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Material characterization for electroconvection

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We report a set of material characterizations on the nematic mixture *Mischung V*. With these measurements, as well as previously known results, *Mischung V* becomes the second nematic liquid crystal possessing a complete set of known physical parameters relevant for electroconvection, enabling quantitative comparison with theoretical predictions to be made. Additionally, we have identified a stable dopant which induces in *Mischung V* the electrical conductivity necessary for observing the conduction regime of electroconvection. *Mischung V* is thus validated as a suitable substitute for materials that have traditionally been chosen for these types of experiments. However, *Mischung V* does not present the same experimental difficulties as traditional materials.

1. Introduction

Electroconvection (EC), or electrohydrodynamic convection in nematic liquid crystal (LC) materials has proved to be a particularly fruitful model system for studying nonequilibrium pattern formation [1], anisotropic hydrodynamics, turbulence [2] and defect coarsening [3]. Electroconvection experiments have made substantial contributions in all these fields. The preponderance of the experimental work on EC has taken place in spite of one well known and particularly vexing experimental difficulty. This difficulty arises from the paucity of liquid crystal materials: (a) that possess appropriate values of electrical transport coefficients for EC; (b) for which all relevant physical properties have been measured; (c) that are chemically and thermally stable; (d) that can be doped to produce a desired electrical conductivity; (e) that are readily available. Of these factors, controlling the electrical conductivity is normally the most serious difficulty with regard to electroconvection. The lack of measured values of physical parameters is not *per se* an obstacle to EC experiments, but it substantially hinders quantitative comparison with theoretical results. This article endeavors to remedy this situation by reporting on a detailed characterization of not only physical parameters but also suitability for EC experiments of the nematic mixture commonly known as *Mischung V*. This material is proposed as a candidate benchmark standard material for EC enabling robust reproducibility of both quantitative and qualitative experiments.

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We report on measurements of four of the five independent viscosity coefficients, and of all electrical transport properties as well as the diamagnetic susceptibility. These measurements rely partly on previous measurements of mechanical and optical properties. Additionally, we report on a dopant that induces a controllable electrical conductivity that is robust, reproducible and stable over several months and counting.

2. Background

The vast majority of EC experiments, going back over thirty years, have employed a single compound, methoxy benzylidene butylaniline (MBBA). In addition to possessing appropriate values of both the dielectric anisotropy ($\Delta\varepsilon$) and conductivity anisotropy ($\Delta\sigma$) necessary for EC to occur, MBBA has the singular advantage of being one of the first thermotropic liquid crystal compounds identified. Therefore, many techniques to measure physical properties of liquid crystals were perfected using MBBA; essentially all its physical properties have been measured. This includes the most challenging characterization to perform: all five independent viscosity coefficients have been measured. We are unaware of any other liquid crystal material which has been as extensively studied. Unfortunately, the compound MBBA is a Schiff's base; the linkage between the two phenyl rings is easily hydrolysed, which leads to difficulty in maintaining purity. This in turn leads to drifts in the physical properties, most notably the electrical conductivity. Notwithstanding these well known problems, many important experimental results have been obtained using MBBA.

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A handful of other LC compounds and mixtures have also been employed. A mixture of alkylazoxybenzenes that is traditionally known as Phase 5 [4], and a fluorinated compound containing both phenyl and cyclohexyl rings, known by the trade name I52 [5], are the materials of choice for studying effects due to weakly electrolytic charge transport. Phase 5 is no longer commercially available, and has proven difficult to dope reliably to obtain the desired, stable conductivity. Only one effective dopant for I52 has been identified, and this dopant (iodine) leads to an electrical conductivity that slowly drifts. Moreover, I52 is slightly unstable when held at temperatures at or near its clearing point [6]. Furthermore, only one viscosity coefficient, the orientational viscosity, γ_1 has been measured for both these materials.

The liquid crystal display industry has led to the development of an enormous number of compounds and mixtures, many of which have been exhaustively studied. Unfortunately, not only do materials that are designed for information display applications possess inappropriate physical properties for EC (convection is something to be avoided in a display), but also such materials are designed to minimize the electrical conductivity in order to reduce display power consumption. Thus, the majority of material syntheses and characterizations for information display are of no benefit for EC.

One more material has been occasionally used for EC experiments. This is a mixture of phenyl benzoates commonly known as *Mischung V* (MV). A more detailed description of the mixture is found below. As with all the materials listed above, control of the electrical conductivity of MV is problematic. Like I52 and Phase V, MV's material properties are not fully known. In this paper, we present a novel and robust approach to the doping of this compound, as well as measurements of almost all the unknown material properties; we have also validated MV as a suitable material for EC. With these measurements, essentially all the shortcomings (a)–(e) listed above are ameliorated. Indeed, MV appears to be a fine substitute for MBBA for EC measurements.

3. Experimental details

Mischung V is a mixture of four compounds, in the following ratios:

4-hexyloxyphenyl-4′-methoxybenzoate ($\bar{1}O\bar{6}$) 22.0%,
4-octyloxyphenyl-4′-pentyloxybenzoate ($\bar{5}O\bar{8}$) 30.3%,
4-heptyloxyphenyl-4′-hexyloxybenzoate ($\bar{6}O\bar{7}$) 13.3%,
4-butyloxyphenyl-4′-hexylbenzoate ($6O\bar{4}$) 34.4%.

Some of these compounds were available at the Liquid Crystal Institute at Kent State University; others were synthesized via a straightforward condensation reaction. The reaction precursors for all compounds are alkoxybenzyl alchohols and alkyl- or alkoxy-benzoic acids; all are commercially available. All compounds were purified by recrystallization from ethanol followed by chromatographic column separation before mixing in the specified ratios. The mixture as prepared exhibited a narrow nematic to isotropic phase transition at 69.2°C.

As stated above, lack of knowledge of the viscosity coefficients of liquid crystal materials is a significant obstacle to their employment in EHC experiments. One viscosity coefficient, γ_1 has been previously measured for MV. We have employed the dynamic light scattering (DLS) technique to measure three additional independent viscosity coefficients. Theoretical treatments of EC normally employ the Ericksen–Leslie formulation for nematodynamics [7]. In this formulation there appear six viscosity coefficients usually called the Leslie coefficients, α_{1-6}; Parodi's relation constrains one of these, leading to five independent Leslie coefficients. DLS measurements yield combinations of the Leslie coefficients, usually called the Miesowicz coefficients $\eta_{(a,b,c)}$. Using specific scattering geometries as described in [8] and [9], to isolate dynamic scattering from specific director modes, we measure all three Miesowicz coefficients: $\eta_a \equiv \alpha_4/2$, $\eta_b \equiv (\alpha_3 + \alpha_4 + \alpha_6)$ and $\eta_c \equiv (-\alpha_2 + \alpha_4 + \alpha_5)/2$. These measurements utilize the previously measured [10] value for the rotational viscosity, $\gamma_1 \equiv \alpha_3 - \alpha_2$. Because Parodi's relation, $\alpha + \alpha_3 = \alpha_6 - \alpha_5$, constrains one coefficient, we can obtain values for all Leslie coefficients except α_1. The results are summarized in the table. α_1 does not appear in the Miesowicz coefficients, and is by far the most difficult to measure by light scattering or any other means. It remains unknown for MV.

In addition to the viscosities, the physical parameters that are most important to characterize for electroconvection are the electrical transport properties, specifically the two distinct eigenvalues of the dielectric susceptibility and conductivity tensors: $\varepsilon_\parallel$, $\varepsilon_\perp$, $\sigma_\parallel$ and $\sigma_\perp$, respectively. Of these, the conductivities have the greatest bearing on electroconvection. The mixture MV by itself has too low an electrical conductivity for investigation of the conduction regime of electroconvection. Undoped MV has $\sigma_\perp \sim 4 \times 10^{-9}\ \Omega^{-1}\ \mathrm{m}^{-1}$. In order to control the electrical conductivity reliably and systematically, we added a small amount of dopant to the mixture. Various dopants were tried, including alkyl ammonium salts,

Table. Leslie viscosity coefficients for *Mischung V* at different temperatures. All coefficients are reported in cP.

Temp/°C	α_2	α_3	α_4	α_5	α_6
23.5	−558.7	24.91	75.88	540.0	6.21
28.0	−405.3	0.20	165.7	317.1	−88.04
35.0	−260.4	14.78	100.8	180.3	−65.35
40.5	−187.6	17.09	61.65	128.3	−42.23
45.5	−141.4	15.70	73.62	63.9	−61.79

charge transfer complexes, etc. The most effective and reliable dopants found were the precursors used to synthesize phenyl benzoates. Specifically, the dopant is a mixture of equal weights of *p*-heptylbenzoic acid and octyloxyphenol. For the measurements reported here, we added 3.8 wt % of this dopant to the mixture described above. Because these precursors are rather similar to phenyl benzoates, they are also highly soluble. Moreover, alkylbenzoic acid and alkylphenols should also act as weak proton donors when dissolved in phenyl benzoates. We have not confirmed whether this is indeed the mechanism whereby the conductivity is increased on the addition of these compounds; however, the resulting mixture has the desired properties.

We measure the dielectric constants and the conductivities by monitoring the capacitance and loss of a thin layer of the LC mixture as it undergoes the magnetic field induced splay Fréedericksz transition. This measurement also yields the diamagnetic anisotropy, $\Delta\chi$. The LC is contained in a sample 'cell' [11] between flat, transparent conducting electrodes, separated by distance d, in the parallel plate capacitor geometry. The electrodes have been treated to induce planar alignment of the nematic director. Before the LC is introduced we measure the capacitance of the empty cell and the distance separating the electrodes. The capacitance of the empty cell is $C_0 = \varepsilon_0 A/d$ where ε_0 is the permittivity of free space, and A is the active area of the etched electrodes.

The doped LC is introduced between the electrodes using capillary action. The cell is then placed in a temperature controlled copper block. This block is positioned between the polefaces of an electromagnet, such that the magnetic field is perpendicular to the parallel plates. The capacitance C and conductance g of the LC layer are monitored as a function of the magnetic field as this field is increased well above the Fréedericksz field, H_f.

The capacitance of the cell at zero magnetic field is then $\varepsilon_0 \varepsilon_\perp A/d$ and the conductance is $\sigma_\perp A/d$. C and g as functions of H are extrapolated to $H \to \infty$ to yield $\varepsilon_0 \varepsilon_\parallel A/d$ and $\sigma_\parallel A/d$ respectively. Figure 1 shows an example of capacitance and conductance data vs magnetic field. Figure 2 shows the electrical transport properties as a function of temperature for the sample doped as described above. In addition to the transport properties, this measurement also yields the Fréedericksz threshold field, $H_f = \pi/d(K_1/\Delta\chi)^{1/2}$. With the previous measurement of K_1 [10] we can obtain the diamagnetic susceptibility anisotropy $\Delta\chi$. At 25°C, $\Delta\chi = 4.7 \times 10^{-8}$ (cgs). The electrical conductivities are a sensitive test of material stability. The electrical conductivity of this relatively low-conductance sample changed by less than 40% over a period of more than eight months. This rate of change is only attainable in traditional EC materials when they are doped extraordinarily heavily.

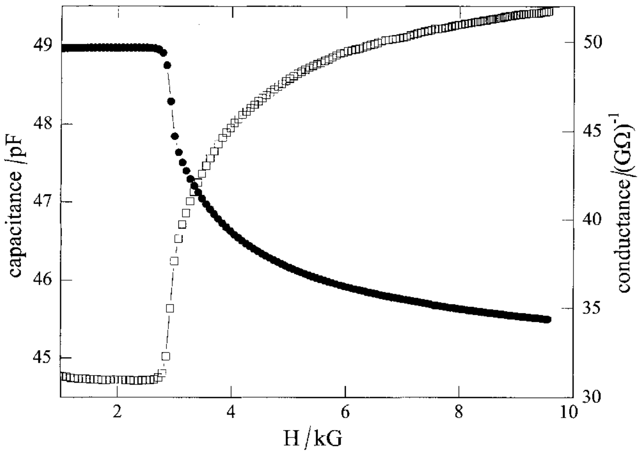

Figure 1. Example of capacitance (●) and conductance (□) of doped *Mischung V* sample as it undergoes the magnetic field induced Fréedericksz transition. This data is used to extract the dielectric constant and conductivity eigenvalues.

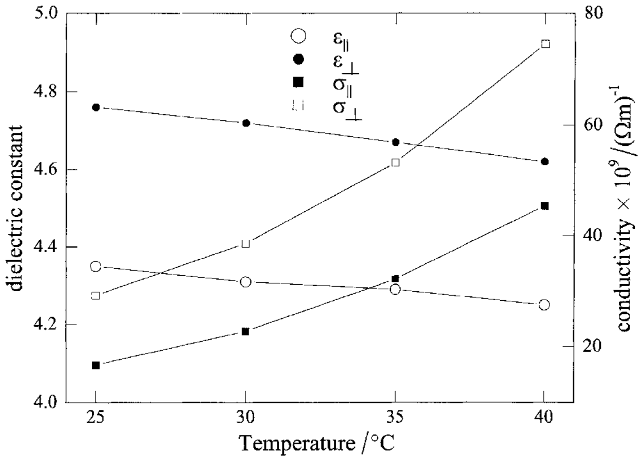

Figure 2. Dielectric constants and conductances of doped *Mischung V* as a function of temperature.

We have also validated this material's suitability for EC experiments. Figure 3 shows the critical onset voltage for EC as a function of frequency at different temperatures. These curves show the classic behaviour: vanishing frequency dependence at low frequencies followed by a sharp increase in the 'conduction' regime and then a sharp knee in the curve at the so-called cutoff frequency above which one observes the 'dielectric regime'. The cutoff frequency increases dramatically with temperature.

4. Conclusion

Mischung V is demonstrated to be an excellent material for experiments on electroconvection in nematics. We

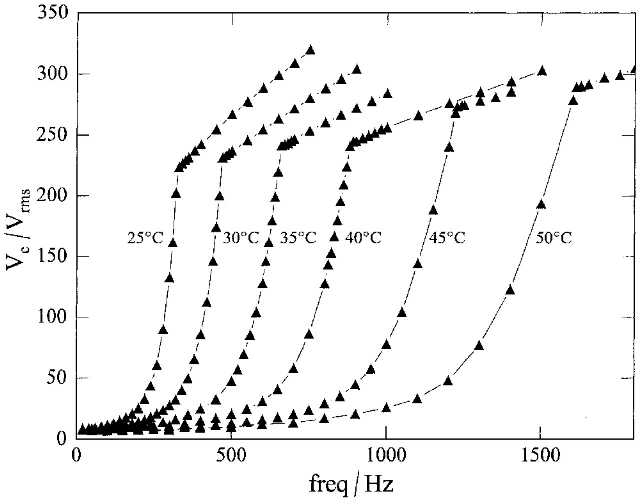

Figure 3. Critical potential difference needed to induce EC as a function of frequency for MV doped as described in the text.

know of no other material which is as (i) chemically stable, (ii) easily doped, (iii) adequately characterized and (iv) easily obtained.

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