or i = Wfor water) are the partial molar enthalpies and volumes, respectively, and x_I and x_N are the mole fractions of surfactant in the coexisting isotropic and nematic phases, respectively. Equation (1) is essentially the Clapeyron equation: $(\partial p / \partial T)_{x_1} = \Delta H / T \Delta V$. As ΔH can only be negative, it follows that ΔV must be negative, too. That is, the density of the nematic phase must be greater than that of the isotropic micellar solution phase. To estimate a value for ΔV for the isotropic-to-nematic transition from the data or $(\partial p / \partial T)_{x_1}$, we have taken for ΔH the value of the heat absorbed at constant composition, a not unreasonable approximation, since the phase transition is very weak [9,11,12]. For a sample with w = 0.41, $(\partial p / \partial T)_{x_I} = 1.9 \times 10^8$ Pa K⁻¹ at 101 kPa [9] and $\Delta H = -6 \times 10^{-3}$ J g⁻¹ of solution [12], leading to $\Delta V = -1 \times 10^{-7}$ cm³ g⁻¹. This is significantly smaller and of opposite sign to the apparent volume change of about $+1 \times 10^{-4}$ cm³g⁻¹ estimated from the Photinos and Saupe data [8,13] for a sample of similar composition. This raises the spectre that the interpretation given by these authors to the density measurements as made with the vibrating-tube densitometer may be equivocal. Indeed, some time ago we also carried out density measurements on the CsPFO-water system and obtained similar results. These were, however, found to be quite different from corresponding measurements we made using a classical dilatometer technique. The results of this study are here reported for the first time together with a new interpretation of the density measurements made using the vibrating-tube densitometer. The nature of the relaxation process which occurs in conductivity measurements is also reexamined. NMR spectroscopy is employed to precisely locate phase-transition temperatures for the actual samples used in the density and conductivity measurements.

II. EXPERIMENTAL METHODS

CsPFO was prepared by neutralizing an aqueous solution of pentadecafluorooctanoic acid (Fluorochem Ltd.) with cesium carbonate. The neutral solution was oven dried at 100 °C and the salt was recrystallized twice from *n*-butanol. Excess solvent was removed by drying under a vacuum for several days. Solutions were made up immediately prior to use and made homogeneous by mixing in the isotropic phase. Phase-transition temperatures were precisely determined from ²H NMR measurements [7] made on aliquots of the samples contained in standard 5-mm o.d. NMR tubes using a JEOL GX270 NMR spectrometer. The temperature of the sample was controlled and measured to within 5 mK using a double-pass-waterflow system [14].

Density measurements were made on Anton-Paar vibrating-tube digital density meter (model DMA 60/602) in which 0.7 cm³ of sample is contained within a 2-mm i.d. U tube. The tube vibrates at a frequency in the range 300 to 400 Hz, depending on its total mass, with a vibrational amplitude at its tip of about 0.1 mm. All solution densities were measured relative to that of pure

water (triply distilled under a nitrogen atmosphere). The calibration constant of the density meter was determined from the known densities of water [15] and air [16]. The reproducibility of an individual density measurement was to better than 3×10^{-6} g cm⁻³. The accuracy of the density meter was checked by determining the densities of some aqueous sodium chloride solutions: the results obtained for solutions in the range 0.1 to 1.0 mol kg⁻¹ differed from literature data [17] by less than 5 ppm. Samples of the isotropic micellar solution phase were introduced into the sample U tube by means of a hypodermic syringe, taking care to avoid the generation of bubbles. The sample temperature was maintained to ± 0.002 K using a water-flow thermostat (Sodev, model CT-L), and a thermistor (calibrated against a quartz thermometer), placed within the glass housing of the U tube, was used to monitor the sample temperature.

The dilatometer consisted of a sample bulb 12 cm in length, with an internal diameter of 1.6 cm, to which a capillary with internal diameter 2 mm and length 12 cm was attached. The height of the capillary column was measured by means of a cathetometer to a precision of 0.001 cm, enabling volume changes of 3×10^{-5} cm³ to be detected. Since the total mass of sample in the dilatometer was 28 g, this corresponds to changes in the specific volume of the order of 1×10^{-6} cm³ g⁻¹. The whole apparatus was enclosed by a thermostatted double-pass water-flow system with temperature control and measurement similar to that used in the NMR experiments [14].

The apparatus for the measurement of electrical conductivities is similar to that described in previous studies [3,18,19]. The sample of volume 3 cm³ is contained in a cylindrical container of internal diameter 1.8 cm. The electric field E is generated by a pair of platinized platinum 10×10 mm² squares placed 10 mm apart. The conductivity cell is mounted vertically between the poles of a Varian V-3603 electromagnet which may be rotated through 360° about the vertical axis of the cell. The nematic director **n** is aligned along the direction of the magnetic field **B** which can be set at any angle ϕ with respect to the direction of E. Conductivities were measured by a Hewlett-Packard HP 4192A impedance analyzer at an operating frequency of 25 kHz. The sample cell is surrounded by a double-pass water-flow jacket and temperature control and measurement was achieved using a system similar to that used for the NMR measurements [14].

III. RESULTS

A. Characterization of phase behavior by ²H NMR of ²H₂O

Phase-transition temperatures were determined by NMR methods [7,20] and are unequivocal. For this purpose we have employed the NMR spectrum for a deuterium spin (I=1) in ²H₂O. This is a simple doublet with quadrupole splitting given by $\Delta \tilde{v} = \frac{3}{2} |\tilde{q}_{zz}|_s S$, where $|\tilde{q}_{zz}|_s$ is determined by the quadrupole-coupling constant for ²H in ²H₂O, sample concentration and the structure of the micelle [7] and S is the nematic order parameter. The variation with temperature of $\Delta \tilde{\nu}$ for the CsPFO-²H₂O (w=0.406) sample on cooling from the isotropic, through the nematic, into the lamellar phase, together with the ²H spectra which characterize the pure and biphasic intervals, is shown in Fig. 1. On cooling from the isotropic micellar solution into the isotropic-nematic biphasic region, a symmetrical doublet from the ${}^{2}H_{2}O$ molecules in the nematic phase is superimposed on the isotropic singlet (S=0) arising from the ²H₂O molecules in the isotropic micellar solution. As cooling continues, the doublet intensity increases at the expense of that of the singlet, consistent with a variation of the relative amounts of the two phases as described by the lever rule. The quadrupole splitting is seen to change little in the mixed-phase region. This is because the value of S is essentially independent of composition along the isotropic-to-nematic transition line. At the lower boundary to the transition T_{NI} , the singlet disappears. Thereafter, in the nematic phase, the doublet splitting increases rapidly at first, then more gradually, reflecting the increase in the nematic order parameter S with decreasing temperature. However, $\Delta \tilde{v}$ will increase more rapidly than S because $|\tilde{q}_{zz}|_s$ also increases as a result of the growth in the diameter of the micelles [7]. At the lower



FIG. 1. Partially averaged ²H quadrupole splittings $\Delta \tilde{v}$ of ²H₂O as observed on cooling a sample of CsPFO-²H₂O (w = 0.406) from the isotropic micellar-solution phase, to the nematic phase, and then from the nematic phase into the lamellar phase, together with the ²H spectra which characterize the pure phases and the isotropic-nematic biphasic interval. Close to the transition, the temperature was changed in decrements of about 20 mK. Following each temperature change, the splittings became constant after about 5 min, but the measurements were taken after waiting a further 5 min to ensure that thermal equilibrium had been established. The discontinuities in the temperature dependence of the quadrupole splittings give T_{NI} and T_{LN} to a precision of ±0.005 K and ±0.01 K, respectively. T_{IN} (=306.25 K) is determined with a precision of ±0.010 K as described in the text.

boundary to the nematic phase T_{LN} , there is a discontinuity in the temperature dependence of $\Delta \tilde{\nu}$, but not in $\Delta \tilde{\nu}$ itself. This means that there is no discontinuity in either $|\tilde{q}_{zz}|_s$ or S at this transition. The former is quite consistent with x-ray measurements, which show that at this transition the micelles in the nematic phase simply condense onto the lamellar planes without any detectable change of their structure or size [3]. The behavior of $\Delta \tilde{\nu}$ solely reflects the variation of S which is characteristic of a second-order nematic-smectic-A-like transition [21].

The phase-transition temperatures T_{NI} and T_{LN} can be obtained with the precision of a few millikelvin as shown in Fig. 1. At low concentrations (w < 0.4), using a magnetic field of 6.3 T, the upper limit to the isotropic-tonematic transition T_{IN} can also be determined with high precision ($\pm 2 \text{ mK}$) from the observation of a discontinuity in the field-induced quadrupole splitting in the isotropic phase signal [11]. At w = 0.406 the magnitude of the splitting is small and the isotropic peak does not resolve into a doublet, but a broadening of the signal can be seen about 30 mK above the temperature at which the nematic doublet is first detected. The actual value of T_{IN} must lie in this 30-mK temperature range and we claim a precision of ± 10 mK in this transition temperature.

B. Densitometer measurements

The temperature dependence of the density of a CsPFO-²H₂O (w = 0.406) sample in the vicinity of the nematic-to-isotropic and lamellar-to-nematic transitions, as measured using the Anton-Parr model DMA 60/602 densitometer, is shown in Fig. 2. The behavior depicted in this figure is similar to that obtained by Photinos and Saupe [8,13] for CsPFO-H₂O (w = 0.41) samples using a Mettler-Parr DMA 60 densitometer, and clearly shows the unexpected increase in volume associated with both the isotropic-to-nematic and nematic-to-lamellar transitions. At the isotropic-to-nematic transition, pretransitional effects are observed on both sides of the transition [Fig. 2(a)]; the breaks in the temperature dependence of the specific volume cannot, therefore, be used as indicators of T_{IN} and T_{NI} . No hysteresis between cooling and heating data was observed; constant density readings were obtained after about 5 min following each temperature change. In contrast, on cooling into the lamellar phase, the specific volume at a given temperature exhibited a slow increase with time. This is demonstrated in Fig. 2(b), where data taken at two cooling rates are compared. Both sets of data were obtained by decrementing the temperature and waiting for a preset delay before making the density measurement. The longer this wait period, the greater the displacement to higher specific volumes; the density in the lamellar phase at the temperature of 300.2 K was still slowly decreasing after a 24-hour wait period. Hysteresis between heating and cooling measurements is present in the lamellar phase [Fig. 2(b)]: Photinos and Saupe [8] observed similar hysteresis with the difference between heating and cooling depending on the history of the sample and the temperature sweep rate, with the difference diminishing the slower the sweep rate.

The volume change at the lamellar-to-nematic transi-

tion is not well defined, but the difference in specific volumes between the nematic and isotropic phases at a given temperature in the mixed-phase region can be obtained by simply extrapolating the pure phase data to the appropriate temperature. Thus on passing from the nematic into the isotropic phase there is an apparent decrease in volume of 7×10^{-5} cm³g⁻¹. This volume change is of sufficient magnitude to be easily measurable by our dilatometer which can detect changes in volume of about 1×10^{-6} cm³g⁻¹ of solution.

C. Dilatometer measurements

The temperature dependence of the capillary height h of the dilatometer containing the CsPFO-²H₂O (w = 0.406) sample is shown in Fig. 3. No discontinuity in either h or its temperature dependence is observed at



FIG. 2. Temperature dependence of the specific volume of CsPFO-²H₂O (w = 0.406) as measured by an Anton-Paar model DMA 60/602 vibrating-tube densitometer: (a) in the vicinity of transition $(T_{IN} = 306.25)$ K; isotropic-to-nematic the $T_{NI} = 306.09$ K); (b) in the vicinity of the nematic-to-lamellar transition (T_{LN} = 300.59 K). In both (a) and (b), the circles represent data collected on first cooling the sample (closed circles), in decrements of about 100 mK, from the isotropic, across the nematic, and into the lamellar phase to a final temperature of 295.7 K, and then heating (open circles) back to the isotropic phase in corresponding temperature increments. The wait time at each temperature was 15 min in the isotropic and nematic phases and 30 min in the lamellar phase. In (b) the squares refer to data collected on cooling from the isotropic phase with a wait time of 15 min in all phases.



FIG. 3 Temperature dependence of the height h, measured by a cathetometer to a precision of 0.001 cm, of the CsPFO-²D₂O (w = 0.406) solution in the dilatometer capillary tube. The data shown were obtained on cooling the sample from the isotropic phase in decrements of between 20 to 100 mK and waiting for 15 min for equilibrium to be reestablished before recording the dilatometer height; no hysteresis was observed between these data and those collected on heating from the lamellar phase.

either of the transitions and no hysteresis between cooling and corresponding data obtained on heating the sample was observed in any of the phases. The dilatometer experiment was also repeated on a sample with a homeotropic director distribution obtained with the dilatometer cell in a 1.4-T magnetic field. No significant differences were observed between the two sets of data.

D. Comparison between densitometer and dilatometer measurements

Clearly there are substantial differences in the behavior of the specific volumes in the nematic and lamellar phases. In the isotropic phase, however, there is a correspondence in the temperature dependencies of h and V, indicating corresponding behavior. Accepting the concurrence of the data for the isotropic phase, we can relate the change in the capillary height to the corresponding change in specific volume. This then enables us to calculate the quantity $\Delta V_{den} - \Delta V_{dil}$, where ΔV_{den} and ΔV_{dil} are, respectively, the specific volume changes relative to some arbitrary reference temperature in the isotropic phase as measured directly by the densitometer and as calculated from the dilatometer height. This quantity, which is simply equivalent to the difference between the volumes as determined by the two techniques (ΔV) , is plotted in Fig. 4. We see large anomalous increases in densitometer volumes in the vicinity of the isotropic-tonematic and the nematic-to-lamellar transitions. Note, also, the pretransitional increases in volume on approaching the transitions from above.



FIG. 4. The difference between the specific volumes (ΔV) as measured by the densitometer and as calculated from the dilatometer heights, as described in the text, on cooling from the isotropic micellar solution phase, across the nematic phase, and into the lamellar phase. The densitometer volumes used in calculating ΔV for the lamellar phase are those data obtained with a 15 min delay between successive measurements (see Fig. 2). The dilatometer volume changes below 298 K were obtained by extrapolation.

E. Conductivity measurements

In the macroscopically aligned sample studied here, the experiment measures the partially averaged component $\tilde{\kappa}_{zz}$ of the conductivity tensor κ along the direction of the electric field **E** which is taken to be along the z axis of the laboratory frame L(x,y,z). This is given by $\tilde{\kappa}_{zz}(\phi) = \kappa_i + \frac{2}{3}(\kappa_{\parallel} - \kappa_{\perp})_M P_2(\cos\phi)$, where ϕ is the angle between the direction of **E** and the mesophase director **n** which is aligned along the direction of the applied field **B**. κ_i is the trace of κ as measured in the isotropic phase (S=0) and in the liquid-crystal phases when $\phi = 54^\circ 44'$ $[P_2(\cos\phi)=0]$, and $(\kappa_{\parallel})_M$ and $(\kappa_{\perp})_M$ are the calculated values of the conductivities parallel and perpendicular to the symmetry axes of a static micelle [3].

The variations with temperature of the electrical conductivities $\tilde{\kappa}_{zz}(0^\circ)$, $\kappa_i [\tilde{\kappa}_{zz}(54^\circ 44')]$, and $\tilde{\kappa}_{zz}(90^\circ)$ for CsPFO-²D₂O (w = 0.410) in the lamellar phase and across the lamellar-to-nematic transition are shown in Fig. 5. $\tilde{\kappa}_{zz}(0^{\circ})$ measurements were made at magnetic flux densities of 1 and 2 T. There was no significant difference between the cooling data at the two field strengths, but the heating data did not coincide: the 2-T heating data is seen (Fig. 6) to fall below the 1-T data at a temperature about 5 K below T_{LN} . Close to the transition, the 2-T data is much closer to the cooling (equilibrium) values. At a temperature about 100 mK below T_{LN} , the relaxation is quite rapid and is complete for the 2-T data at T_{LN} = 0.025 K. In contrast, the 1-T heating data coincided with the cooling data at T_{LN} +0.05 K. A sample left in the lameller phase in a field of 2 T at 300.95 K took



FIG. 5. Temperature dependencies of the electrical conductivities $\tilde{\kappa}_{zz}(0^{\circ})$, $\tilde{\kappa}_{zz}(90^{\circ})$, and $\kappa_i [\tilde{\kappa}_{zz}(54^{\circ} 44')]$ for CsPFO-²D₂O (w = 0.410), as measured at 25 kHz and in a magnetic field of 1 T, in the lamellar phase and across the lamellar-to-nematic transition. The sample was first cooled (closed circles) in steps of 50 mK over the temperature range 304 to 300 K, then in 200-mK steps to 290 K, waiting 10 min at each temperature before making the measurement. This was followed by heating (open circles) in steps of 200 mK/10 min to 300.3 K and then in steps of 20 mK/10 min from 300.3 to 301.4 K. The location of T_{LN} [=301.01(1) K] was precisely determined from ²H NMR measurements.

only an hour to relax to the cooling value. Significantly, a homeotropically aligned lamellar sample prepared by cooling in the magnetic field to 300.95 K showed no relaxation at all over a time interval of 2 h following rotation of the director away from **B**.



FIG. 6. Temperature dependence of the electrical conductivity $\tilde{\kappa}_{zz}(0)$, measured at 25 kHz for CsPFO-²D₂O (w = 0.410), in the vicinity of the lamellar-to-nematic transition. The sample preparation was as described in Fig. 5. The open circles and open squares refer to data collected on heating in magnetic fields of 1 and 2 T, respectively. The cooling data (closed circles) were collected at 1 T.

IV. DISCUSSION

A. Density measurements

The apparent increases in specific volume measured by the densitometer (Fig. 2) on passing from the isotropic to the nematic and from the nematic to the lamellar phase are not evident in the dilatometer measurements (Fig. 3). The sensitivity of the dilatometer is such that the 7×10^{-5} cm³ g⁻¹ change in specific volume encountered at the isotropic-to-nematic transition [see Fig. 2(a)] would appear as a displacement of about 1 mm in the height of the capillary across the temperature gap of the mixedphase region. This displacement is two orders of magnitude greater than the precision with which the heights can be read and would, therefore, be readily detectable, and similarly for the predicted displacement at the nematic-to-lamellar transition. We note here that neither the densitometer nor the dilatometer would have the resolution necessary to detect the -1×10^{-7} cm³ g⁻¹ volume change predicted from $(\partial p / \partial T) x_I$ [9]. Clearly, the apparent increases in specific volume, as detected in the densitometer measurements, cannot be associated with changes in the micelle structure [8]. We must therefore look for other explanations.

One possibility is that the extra volume arises from surface-induced defects. However, the volume associated with any such defects would not be expected to be so large, and, if present, they would be detectable in the dilatometer measurements, too. In the dilatometer experiments, a sample with a homeotropic nematic director distribution gave similar results to one with an isotropic director distribution, indicating that the volume associated with any disclinations in the nematic phase is indeed negligible.

A more likely explanation lies in the fact that the sample in the densitometer is being shaken. How shaking produces an excess volume is not obvious, but it occurs in the ordered phases only. In the nematic phase the excess volume reaches a maximum at T_{IN} -0.3 K and almost disappears at T_{LN} +0.5 K. In the lamellar phase, a much larger excess volume is generated and this reaches a maximum at about T_{LN} -4 K (see Fig. 4). We did not make any measurements at lower temperatures, but it appears the behavior existing in the lamellar phase is qualitatively similar to that observed in the nematic phase, and we anticipate that ΔV will continue to fall as the temperature is decreased. It is also apparent that the isotropic-tonematic transition, as indicated by the excess volume, is spread over a far greater temperature range than the actual transition: there are extensive apparent pretransitional effects. Similarly, the nematic-to-lamellar transition shows pretransitional behavior on the nematic side. In the nematic phase, the "saturation" excess volume is generated within the time scale of the measurements and so there are no hysteresis effects. In contrast, in the lamellar phase, the approach to the saturation excess volume is much slower, hence the hysteresis behavior and associated long relaxation times. It is as though the phases are being churned up in some way which is dependent upon the viscosity and/or elastic properties which are determined by the long-range structural organization in the two phases. The vibration of the sample tube appears to be driving the system into complex nonequilibrium configurations.

B. Conductivity measurements

The difference between the values of conductivity measured on cooling from the nematic phase and those obtained on heating from the lamellar phase (see Figs. 5 and 6) have been shown to be consistent with the buildup of focal domains on heating the sample as a consequence of the concomitant decrease in the layer periodicity [22]. NMR and microscopy experiments have shown that when a CsPFO-²H₂O (w = 0.55) sample is cooled in an iron magnet with the axis of the cylindrical sample tube orientated perpendicular to the direction of **B**, as is the case in the conductivity experiment, no distortion of the nematic director occurs and the sample maintains its homeotropic configuration throughout the lamellar phase. But, on heating from the L_D phase, the NMR spectrum indicates that director orientations other than those along the field direction begin to build up. Microscopy observation of an identical sample contained in a capillary tube reveal that, on heating from the L_D phase, a partial focal conic (PFC) texture develops. The PFC texture indicates small lamellar regions arranged on a square lattice in which the lamellae have moved away from their homeotropic orientation. On heating into the N_D phase, both NMR and microscopy measurements reveal that the homeotropic director distribution is reestablished. The PFC structure is characteristic of liquidcrystal phases having a layerlike structure and occurs when a dilative strain is present in a direction perpendicular to the layers. In the CsPFO-water system, this arises from the decrease in layer periodicity as the temperature is raised [22].

In the conductivity experiment, on cooling, the compressional strain, arising from expansion along the normal to the lamellar planes, constrains the lamellae in a homeotropic configuration between the electrodes of the cell. On heating, the dilative stress, which arises from contraction, induces focal domains. The presence of distortion of the director on heating is revealed by the nonequality in the quantities $\tilde{\kappa}_{zz}(54^{\circ}$ 44') and $\{\tilde{\kappa}_{zz}(0^\circ)/3 + 2\tilde{\kappa}_{zz}(90^\circ)/3\}$ (Fig. 5). This condition is always found to be satisfied on cooling, but not on heating the sample, when the values of $\tilde{\kappa}_{zz}(0^\circ)$ and $\tilde{\kappa}_{zz}(90^\circ)$ measured in the L_D phase are seen to deviate by roughly equal amounts towards the cooling κ_i values. Thus, the differences between the cooling and heating data can be understood in terms of the development of focal domains which give rise to a distortion of the director from a homeotropic configuration. Close to T_{LN} , the domains realign in the magnetic field. The restoring magnetic torque is equal to $\chi_a B^2 \cos\theta \sin\theta/\mu_0$, where θ is the angle between **n** and **B**, χ_a is the anisotropy in the diamagnetic susceptibility, and μ_0 is the permativity of free space. Relaxation of the director distortion is, therefore, four times faster in the 2-T field than in the 1-T field. At the heating rate used in Fig. 6 (2.0 mK min⁻¹), the data collected at

2 T show that full relaxation has occurred just below T_{LN} , while for the 1-T data, relaxation is complete just above the transition. This relaxation of the director to a homeotropic alignment has also been observed in NMR experiments at $T_{LN} - T < 0.5$ K [22].

V. CONCLUSIONS

The comparison of densitometer with corresponding classical dilatometer density measurements has revealed the occurrence of anomalous contributions to the specific volumes of the nematic and lamellar phases as obtained by the densitometer. These anomalous contributions cannot be attributed to changes in the microscopic (aggregate) structure as previously argued [8]. They are possibly associated with some nonequilibrium state induced by the vibration of the sample container in the densitometer experiments. They are particular to the liquid-crystal phases, not to the isotropic phase, and must therefore be associated with the long-range structural organizations of the former. The different hysteresis and relaxation behavior of the lamellar and nematic phases no doubt reflect the different structures and elastic properties of the two phases. These are interesting phenomena which require further investigation.

The hysteresis and long relaxation times observed in electrical conductivity measurements in the lamellar phase have been shown to arise from partial focal conic textures. The relaxation rate depends on the magnetic-field strength as well as the proximity to T_{LN} . Relaxation of the conductivity to values commensurate with the equilibrium (cooling) state can occur at temperatures below T_{LN} . Significantly, a homeotropically aligned sample, obtained by cooling from the nematic phase to just below T_{LN} in the lamellar phase, shows no relaxation at all when the nematic director is rotated away from the direction of the magnetic field, confirming that the relaxation cannot be associated with changes in the structure of the aggregates.

Thus, there are no reasons at the present time not to accept the available evidence which supports the notion that the nematic-to-lamellar transition is essentially a nematic-to-smectic-A transition. The transition solely involves the onset of translational ordering of the discotic micelles along the direction of the nematic director. The recent work of Herzfeld and Taylor [6] suggests that the transition can be understood within the context of hardcore interactions between the micelles. The intrinsic stability of discrete micelles in the lamellar phase, relative to that of continuous bilayers, is attributed to the translational entropy associated with the liquidlike degrees of freedom of the discrete micelles.

Finally, it is instructive to compare the predicted increase in volume of 1×10^{-7} cm³g⁻¹ at the nematic-toisotropic transition with those for the corresponding transition in thermotropic liquid crystals [23,24]. The latter, typically 1×10^{-3} cm³g⁻¹, are significantly larger. The expansion in volume in the case of thermotropics can be attributed to the less favorable molecular packing in the isotropic phase. We may expect the volume change in the case of the CsPFO-water system to have a similar origin; the much smaller volume change is consistent with the smaller volume fraction of the nematogenic particles, i.e., the micelles.

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