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Phase Behavior for Liquid Crystal Mixtures Having Low-Frequency Dielectic Relaxation

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Phase behavior and dielectric properties are reported for nematic liquid crystal mixtures having a dielectric anisotropy $\Delta\varepsilon$ which changes sign at low frequencies. Mixtures of two materials—component A, a pure material with a sign-reversing $\Delta\varepsilon$, component B, a negative anisotropy material—show composition-dependent phase behavior. For low concentrations of A, a glassy nematic is found at low temperatures. For high concentrations of A, melting of excess component A is observed, characteristic of a quasi-eutectic-forming system. The temperature dependence of the dielectric relaxation yields an activation energy of 0.89 ± 0.04 eV for molecular reorientation.

I INTRODUCTION

Dielectric relaxation studies of liquid crystals have been a subject of considerable interest since the work of Maier and Meier[1] and Baessler, Beard, and Labes.[2]

Several experimental[3–16] and theoretical papers[17,18] on the subject have appeared. Interest in the phenomenon has been stimulated by the discovery of nematic materials with low frequency relaxation associated with a reversal of the sign of the dielectric anisotropy $\Delta\varepsilon$ $(\varepsilon_{\parallel} - \varepsilon_{\perp})$,[4–6,8,10–12,14–16] thus allowing the use of two-frequency address techniques for rapid turn-on or turn-off of display devices.

However, relatively little data is available concerning the phase behavior of mixtures showing dielectric anisotropy reversal.[5] In this paper we report both phase behavior and dielectric data for such mixtures.

II THERMAL STUDIES AND PHASE BEHAVIOR

The system studied consisted of mixtures of two nematogenic components: 4-pentylphenyl-2-chloro-4-(4-pentylbenzoyloxy) benzoate[19] (hereinafter referred to as component A) having a dielectric anisotropy $\Delta\varepsilon$ which reverses sign at audio frequencies;[12] and a multicomponent mixture[20] (component B) having a negative dielectric anisotropy.

The phase behavior of the mixtures was determined by differential scanning calorimetry[21] (DSC) at scan rates of 5°C/min. Samples of ten different compositions ranging from 0.0 to 1.00 weight fraction component A were formed by careful mixing.[22]

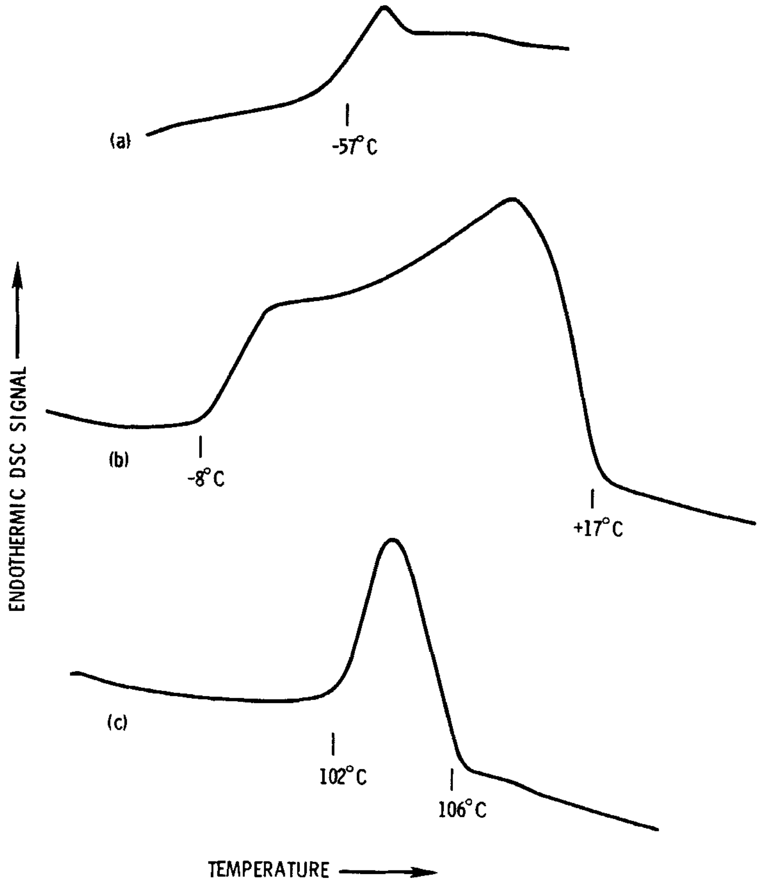

FIGURE 1 DSC tracings for three transitions of a mixture with X = 0.584: (1a) change in heat capacity at the glass transition: (1b) melting of excess component A: (1c) nematic–isotropic transition.

Pure component A undergoes a crystal–nematic phase transition at 39.6°C (latent heat 23.8 KJ/mol) and nematic–isotropic transition at 123.0°C (latent heat 1.18 KJ/mol).[23] Component B is reported[24] to undergo a glass transition at about −53°C, a crystal–nematic transition at 3°C, and a nematic–isotropic transition at 83°C. The crystal–nematic transition is detectable only after extended annealing at a temperature about half-way between the glass transition and crystal–nematic temperatures.[25] The present DSC studies were confined to glassy component B.

For mixtures of intermediate composition, the DSC behavior depended sensitively on both composition and thermal treatment. For mixtures with sufficiently high weight fraction, X, of component A, three transition regions were observed (Figure 1): a glass transition as indicated by a change in heat capacity (Figure 1a); a broad transition with a DSC shape characteristic[26] of the melting of excess component A (Figure 1b); and a nematic–isotropic transition (Figure 1c). (Of course, for pure component A, no glass transition is observed, and the excess melting peak becomes the crystal–nematic transition peak.)

In order to obtain the proper excess melting behavior it was necessary to subject each sample to an appropriate thermal treatment[27] to produce an equilibrium state. The treatment consisted of a liquid nitrogen quench (to shatter the sample and produce a large surface/volume ratio), followed by storage at a temperature of about −20°C (i.e. below the lowest temperature for partial melting—the quasi-eutectic temperature) for one or more days.[28] During the storage period, thermal equilibration (crystallization of the excess component) took place for most samples. Samples not thermally treated were unsuitable for determination of equilibrium thermal parameters. They showed two possible types of DSC behavior:

1) Untreated samples of higher X-values ($X > 0.647$) crystallized during the DSC run, yielding an exotherm which overlapped the higher temperature excess component melting endotherm.

2) Samples with $X < 0.647$ would not crystallize at all unless subjected to a lengthy cold treatment. Furthermore for $X = 0.496$ only two of the several cold-treated samples tested actually crystallized; these two yielded noisy, poor quality DSC spectra. As a result of this problem, no attempts were made to crystallize samples for $X < 0.496$.

The phase diagram for the mixtures is shown in Figure 2. For $X < 0.496$ no melting peak is observed, only a glass transition at about −56°C and a nematic–isotropic transition at a concentration-dependent temperature. Apparently formation of a crystal lattice upon cooling is not favored. Instead, the nematic liquid crystal is preserved to low temperatures. As the temperature is lowered the viscosity evidently become sufficiently high that glass-like

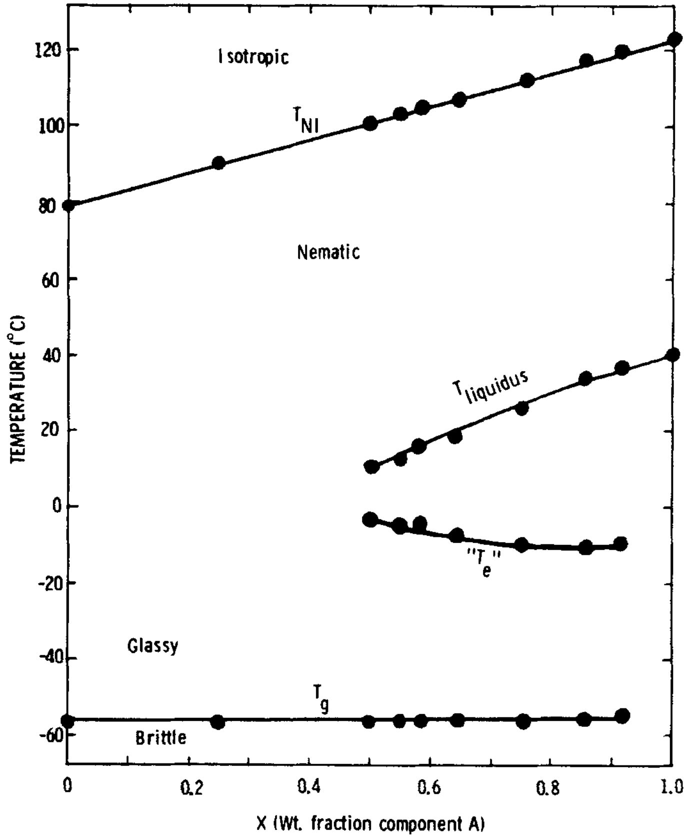

FIGURE 2 Phase diagram for cold treated mixtures of components A and B.

behavior results. At about $-56°C$ a transition from a glassy to a brittle phase takes place upon cooling. The glass transition is observable in all samples containing component B.

For $X > 0.496$ the DSC spectra clearly demonstrate melting of the excess solid component A in the mixtures (for example, see Figure 1b). The shape of the excess melting curve of Figure 1b is reminiscent of that calculated in Ref. 26. The melting range of the excess component is determined by extrapolation to the baseline of the leading and trailing edges of curves like that of Figure 1b. Two interesting features of the excess melting curves are evident from examination of Figures 1b and 2. First, from Figure 1b, we see that no eutectic melting peak[26] is present. This behavior is not unreasonable since any such peak for sufficiently high X would be due to melting of all of component B plus some component A; and evidently glassy component B exhibits no apparent

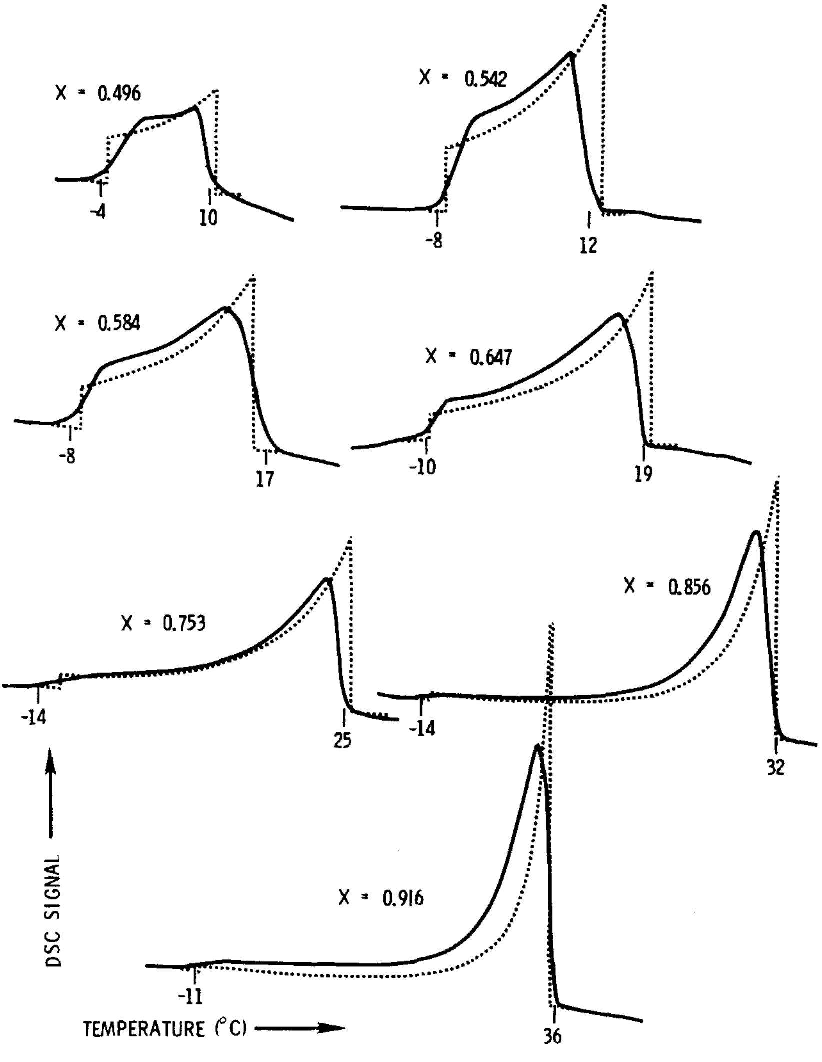

FIGURE 3 Melting peak shapes for excess component A in cold-treated mixtures. Dashed curves are calculated, solid ones are experimental DSC tracings for weight fractions (X) indicated.

melting transition. The second unusual feature is the concentration dependence of the onset of excess melting ("T_e" in Figure 2). For ordinary eutectic-forming systems this onset would occur at the eutectic temperature T_e which would be concentration-independent.[26] The use of quotation marks in Figure 2 to label "T_e" stresses the quasi-eutectic-forming nature of the system.

The temperature of completion of melting of excess component A is labeled $T_{liquidus}$ in Figure 2. Between "T_e" and $T_{liquidus}$ (the melting range) the equilibrium state is a "slush" of nematic liquid crystal plus crystalline component A. Above T_{liquidus} a nematic comesophase exists.

It is possible to calculate DSC lineshapes for the melting of excess component A by converting the weight-fraction compositions of the mixtures to approximate molar fractions and using the techniques of Ref. 26. Since "T_e" is concentration-dependent, it is also necessary to regard the eutectic composition as an adjustable parameter in order to fit "T_e". The calculated excess melting curves shown in Figure 3 (dashed curves) are qualitatively similar to the experimental DSC tracings (solid curves), indicating that although eutectic-forming behavior is not ideal in the present system, it is at least approximately so.

III DIELECTRIC STUDIES

Three mixtures, having $X = 0.245, 0.496$, and 0.753, were selected for dielectric measurements. (In the following discussion these mixtures are labeled by their approximate weight proportions, 1 : 3, 1 : 1, and 3 : 1.) The nematic mixtures were placed in capacitive cells with circular electrodes (area 1 cm^2, separation ≈ 12 μm). Uniform homogeneous alignment of the liquid crystal was produced by rubbing. Strip heaters were attached to both outside cell faces and a copper-constantan thermocouple placed between the cell and heater. Tape was then wrapped around this assembly to provide mechanical rigidity. Heater power was supplied by a regulated, variable voltage power supply, and the temperature was measured by reading the thermocouple output with a potentiometer (ice water reference). The complete test cell was placed between the 5 cm diameter poles of an electromagnet spaced ~ 8 mm apart. Due to thermal contact between the test cell and the water-cooled pole pieces, the minimum achievable cell temperature was about 14°C.

For zero magnetic field the measured capacitance is proportional to $\varepsilon_\perp$ (the dielectric constant perpendicular to the nematic axis) because the liquid crystal molecules are parallel (to within 3°) to the cell electrodes due to homogeneous alignment by rubbing.[29] A sufficiently strong magnetic field applied perpendicular to the cell surface will align the diamagnetic liquid crystal molecules so that $\varepsilon_\parallel$ (the dielectric constant parallel to the nematic axis) is measured. From capacitance versus field plots it was found that alignment for the 1 : 1 mixture was essentially complete at a magnetic field of 1.95 tesla. For the 3 : 1 mixture the alignment was not quite complete at this field strength. Extrapolation to higher fields indicated that the resultant error in $\varepsilon_\parallel$ is $<2\%$.

A General Radio (GR) 1608 impedance bridge with an external audio generator and tuned detector was used to measure capacitance at frequencies from 100 Hz to 10 kHz, and a Boonton Electronics 75C capacitance bridge at frequencies from 5 kHz to 500 kHz. The Boonton is a three terminal bridge which can compensate for lead capacitance while the GR cannot. The difference between capacitance measured by each bridge at a constant magnetic field and equal frequency is the stray capacitance which must be subtracted from the capacitance measured by the GR bridge. Both bridges are accurate to within $<1\%$ over their ranges. All measurements were made with 1 V peak-to-peak applied to the cell. The value of measured capacitance was independent of measuring voltage. It was also necessary to make empty cells—without liquid crystal—to the same dimension as our test ones in order to measure the free space capacitance. The dielectric constant is then computed as the ratio of filled cell capacitance to empty cell capacitance. It is estimated that the size of all our cells is constant within 5%. Adding a 1% temperature error and a 1% frequency error to the above mentioned errors, the maximum error for measuring $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ is $< \pm 8\%$. A representative error bracket is shown in the appropriate figures (following).

Figure 4 shows $\Delta\varepsilon$ versus frequency at constant temperature for the 1 : 3 mixture. The most important results is that $\Delta\varepsilon < 0.1$ for the entire range of frequency and temperature.

Figures 5 and 6 show $\Delta\varepsilon$ versus frequency at constant temperatures for the 1 : 1 and 3 : 1 mixtures, respectively. The value for $\varepsilon_{\perp}$ (which is independent of frequency) is shown in parentheses after each temperature.

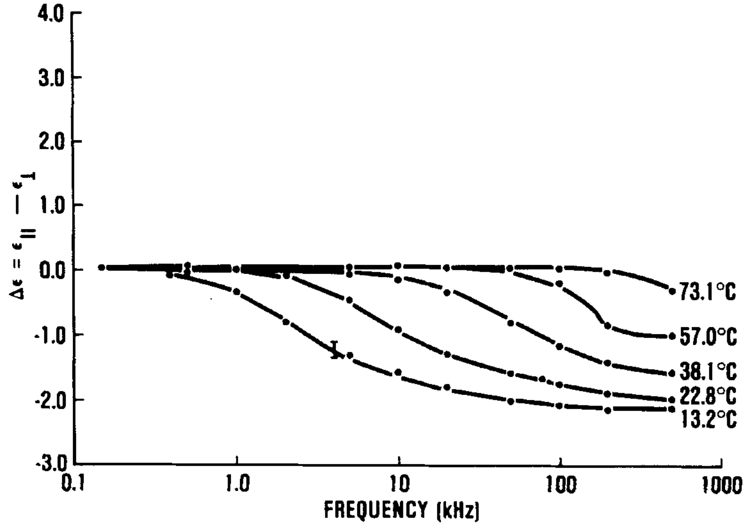

FIGURE 4 $\Delta\varepsilon$ versus frequency at constant temperatures for the 1 : 3 mixture.

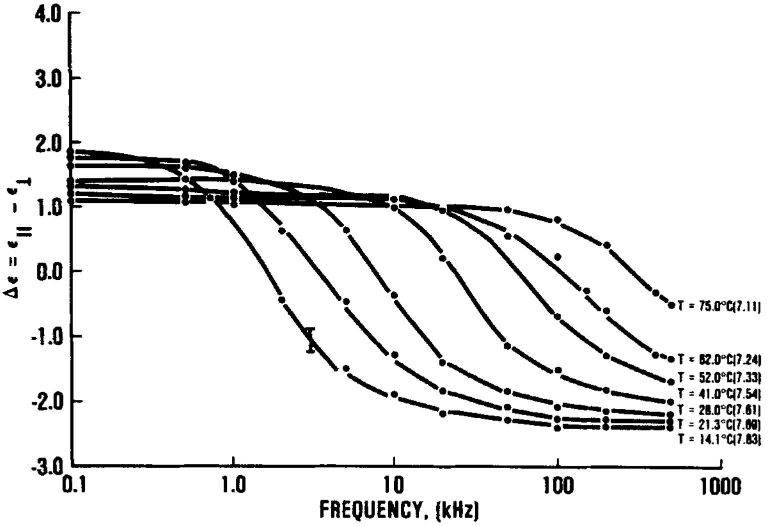

FIGURE 5 Δε versus frequency at constant temperatures for the 1 : 1 mixture.

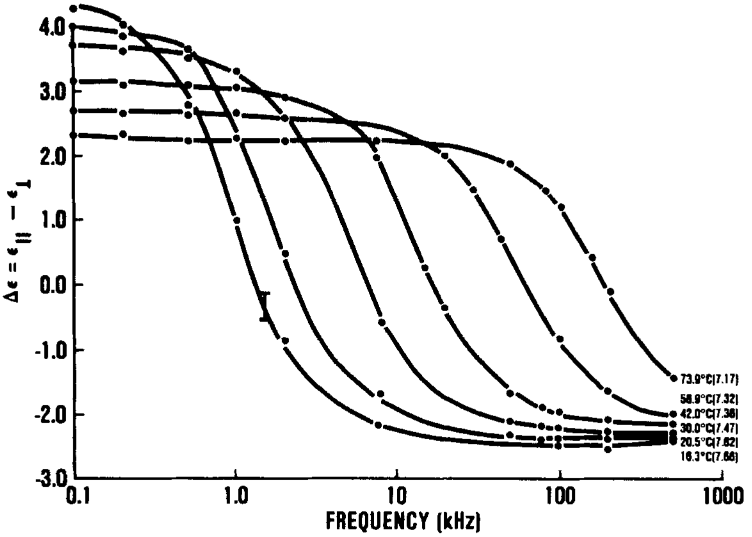

FIGURE 6 Δε versus frequency at constant temperatures for the 3 : 1 mixture.

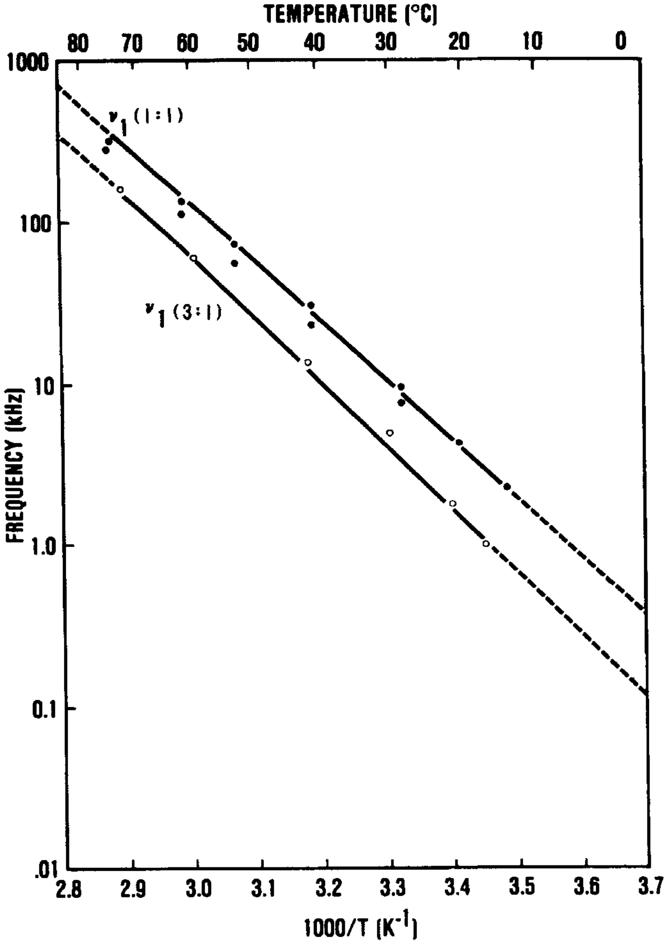

FIGURE 7 Temperature dependence of ν_1 for 1 : 1 and 3 : 1 mixtures.

The measured values of $\varepsilon_{\parallel}$ are described by the expression[3]

$$\varepsilon_{\parallel} = \varepsilon_H + \frac{\varepsilon_S - \varepsilon_H}{1 + \omega^2 \tau_1^2}, \tag{1}$$

where ε_H is the high frequency dielectric constant, ε_S the static dielectric constant, ω $(=2\pi\nu)$ the angular frequency of the measuring field, and τ_1 a relaxation time characteristic of hindered rotation about the short molecular axis.[3] The relaxation frequency ν_1 $(= 1/2\pi\tau_1)$ was determined for mixtures

TABLE I

Activation energy of molecular reorientation from dielectric measurements.

Liquid Crystal	Activation Energy (eV)
This work	0.89 ± 0.04
binary cholesteryl chloride and cholesteryl myristate mixtures[a]	0.99 to 1.30
ternary mixture of benzylidine-cyanoanilines[b]	0.71
single component phenyl benzoates[c]	0.65 to 0.90
binary mixture of chloro-benzoyloxy benzoates[d]	0.83
multicomponent phenyl benzoates[e]	0.84 to 0.88

[a] Ref. 2
[b] Ref. 3
[c] Ref. 8
[d] Ref. 12
[e] Ref. 16

1 : 1 and 3 : 1 from the data of Figures 5 and 6. The temperature dependence of ν_1 for the two mixtures is shown in Figure 7. It is well known[3,30] that

$$\nu_1 \propto \exp(-W/kT) \tag{2}$$

where W is the height of the potential barrier hindering molecular reorientation, k is the Boltzmann constant, and T the absolute temperature. From the data of Figure 7 we find $W_{1:1} = W_{3:1} = 0.89 \pm 0.04$ eV. Table I shows that this value is in reasonable agreement with the result of Bucher *et al.*,[12] and falls within the range of values obtained for other liquid crystals. From the range of values reported in the table (0.65 to 1.3 eV) it appears that the energy barriers to molecular reorientation are moderately sensitive to molecular structure.

Note added in proof:

M. Kresse, Ch. Selbmann, and D. Demus, *Mol. Cryst. Liq. Cryst.* **44**, 179 (1978), have discussed dielectric properties of multicomponent systems.

Acknowledgement

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