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Measurements of the dielectric and viscoelastic constants in mixtures of 4,4'-*n*-octyl-cyanobiphenyl and biphenyl

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We performed measurements of the dielectric constants, splay elastic constant, and rotational viscosity of the nematic phase of mixtures of 4,4'-*n*-octyl-cyanobiphenyl (8CB) and biphenyl (BP). In contrast with previous results of DasGupta *et al.* [*Phys. Rev. E* **63**, 041703 (2001); *Phys. Lett. A* **288**, 323 (2001)], we do not find any anomaly of these constants when the smectic-*A* phase is approached at all concentrations of BP. These results are compatible with recent calorimetric measurements of Denolf *et al.* [*Phys. Rev. Lett.* **97**, 107801 (2006); *Phys. Rev. E* **76**, 051702 (2007)] and the absence of a tricritical point in the phase diagram. The origin of the anomalies observed by DasGupta *et al.* at large concentration of BP is also briefly discussed and a likely explanation in terms of biphenyl evaporation is proposed.

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I. INTRODUCTION

Liquid crystals exhibit a large number of mesophases and, thus, constitute model systems for the study of phase transitions [1–3]. One of the most investigated is the nematic-to-smectic-*A* phase transition. Because the smectic phase can be described with a two-component complex order parameter, this transition was expected to be in the 3D *XY* universality class [4,5]. Nevertheless, several experiments have shown its nonuniversal critical behavior with anisotropic divergencies of the correlation lengths and nonstandard critical exponents [6]. In addition, a coupling with the nematic order parameter and (or) the nematic fluctuations can drive the transition from second to first order [7,8]. Another possibility to change the order of the transition is to add a nonmesogenic impurity, as first proposed theoretically by Anisimov in 1983 [9]. Surprisingly, this effect was experimentally investigated only recently, in 2001, by DasGupta *et al.* [10]. These authors found that the viscoelastic properties of the nematic phase of the liquid crystal 8CB (4,4'-*n*-octyl-cyanobiphenyl) was strongly modified by the addition of biphenyl (BP), a rigid nonpolar and nonmesogenic solute. More precisely, they observed that the rotational viscosity γ_1 of the nematic phase starts to abruptly decrease on cooling close to the smectic-*A* phase, instead of diverging, when the concentration of BP was larger than 3% by weight, typically. A similar behavior was also observed for the dielectric constant parallel to the director and the splay elastic constant. The authors interpreted these results in terms of pretransitional effects, suggesting that the transition becomes slightly first order at large concentration of BP [10]. This interpretation was reinforced by a Landau mean field calculation suggesting the existence of a concentration induced tricritical temperature [11]. Later, Denolf *et al.* [12,13] found from very precise adiabatic scanning calorimetry measurements that the nematic-to-smectic-*A* phase transition remains second order at all concentrations of BP in this system. If these authors are correct, a divergence of γ_1 is theoretically expected [14], since this quantity must become infinite in

the smectic phase, and should not decrease as the transition temperature is approached from above. In order to check this issue, we measured again the rotational viscosity in the mixture 8CB+BP by choosing an alternative technique based on the use of a rotating magnetic field [15,16]. Contrary to DasGupta *et al.*, we found that the viscosity diverges at the nematic-to-smectic-*A* phase transition, whatever the concentration of BP. In addition, we did not find any anomalous behavior for the dielectric and splay elastic constants, which remain approximately constant at the nematic-to-smectic-*A* phase transition at all concentrations of BP.

II. EXPERIMENTAL DETAILS

The liquid crystal 8CB was purchased at Frinton Laboratories, USA, and the BP (of purity $\geq 99\%$) at Sigma-Aldrich, Germany. Both were used without further purification. We performed our measurements with two mixtures: mixture 1 with 2 wt % of BP and mixture 2 with 3.37 wt % of BP. According to Dasgupta *et al.*, the first mixture behaves normally (the viscosity diverges) whereas the second one presents a strong anomaly with the viscosity passing through a maximum about 3 °C above the transition and decreasing on cooling close to the transition. The viscosity was measured optically under a rotating magnetic field by using 30- μm -thick samples treated for homeotropic anchoring. Polyimide Nissan 0626 was used to achieve homeotropic anchoring. The experimental setup is described in Ref. [15] and the optical method for obtaining the bulk viscosity γ_1 with homeotropic samples in Ref. [16]. The samples were sealed on the sides with UV glue NOA 81 (Norland Optical adhesive) to avoid that the BP evaporates. As we shall see later, this precaution proved to be essential. In this experiment, the director was set in motion thanks to a rotating magnetic field. The field, of amplitude 1 T, was parallel to the glass plates. The viscosity was obtained by optically measuring the delay angle α between the director in the middle of the sample and the field. By denoting by ω the angular velocity of the field, this angle reads in the limit $\alpha \ll 1$ [16]

$$\alpha = \frac{\mu_0 \gamma_1 \omega}{\chi_a B^2}, \quad (1)$$

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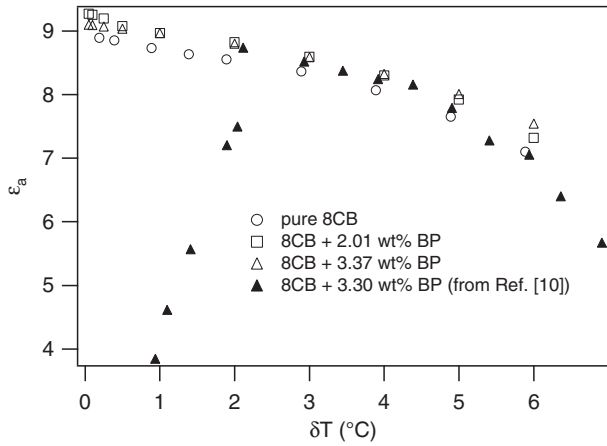


FIG. 1. Dielectric anisotropy as a function of temperature.

where χ_a is the magnetic anisotropy and μ_0 the vacuum permittivity. Thus, measuring the ratio α/ω allowed one to determine the viscosity, providing that the magnetic anisotropy was known. The latter was determined by measuring the onset of instability of the Frederiks transition in 30- μm -thick planar samples. They were prepared between two ITO electrodes recovered with a thin 0825 polyimide layer (from Nissan Ltd.) rubbed in the same direction (parallel rubbing). Similar results were obtained by treating the surfaces with PVA (polyvinylalcohol). Measurements (at 1 kHz) of the critical voltages $V_c(B)$ under zero and 1 T magnetic field (with the field parallel to the anchoring direction) allowed us to obtain the ratio χ_a/ε_a of the magnetic over the dielectric anisotropy by using the formula

$$\frac{\chi_a}{\varepsilon_a} = \frac{\varepsilon_0 \mu_0 V_c^2(0) - V_c^2(B)}{B^2 d^2}. \quad (2)$$

The sample thickness d was measured to within $\pm 0.1 \mu\text{m}$ with a spectrometer. As for the dielectric anisotropy, it was measured from capacity measurements at 1 kHz in planar and homeotropic samples of thickness $d = 7.5 \mu\text{m}$. A HP 4284A LCR meter controlled under LabVIEW was used for the measurements. Temperature of our ovens was controlled to within $0.01 \text{ }^\circ\text{C}$ with ATNE controllers.

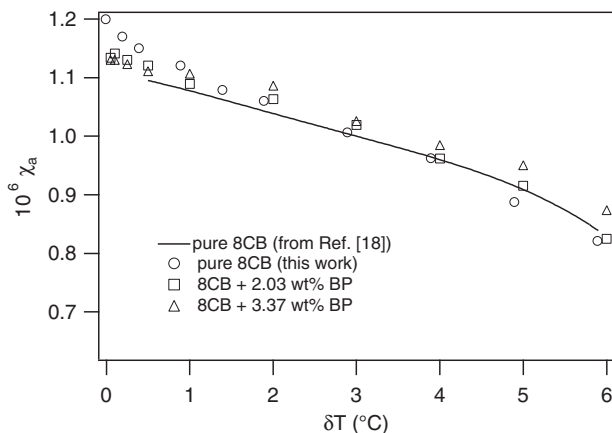


FIG. 2. Magnetic anisotropy as a function of temperature.

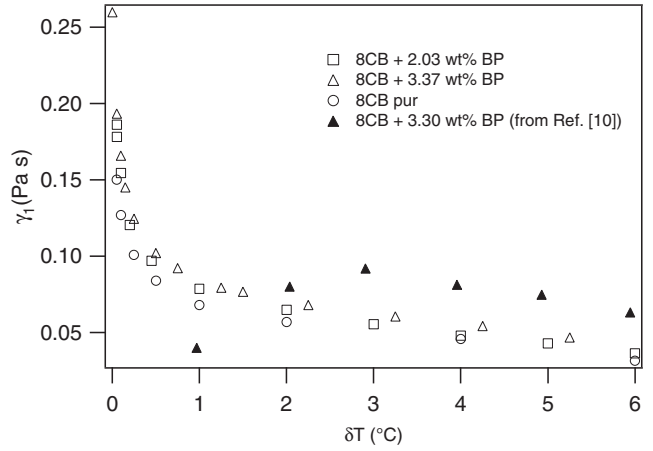


FIG. 3. Rotational viscosity as a function of temperature.

III. EXPERIMENTAL RESULTS

Our results for pure 8CB and mixtures 1 and 2 are shown in Figs. 1–3. All our results are reported as a function of the shift to the transition temperature $\delta T = T - T_{NA}$. For the pure 8CB we measured $T_{NA} = 33.71 \text{ }^\circ\text{C}$, while for mixtures 1 and 2 we found respectively $T_{NA} = 30.28 \text{ }^\circ\text{C}$ and $27.57 \text{ }^\circ\text{C}$. These values are in good agreement with the phase diagram given by DasGupta *et al.* [10] and Denolf *et al.* [13]. Figure 1 shows our results for the dielectric anisotropy which we found to be little dependent on the BP concentration. We note that our results for pure 8CB are in very good agreement (within 2%) with those of Thoen and Menu [17]. Our data are also consistent with those of DasGupta *et al.* [10] for pure 8CB and mixture 1, but disagree with theirs in mixture 2, in particular close to the transition. This point will be discussed in the following section. Data for the magnetic anisotropy are shown in Fig. 2. Again they compare very well for pure 8CB with the data of Bradshaw *et al.* [18]. We should note that the presence of BP does not significantly change the magnetic anisotropy of the phase. Finally, our viscosity measurements are shown in Fig. 3. As expected, the viscosity diverges at the transition in all mixtures, including mixture 2. This result is in disagreement with that of DasGupta *et al.*, who observe a decrease of the viscosity

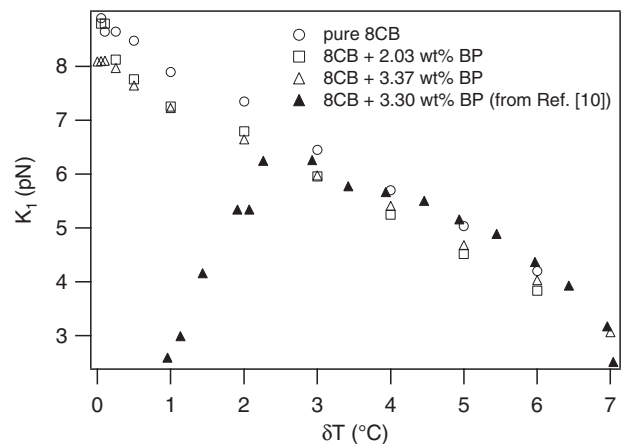


FIG. 4. Splay elastic constant as a function of temperature.

(very similar to that found for the dielectric anisotropy) in mixture 2 close to the smectic phase. A possible explanation for this disagreement is given in the following section. For completeness, we show in Fig. 4 our results for the splay constant K_1 deduced from the measurement of the Frederiks critical voltage. Again we should note that our data for K_1 agree well with the data of Madhusudana *et al.* [19] for pure 8CB but are incompatible with the results of DasGupta *et al.* in mixture 2 close to the transition.

IV. ORIGIN OF THE ANOMALY OBSERVED BY DASGUPTA *et al.*

A rapid analysis of the data of DasGupta *et al.* shows that in mixture 2 (and in all others with a larger concentration of BP) the dielectric anisotropy—but also the splay elastic constant K_1 —present the same anomaly as the viscosity when the smectic phase is approached—namely the passage through a maximum followed by a sharp decrease on cooling. On the other hand, the ratios K_1/ϵ_a and γ_1/K_1 obtained respectively by measuring the critical voltage and the relaxation time at the Frederiks transition of a planar sample seem correct. This observation suggests that the anomaly comes from the measurement of the dielectric anisotropy. Indeed, underestimating ϵ_a leads one to underestimate K_1 and consequently γ_1 . For this reason we reproduced the experimental protocol used by DasGupta *et al.* for measuring ϵ_a . Their method consisted of measuring the curve $C(V)$ with a planar sample over a wide range of voltages (in our case between 0.1 and 20 Vrms). From this curve ϵ_\perp is obtained from the value of the capacitance measured below the onset of Frederiks transition while ϵ_\parallel is deduced from the value of the capacitance extrapolated at infinite voltage (more precisely C is plotted as a function of $1/V$ and is then extrapolated to 0). We used this method by taking care of using a sealed sample to measure ϵ_a in mixture 2 and we found results that were in very good agreement with our previous results obtained from separate measurements on planar and homeotropic samples, without any visible anomaly. The same conclusion was reached by just extrapolating at infinite voltage our curves truncated at 5 Vrms (as DasGupta *et al.* did, their RLC meter being not equipped with the high voltage option). Being unable to reproduce the anomaly, we finally did the experiment again with a sample open on the sides. Curves $C(V)$ obtained in this way with mixture 2 are shown in Fig. 5. In this example, the temperature was set 0.3°C above the transition temperature which was measured in the middle of the sample immediately after filling. The first curve that was measured half an hour after filling looks “normal” and leads to the expected value for ϵ_a . By contrast, the curves measured 2 h, 9 h, and 23 h after filling turn out to be abnormal with the appearance of an intermediate plateau around 5 Vrms, which the amplitude decreases with time. This phenomenon explains very well the results of DasGupta *et al.* as the latter extrapolate the part of the curve measured below 5 Vrms to obtain ϵ_\parallel . This phenomenon, which is an artifact, is also quite easy to understand and is due to the evaporation during time of the BP. This evaporation is very rapid—much more than what we expected at the beginning of this study (see Appendix)—and is responsible for the formation of the smectic phase close to the sides of the sample

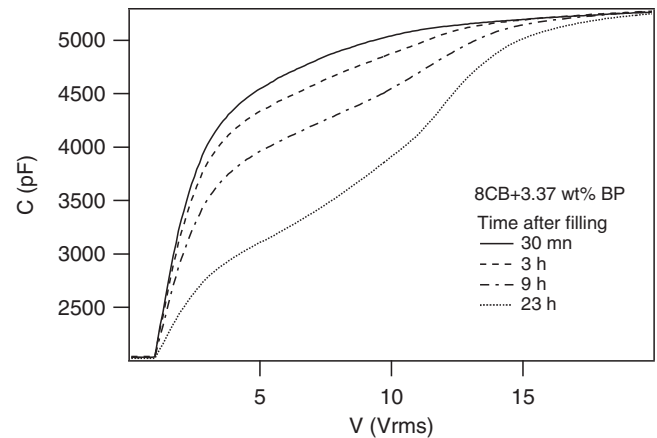


FIG. 5. Capacitance as a function of the applied voltage. The sample is $7.5\ \mu\text{m}$ thick and is not sealed on the sides with an UV glue. Curves were obtained by measuring the capacitance every 0.1 Vrms. The waiting time between two measurements was 4 s. All the curves were measured at the same temperature, $\delta T = 0.3^\circ\text{C}$, by taking for T_{NA} the value measured immediately after filling.

(indeed, T_{NA} quickly increases when the concentration of BP decreases according to the phase diagram [10,13]). An immediate consequence is that only the central part of the sample which is still nematic destabilizes under electric field, which leads to a rapid decrease of the global capacitance. We noted nevertheless that the smectic phase starts to rotate under electric field when the voltage increases above typically 7–8 Vrms (this is clearly visible under the microscope). This explains why the capacitance increases again at very large voltages. It must be emphasized that the effect of the BP evaporation on the measurements of ϵ_a , K_1 , and γ_1 is all the more important the closer the temperature is to the transition temperature, whereas it becomes almost negligible when the sample is entirely in the nematic phase. This explains why the data of DasGupta *et al.* only deviate strongly from ours close to the transition, when the smectic phase starts to grow in the nematic phase from the sides of the samples.

V. CONCLUSION

In conclusion, we strongly suspect that the anomalies on ϵ_a , K_1 , and γ_1 observed by Dasgupta *et al.* in the more concentrated mixtures of 8CB and BP are due to the rapid evaporation of the BP. This artifact may be easily avoided by closing the samples on the sides with an UV glue. If this precaution is taken, all the anomalies disappear, ϵ_a and K_1 remaining approximately constant while γ_1 diverges at the transition. These results are compatible with the fact that the smectic-A-to-nematic phase transition remains second order in this system at all concentrations of BP, as found by Denolf *et al.* [12,13]. This indicates that the coupling between the smectic order parameter and the nematic quadrupolar order parameter is never strong enough to change the order of the transition in this system [1,3], which is also compatible with the fact that the temperature range of existence of the nematic phase increases when the concentration of BP increases.

By contrast, it could be interesting to perform a similar study in the binary mixture 8CB+cyclohexane in which a tricritical point exists because of a large decrease of the temperature range of existence of the nematic phase when the concentration of cyclohexane increases [12,13]. In particular, a detailed study close to the tricritical point of this mixture would be valuable.

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APPENDIX: ADDITIONAL EXPERIMENTAL EVIDENCE OF THE BP EVAPORATION

In order to provide more direct experimental evidence for the rapid evaporation of the BP, we performed two additional experiments. First, we measured the sublimation rate of the biphenyl at room temperature (20°C). For this purpose, we recorded the weight as a function of time of a small quantity (0.1 g) of biphenyl powder deposited on the pan of a high precision balance (Mettler-Toledo XS205). The balance has a sensitivity of 10 micrograms and was controlled by a LabVIEW program. It was placed on an optical table to enhance stability. A typical curve is reported in Fig. 6 together with a curve at zero load. While the second curve is flat, indicating that there is no significant drift of the electronics, the first curve is continually decreasing. This shows that the BP sublimates at room temperature. Fitting this curve with a line shows that the sublimation rate was close to $2 \times 10^{-3} \text{ h}^{-1}$, i.e., close to 5% a day, which is far from being negligible.

Second, we measured as a function of time T_{NI} (liquidus temperature of the nematic-to-isotropic phase transition) and T_{NA} in a free drop of the mixture 8CB+3 wt % BP deposited on a glass plate. The result is shown in Fig. 7. We can

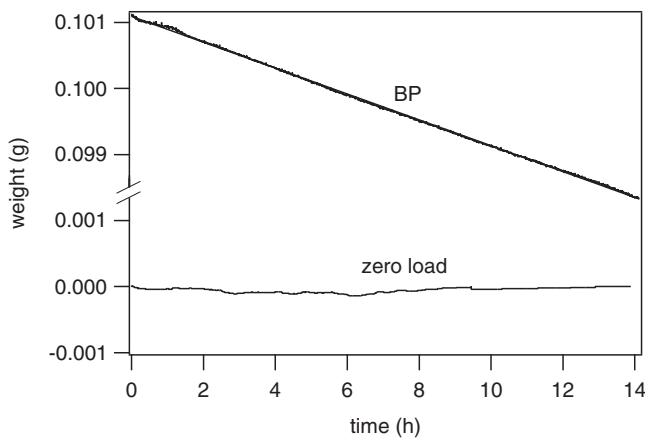


FIG. 6. Weight as a function of time of a small amount of BP powder deposited on the pan of a high precision balance and its best fit with a line. The weighting chamber of the balance was left slightly open in order that the atmosphere inside does not saturate in BP during the measurement. The bottom curve shows a recording at zero load, showing that the electronics does not drift significantly during the experiment.

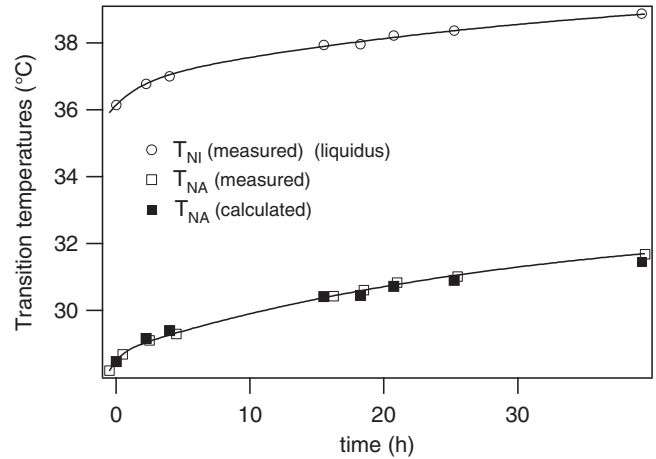


FIG. 7. Transition temperatures measured under the microscope in a free drop deposited on a glass plate as a function of time (in hours). The BP concentration was 3% by weight at the beginning of the experiment. The solid squares have been calculated from the measured T_{NI} and the phase diagram given in Ref. [13]. The solid lines are only guides for the eye.

see that both T_{NI} (empty circle) and T_{NA} (empty square) increase in time. To show that this evolution was well due to the biphenyl evaporation, we calculated from the phase diagram the temperature T_{NA} corresponding to each measured temperature T_{NI} and we reported these values on the graph (solid square). At a glance it appears that the measured curve of T_{NA} perfectly coincides with the curve calculated in this way, which clearly demonstrates that the BP evaporates.

Finally, we calculated from our measurements and the phase diagram the concentration of BP in the droplet as a function of time (Fig. 8). This curve shows that the concentration dropped off from 3 to 2 wt % in one day, which is a huge variation. In addition, it can be seen that the larger the concentration, the stronger the evaporation. This certainly explains why the authors only observed strong anomalies in the more concentrated samples in which evaporation effects are the greatest.

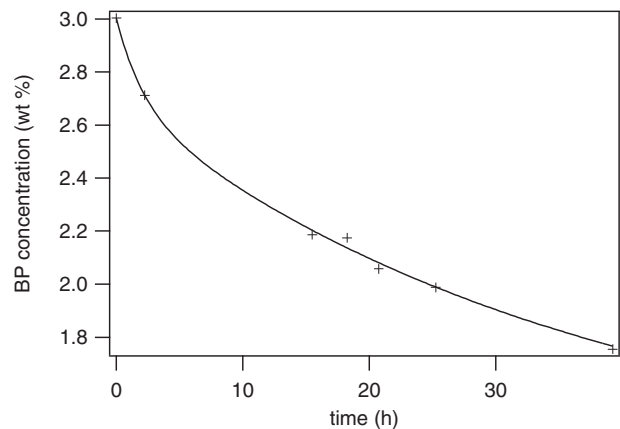


FIG. 8. BP concentration in a free drop as a function of time calculated from the measurements shown in Fig. 7 and the phase diagram given in Ref. [13]. The solid line is only a guide for the eye.

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