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Measurements of electric conductivity and reorientation times for the cesium perfluorooctanoate–D_2O micellar system

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Measurements of the electric conductivity and the relaxation times for reorientation in magnetic fields are presented for the cesium perfluorooctanoate (CsPFO)–D_2O micellar system, as a function of temperature and concentration. Five sample concentrations are presented, namely 41%, 48%, 50%, 55%, and 60% of CsPFO in D_2O by weight. At these concentrations, the system shows a nematic liquid crystal, between a lower-temperature lamellar smectic and a higher-temperature isotropic micellar phase. At the transition from the nematic to lamellar phase, the principal conductivities change rather continuously, and do not show any marked features. The measurements show that at the same reduced temperature, the structure of the nematic phase becomes more anisotropic and the relaxation times become longer with decreasing CsPFO concentration in the system, suggesting that at the same reduced temperature, the size of the nematic micelles increases with decreasing CsPFO concentration. Comparison of the conductivity anisotropy data with values calculated from structural models allows estimates of the aspect ratio of the micelles and the fraction of the area of the smectic planes that is covered by water. The behavior of the relaxation times at the nematic-to-lamellar transition shows dependence on the concentration. The relaxation times at the nematic-to-lamellar transition for the four lower concentrations diverge; the critical exponents in order of increasing CsPFO concentration are 0.71, 0.76, 0.77, and 0.85. The 60% sample does not show any pretransitional behavior at this transition.

I. INTRODUCTION

Several surfactant-water systems are known that show a nematic range between a lamellar smectic phase and an isotropic micellar solution. Examples are decylammonium chloride (DACl),[1,2] ammonium perfluorononanoate (APFN),[3] and cesium perfluorooctanoate (CsPFO).[4] In these systems, the nematic phase consists of oblate or disklike micelles. In the two perfluorinated systems, the nematic range reaches a width of about 7 °C. The nematic phase in the APFN seems to form at lower molar concentrations compared to CsPFO. Also, the Krafft point for APFN is higher, about 21 °C, as compared to 7 °C for CsPFO.[5] The nematic-to-isotropic transition is weakly first order. Studies in the CsPFO system[6–8] show that this transition becomes weaker with decreasing concentration, suggesting the existence of a point on the transition line, where the transition becomes second order (Landau point), although this point has not been reached for the CsPFO system. Also, the lamellar-to-nematic transition becomes weaker with decreasing concentration, as indicated by the width of the two-phase coexistence range at this transition. Eventually, this transition line turns second order (at the tricritical point). At high enough concentrations, the nematic range becomes progressively narrower, and finally the lamellar phase transforms directly to the isotropic phase through a first-order transition.

It was first reported[9] in the DACl system that the formation of the lamellar smectic phase does not have significant effects on the electric conductivity. This surprising result, which was later verified with both the CsPFO (Ref. 10) and APFN,[11] indicates that in the lamellar smectic phase the aqueous regions are rather continuous.

In connection with the nematic phase of the APFN system, we have reported measurements of the electric conductivity parallel (k_1) and normal (k_2) to the director, and measurements of the relaxation time for reorientation in a magnetic field. The conductivity anisotropy

$$\alpha=(k_1-k_2)/\langle k\rangle \tag{1}$$

and the relaxation time decrease with increasing surfactant concentration at given reduced temperature from the nematic-isotropic transition, suggesting that the nematic micelles are larger the lower the concentration. The anisotropy is determined by the structure of the micelles, their orientational order, and the conduction mechanism. By comparing the measured anisotropy with calculated values for model structures of insulating disks in a uniformly conducting medium, information can be derived on the aspect ratio of the micelles. We applied this approach to the DACl system, and estimated that the micelles have a small diameter to thickness ratio, between 2.5 and 4. These estimates were confirmed by x-ray diffraction and by electron microscopy studies. A similar procedure can be applied to the lamellar smectic phase.

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The structure of the latter can be modeled by analogy to the smectic-A phase of thermotropic liquid crystals, i.e., as micelles arranged in parallel planes.[4] Alternatively, it can be modeled as parallel stacks of perforated insulating layers embedded in a uniformly conducting medium. The conductivity measurements alone cannot distinguish between the two models; nevertheless they indicate that water occupies a large fraction of the area of a smectic plane. This fraction is as high as 30% near the transition to the nematic phase. The presence of other defects, e.g., screw dislocations, should increase k_1 in the lamellar phase, yet since these defects presumably heal with time, k_1 should accordingly decrease with time. This seems to be the case with APFN, as indicated by measurements taken over a period of 24 h.[11] However, from density measurements on DACl (Ref. 9) and CsPFO,[10] we found indications of slow relaxation processes occurring in the smectic phase with relaxation times of the order of 100 h, which are presumably connected with the approach to an equilibrium distribution of defects.

In the present work we report measurements of the principal conductivities and of the relaxation times for CsPFO-D_2O mixtures. The measurements are taken as a function of concentration and temperature. The principal conductivities are compared to the data of Boden and co-workers on a 55 wt. % CsPFO mixture, and to our measurements on the DACl and APFN systems. A discussion of the micellar size as a function of temperature and concentration is given in terms of the anisotropy data and in terms of the relaxation times.

II. EXPERIMENT

The CsPFO was prepared by neutralizing perfluorooctanoic acid (Aldrich 96%) by CsOH (Aldrich 99.9%). The salt was recrystallized three times from ethanol. The samples were prepared by mixing CsPFO with deuterium oxide (Aldrich 99.8%). The phases and transition temperatures were identified by polarized light microscopy. Additional information on the transition temperatures and the width of any two-phase coexistence regions was obtained from the conductivity versus temperature data to be discussed below. For the measurements we used five samples. The compositions and transition temperatures are given in Table I. The phase sequence and the transition temperatures are in good agreement with the phase diagram of Boden and Holmes.[4]

The experimental setup for the conductivity measurements was described in detail elsewhere.[11] For the measurements we used an H-shaped glass cell. The platinized platinum electrodes were placed at the ends of the horizontal section. The diamagnetic anisotropy of the CsPFO samples is positive, meaning that the nematic director aligns parallel to an applied magnetic field. Consequently, the measurement along each of the two principal directions was achieved by aligning the long section of the conductivity cell parallel (for k_1) or perpendicular (for k_2) to the magnetic field. For the measurements of the principal values, the aligning magnetic field was $H=13.5$ kG. In addition to the applied field, the alignment of the director in the cell is also affected by the sample-glass boundary. At the glass surface the director is normal to the wall of the glass cell. Thus in the geometry of the k_1 measurement, the surface action competes with the aligning field, and at the cell boundary the director remains normal to the applied field H. In connection with the APFN measurements in the k_1 geometry of Ref. 11, the wall effects caused a spontaneous realignment of the director in the lamellar phase. This realignment is suppressed in the present measurements by using a stronger aligning magnetic field. Also, to minimize the significance of the surface layer, we used a larger cell diameter (3.5 mm). In the lamellar phase the measured k_1 decreased with increasing H. Away from the lamellar phase, the values showed saturation for $H > 10$ kG. Measurements at 3, 5, 10, and 13.5 kG in the vicinity of the nematic-lamellar transition indicate that the k_1 values presented here may be 3% below the saturation value. The measurements of k_1 and k_2 were started in the isotropic phase, the temperature was stepped down at a rate of 0.1 °C/3 min to the minimum desired value, upon which the steps were reversed, and the measurements continued up to the isotropic phase.

TABLE I. Sample compositions and transition temperatures. T_{ni} is the temperature at which the sample becomes isotropic, and is determined to within ±50 mK from the anisotropy data. T_{sn} is the temperature at which the sample becomes lamellar, and is determined to within ±20 mK, as described in the last paragraph of Sec. II.

Sample	CsPFO concentration (wt. %)	T_{sn} (°C)	T_{ni} (°C)
Cs1	41	29.43	35.1
Cs2	48	38.33	43.9
Cs3	50	42.13	47.6
Cs4	55	52.28	57.8
Cs5	60	67.50	72.9

III. EXPERIMENTAL RESULTS

The measured principal conductivities for the five samples are shown in Fig. 1, versus the reduced temperature $T-T_{ni}$, where T_{ni} is the temperature at which the sample becomes isotropic, and the two principal conductivities coincide. The conductivity increases with increasing CsPFO concentration. Also, away from the transition regions, the conductivity increases with increasing temperature. This is a result of increased dissociation of the Cs^+ counterions, thus increasing the number of charge carriers. In addition, as the temperature increases the viscosity of the aqueous phase surrounding the micelles decreases, and thus the conductivity increases; indeed most of the temperature dependence of the conductivity is due to the variation of the viscosity, as shown in Fig. 2, where the principal conductivities are multiplied by the viscosity of water.[12] The overall slope of these curves is substantially reduced.

As the transition to the isotropic phase is approached, the conductivities show considerable temperature depen-

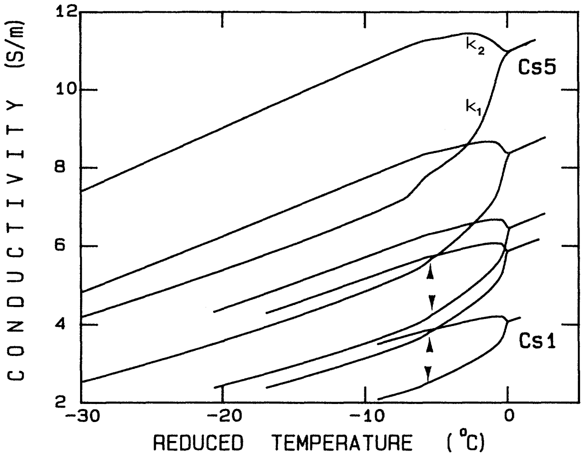

FIG. 1. Principal conductivities for five CsPFO-D_2O samples vs the reduced temperature $T-T_{ni}$ in ascending order Cs1–Cs5. The arrows mark the nematic-lamellar transition on k_1.

dence, which is attributed to the concomitant decrease in the orientational order and in the size of the micelles. The transition to the isotropic phase is characterized by a two-phase coexistence range. In this range the alignment of the nematic director deteriorates as the sample is partially isotropic. The observed broadening of the transition region with increasing concentration reflects the widening of the two-phase range, in agreement with the phase diagram of Boden and Holmes.[4] The inhomogeneity of the sample in the two-phase range affected the reproducibility of the data in this range on heating and cooling.

The transition to the lamellar phase, albeit devoid of drastic changes in conductivity, is nevertheless noticeable in both k_1 and k_2. The transition becomes wide with increasing concentration, also as a result of the increasing two-phase coexistence range; for the lower concentrations the transitions appear more continuous. The conductivity anisotropies of the five samples versus $T-T_{ni}$ are shown in Fig. 3, and clearly reflect the effects of the coexistence ranges. The measurements shown in this figure were taken on cooling.

Away from the lamellar phase the results reproduced well between heating and cooling experiments. In the lamellar phase undulation of the smectic planes occurs on heating; this effect was studied in detail in connection with the APFN system,[11] and was observed here as well. The results in the lamellar phase showed dependence on the history of the sample and on time. The behavior is characterized by long relaxation times, over 100 h, and as discussed in more detail in Ref. 13 they probably reflect the formation of the smectic layers and the slow approach to the equilibrium distribution of defects in the sample.

The conductivity of the sample for current forming an arbitrary angle ψ with the nematic director can be expressed in terms of the principal conductivities by the equation

$$k(\psi)=k_1k_2/[k_1+(k_2-k_1)\cos^2\psi] \ . \tag{2}$$

The above equation can be used to describe the realignment of the nematic director from an initial direction forming an angle ϕ_0 to a direction parallel to the magnetic field. In the simplest case, the reorientation is dominated by the uniform rotation of the director, and the time dependence of the angle ϕ between the director and H is described by a single relaxation time τ through the equation

$$\tan\phi=\tan\phi_0\exp(-t/\tau) \ . \tag{3}$$

The initial angles ϕ_0 were about 10°–15° in these experiments, and the conductivity measurements were taken in intervals of 10 sec in a 10-kG magnetic field. The results of representative measurements on sample Cs1 at

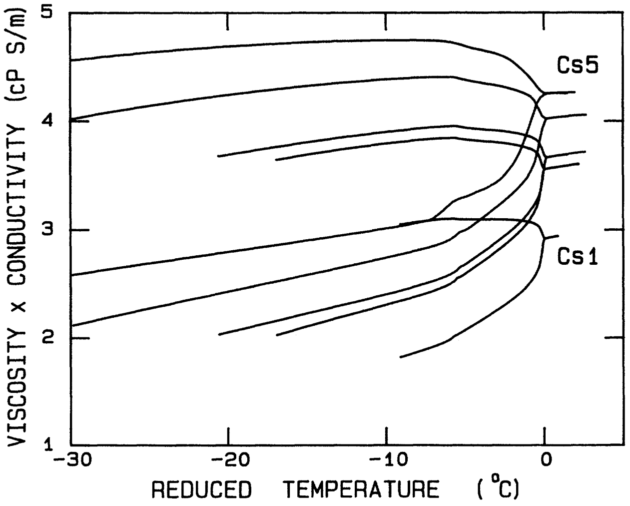

FIG. 2. Principal conductivities multiplied by the viscosity of water for five CsPFO-D_2O samples vs the reduced temperature $T-T_{ni}$.

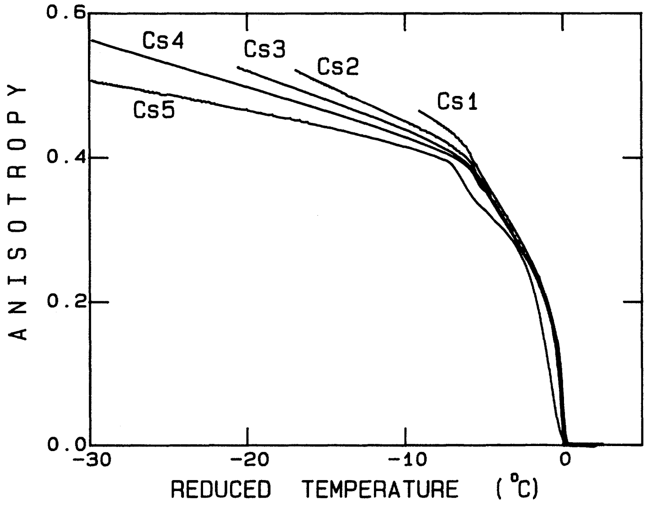

FIG. 3. Conductivity anisotropy [cf. Eq. (1) in text] vs the reduced temperature $T-T_{ni}$.

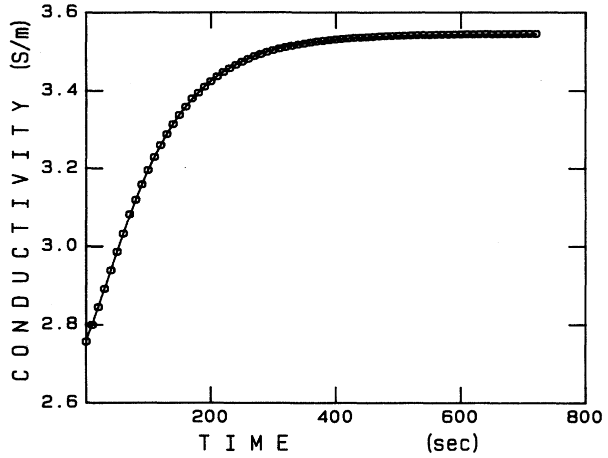

FIG. 4. Reorientation of Cs1 in a 10-kG magnetic field at 29.965 °C. The solid line is the best fit to Eqs. (2) and (3).

29.965 °C are shown in Fig. 4. The relaxation time τ is determined from the best fit of the time-dependent conductivity data to Eqs. (2) and (3); the best-fit curve is also shown in Fig. 4. The fits are generally very good, indicating that the director reorientation is indeed dominated by the single mechanism described by Eq. (3). An alternative verification that the effective mechanism in these experiments is a simple reorientation is provided by repeating measurements at field values 5, 7, 10, and 13.5 kG, keeping the temperature constant. Within experimental error, the results verified the linear dependence of τ on H^{-2}.[14] The results of this experiment are plotted in Fig. 5. The director reorientation becomes more complex at the onset of the two-phase coexistence range in the case of a first-order nematic-to-lamellar transition. Figure 6 illustrates the point, with a measurement taken on sample Cs4, at $T=52.36$ °C. A second relaxation mechanism with characteristic time of the order of 60 sec is clearly noticeable and Eq. (3) is no longer applicable in this case. At the nematic isotropic coexistence range the reorientation is rather rapid, and we could not detect the possible presence of a second relaxation in our data.

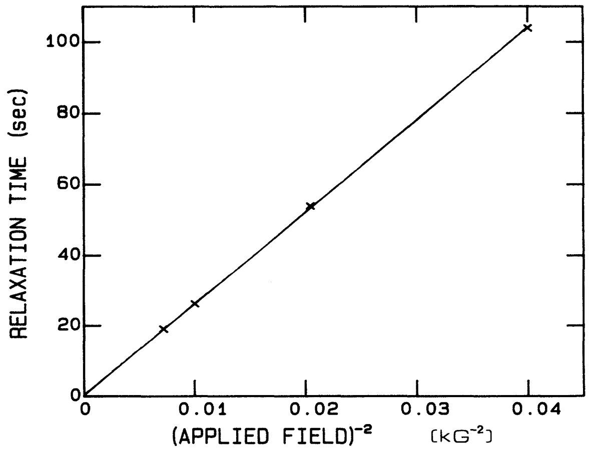

FIG. 5. Reorientation time τ vs H^{-2} for sample Cs2 at 39.54 °C.

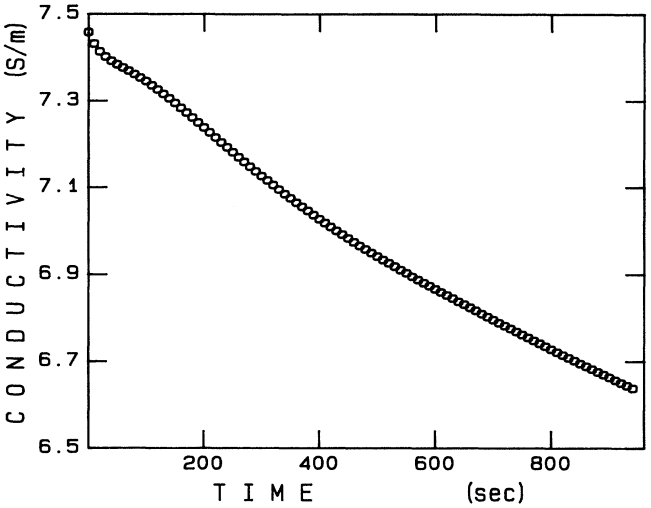

FIG. 6. Reorientation of sample Cs4 in the two-phase nematic-lamellar range (52.36 °C) in a 10-kG field.

The values of τ determined by the best fit to the data are shown in Fig. 7 versus $T-T_{sn}$, where T_{sn} is the lamellar-nematic transition temperature. τ increases with decreasing temperature and decreasing concentration at corresponding temperatures in the nematic phase. At the transition to the lamellar phase τ diverges for samples Cs1–Cs3: the magnetic field cannot realign the director of the lamellar phase. The divergence at the transition to the lamellar phase can be described by a critical exponent as

$$\tau \sim (T-T_{sn})^{-\gamma} . \quad (4)$$

The critical exponent γ is obtained from the slope of the

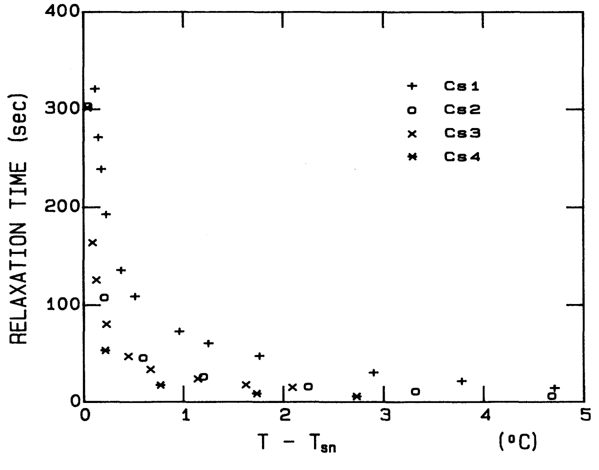

FIG. 7. Reorientation time τ vs $T-T_{sn}$ in a 10-kG magnetic field. For sample Cs4, T_{sn} is replaced by the supercooling limit $T^*=52.23$ °C, derived from the best fit to the corresponding data of Fig. 8.

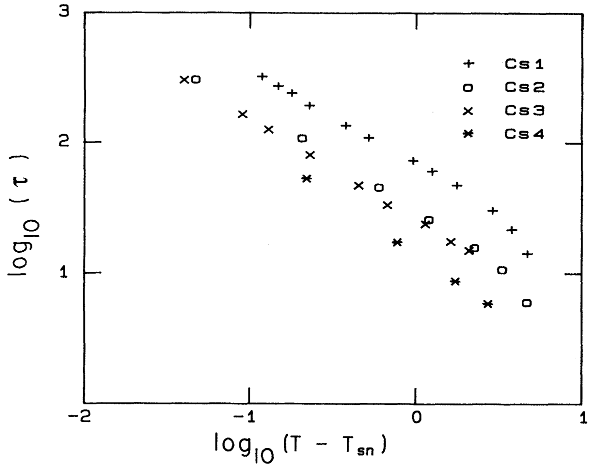

FIG. 8. Log-log plot of reorientation time τ vs $T-T_{sn}$. The comments on Cs4 in Fig. 7 apply.

log-log plots of τ versus $T_{sn}-T$, shown in Fig. 8. The figure also shows data for Cs4, which has a first-order transition. In this case γ describes the pretransitional behavior, with T_{sn} replaced by a supercooling temperature ($T^*=52.23\,^\circ\mathrm{C}$) determined from the best linear fit to $\log_{10}\tau$. The slopes of the best linear fits to the data in the range between T_{sn} and $T_{sn}+2\,^\circ\mathrm{C}$ give the following values for γ:

0.71 for Cs1 ,

0.76 for Cs2 ,

0.77 for Cs3 ,

0.85 for Cs4 .

We could not determine pretransitional divergent behavior of the τ values for Cs5 because of the short relaxation times. The determination of the slopes depends on the choice of T_{sn}, and the estimated error in γ is about ± 0.04. The divergence of τ at the lamellar-to-nematic transition was utilized to determine T_{sn} accurately. The sample in the k_2 geometry was cooled to the lamellar phase, and there it was rotated by about 45°. The conductivity was monitored in 10-sec intervals while the temperature was increased in steps of 40 mK/3 min. The transition was noticed as a sharp decrease in the conductivity and could thus be determined to within ± 20 mK. For samples Cs4 and Cs5, which undergo a first-order nematic-lamellar transition, the T_{sn} values listed in Table I correspond to the lower limit of the nematic-smectic coexistence range.

IV. DISCUSSION

As expected the results of the conductivity measurements are qualitatively similar to the APFN and DACl systems mentioned in the Introduction. Specifically, sample Cs1 has about the same transition temperatures as sample $S2$ of Ref. 11. Comparison shows that the conductivity of Cs1 is over twofold higher, and the anisotropy at the lamellar-to-nematic transition is 8% lower. As observed with the APFN measurements, when the temperature variation of the viscosity of water η is factored out, the average conductivity decreases with decreasing temperature, as a result of the increase in the micellar size and the increased binding of the Cs^+ counterions. The changes in the micellar size and the binding of the counterions along with the orientational order determine the behavior of the principal components of the conductivity in the nematic phase: an increase in the orientational order causes k_1 to decrease and k_2 to increase. k_1 and k_2 are similarly affected by the smectic order. From Fig. 2, however, we note that ηk_2 initially increases in the nematic phase, due to the rapid increase of orientational order near the transition, but on further cooling and in the lamellar phase it decreases slowly, indicating that the increase in binding of the counterions eventually overcomes the effects of the increasing size and orientational order. In addition, the mobility of the counterions may depend on the size of the micelle. For rod-shaped micelles Francois[15] proposed a model where the mobility of the counterions parallel to the micellar surface is larger than the mobility perpendicular to the surface. Our recent measurements on other micellar nematics[16] suggest that it may be worthwhile to further explore this assumption, and develop a theoretical model to interpret the conductivity of micellar liquid-crystal phases.

Comparing our results for Cs4 with the measurements of Boden, Corne, and Jolley[10] on a 55 wt. % sample we find good agreement in the conductivity values, and the slope of the conductivity curve in the isotropic phase. A discrepancy is noted in the values of k_2, which are lower in Ref. 10, and as a result, in comparison to the values presented here, the anisotropy values of Ref. 10 are over 22% lower near T_{sn} and over 32% lower at $T_{sn}-20\,^\circ\mathrm{C}$. The difference is probably due to incomplete sample alignment in the measurements of Boden, Corne, and Jolley.[10]

As mentioned in the Introduction, the conductivity data can be analyzed in terms of the anisotropy of a lattice of insulating disks, perfectly ordered in a uniformly conducting medium. The calculated anisotropies and average values versus D/h are given in Ref. 11 for various volume fractions occupied by the disks. The measured anisotropy α_e is related to α, the anisotropy calculated for complete order by

$$\alpha_e=\alpha S\ , \tag{5}$$

where S is the orientational order parameter of the micelles. According to the estimates of Boden, Parker, and Jolley[17] for the Cs3 mixture $S=0.72$ near T_{sn} and $S=0.57$ in the middle of the nematic range. Assuming that these S values do not vary appreciably over the range of concentration covered by our samples, we can use these S values to calculate α from Eq. (5) and the experimental results (α_e) of Fig. 3. The values of α can then be used to estimate D/h from the α versus D/h results of Ref. 11. The results are listed in Table II. For

TABLE II. Aspect ratio D/h of the micelles in the nematic phase, and fraction of the area of the smectic planes occupied by defects. The estimates are based on comparison of the measured conductivity anisotropy with the values calculated in Ref. 11. The density of CsPFO in the micelles (Ref. 18) is 2.5 g/cm^3.

Sample	Volume fraction (%)	Aspect ratio at T_{sn}	Aspect ratio at $(T_{sn}+T_{ni})/2$	Defect area (%) at T_{sn}
Cs1	23	6.0	5.3	33
Cs2	29	4.6	4.1	31
Cs3	31	4.1	3.8	30
Cs4	35	3.6	3.4	28
Cs5	40	2.8	2.8	25

the evaluation of the volume fraction occupied by the disks, we used $\rho_s = 2.5$ g/cm^3, a value based on density measurements on the CsPFO system.[18] It is stressed that these estimates depend on the assumed values of S and the D/h estimates increase with increasing S values. The range of D/h values is in good agreement with previously reported values for the APFN and DACl systems. It is also interesting to note that the D/h values are of the same order of magnitude as the values predicted by Onsager's theory for hard disks.[19–21] For low concentrations of thin hard disks, the nematic phase occurs when the number of disks per unit volume C is[22]

$$C = 0.91/D^3 , \tag{6}$$

which yields a value of $D/h \approx 2$. Although this figure may seem in good agreement with the values listed in Table II, it must be pointed out that Eq. (6) applies to thin disks, i.e., high aspect ratios.

Also listed in Table II are the fractions of the area of the smectic planes occupied by water. These values were also obtained by comparison of the anisotropy data just below T_{sn} with the calculated anisotropy[11] for a system of perforated insulating layers, stacked parallel in a conducting medium. The results show that about $\frac{1}{4}$ to $\frac{1}{3}$ of the lamellar plane is occupied by water. The long relaxation shown in Fig. 6 for sample Cs4, suggests that the alignment of the smectic phase in samples Cs4 and Cs5 may be incomplete, due to the two-phase range, and accordingly interpretation of the anisotropy data for these two samples may include considerable error.

The reorientation of the nematic director is a complicated process in general, and depends on the external field, the boundary conditions, and the properties of the sample. Our experimental measurements were adequately described by a single relaxation time as long as the angle ϕ_0 was kept small, and the director did not cross either of the principal directions during the reorientation. The reorientation time τ decreases with increasing concentration at a given reduced temperature, and this trend prevails even after correcting for the viscosity of water. This behavior, which was also observed with the APFN system,[11] is consistent with the decrease of the micellar dimensions with increasing concentration discussed above. The average value of the critical exponent describing the temperature behavior of τ near T_{sn} for all the samples is 0.773; sample Cs1 shows the highest deviation from the average value, but is still within experimental error. The values reported here for CsPFO are consistently larger than the values reported for APFN (0.68 to 0.71) by the same method. Although the error introduced by the uncertainty in T_{sn} and the fact that the data used do not come close enough to T_{sn} to allow definitive conclusions on the unversality at this transition, it is noted that dependence of the exponents on the sample composition at this transition was observed in connection with the divergence of the bend elastic constant at the same transition in the DACl system[23] obtained by the Freedericksz transition method. By improving the temperature resolution, the conductance method presented here could prove very useful in examining universality in the behavior of τ at the nematic-lamellar transition. The nematic-isotropic transition of the CsPFO system is nearly second order, as mentioned in the Introduction. Boden, Parker, and Jolley[17] have proposed a method to determine the pretransitional behavior of the order parameter near T_{ni} from the principal conductivities. For a 55% sample they find for the corresponding critical exponent $\beta = 0.31$. It would be of interest to compare this result with measurements of relaxation times near T_{ni}.

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