Molecular Crystals and Liquid Crystals

Effect of Strong Electric Fields on Phase Transitions in Some Liquid Crystals

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EFFECT OF STRONG ELECTRIC FIELDS ON PHASE TRANSITIONS IN SOME LIQUID CRYSTALS

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<u>Abstract</u> An electric field couples to the orientational order in liquid crystals through dielectric anisotropy and is conjugate to the order. However the ionic flow produced by the field causes a dissipation of energy in the medium rendering an experimental study of the effect of the field on the order difficult. We have devised a method of measuring the local temperature of the sample, and both the dielectric constant whose value depends on the orientational order and the conductivity which is sensitive to the short range order in the medium. We report the electric field temperature phase diagrams of pentyl cyanobiphenyl (5CB) and octyloxy cyanobiphenyl (8OCB). The results include (a) the field induced enhancement of the orientational order (b) the critical field beyond which the nematic paranematic transition is continuous and (c) the effect of the field on the nematic-smectic A transition in 8OCB. The results are analysed using the appropriate Landau theories.

INTRODUCTION

Nematic liquid crystals have a long range orientational order of anisotropic molecules. The order parameter which is a second rank tensor couples to external orienting fields like magnetic or electric fields through the anisotropy in the appropriate susceptibility of the medium. As such these fields are conjugate to the orientational order in the medium. The effect of the field is simpler to discuss in the case of a material with positive anisotropy of susceptibility, in which the nematic director aligns preferentially along the field direction. Deep inside the nematic phase, the field quenches the thermal fluctuations of the director and the resulting enhancement of the orientational order depends *linearly* on the field.[1,2] The field also induces an orientational order in the otherwise isotropic phase so that the phase transition at relatively low fields occurs between the latter phase and a phase with a much higher order parameter. The transition point increases while the jump in order parameter at that point decreases with increase of field. Since the two phases have the same symmetry, in analogy with liquid gas transition under pressure, there is a critical

field beyond which there is continuous evolution of the orientational order with temperature without any phase transition. There have been a number of theoretical calculations on such phase diagrams both in the framework of Landau theory[3-5] and molecular models.[6-8]

From the experimental point of view, the volume diamagnetic susceptibilities of the organic compounds which form low molecular mass liquid crystals are relatively low ($\sim 10^{-7}$ cgs units). As such, only a small shift in the transition point has been observed under the action of a magnetic field.[9] This problem can be overcome if large anisotropic colloidal particles form the nematic phase, as has been demonstrated recently in a suspension of fd virus in an appropriate solvent.[10] The dielectric anisotropy of the medium can be quite large (~ 10) in materials with a strong longitudinal molecular dipole moment. The critical field in such cases lies within the experimentally attainable range. However, liquid crystals usually have some ionic impurities and the dissipation of energy due to ionic flow produces a substantial heating of the sample. Helfrich[11] used single short duration electric pulses to estimate the rise in transition temperature by direct observations on a nematic cell. Later, Nicastro and Keyes [12] qualitatively estimated the critical electric field in a nematic liquid crystal. Recently Lelidis and Durand[13,14] could study the phase diagram quantitatively by applying short electric field pulses, adjusting the duration between successive pulses to be long enough (~ 10 sec) to prevent heating of the sample. They used an optical technique to monitor the order parameter of the sample and fitted their data to a simple Landau theory. More recently they have also verified the theoretical prediction[15] that an external field can induce a nematic phase with a large orientational order in materials which undergo a direct smectic A to isotropic phase transition.[16]

In this paper we propose a different experimental set up to explore the effect of strong electric fields on phase transitions in liquid crystals. In this method the local temperature of the sample is measured and an impedance analysis of the cell is used to measure both the dielectric constant and the electrical conductivity of the samples. The former is sensitive to the long range orientational order in the medium while the latter is sensitive to both short and long range positional order in the medium. In the present paper we report some of our first results using this technique.

EXPERIMENTAL

The electrical heating of the sample will not be a problem if its temperature can be measured accurately. We use a thin film of nickel, which has a large tempera-

ture coefficient of resistance, to measure the local temperature. The film which is coated on a glass plate is patterned using a photolithographic technique to obtain a resistance $\sim$ 180 ohms in a circular area of 0.5cm diameter (Figure 1). It is covered by an insulating layer of SiO or SiO_2 on which an aluminium electrode with the same area is deposited in vacuum. A similar electrode is etched either in an ITO or aluminium-coated glass plate which is used as the counter electrode. The gap between the plates is fixed by mylar spacers and is typically 19μm. The electrodes are treated with ODSE (which is a polymerisable silane compound with long alkyl chains) before assembling the cell to get a homeotropic alignment of the nematic director (Figure 2). The block diagram of the experimental set up is shown in Figure 3. The output of an SRS 830 lock-in amplifier is fed to a Trek model 601B amplifier. The high voltage output of the latter is applied to the cell. An electric impedance analysis of the cell allows us to measure the dielectric constant and resistance of the
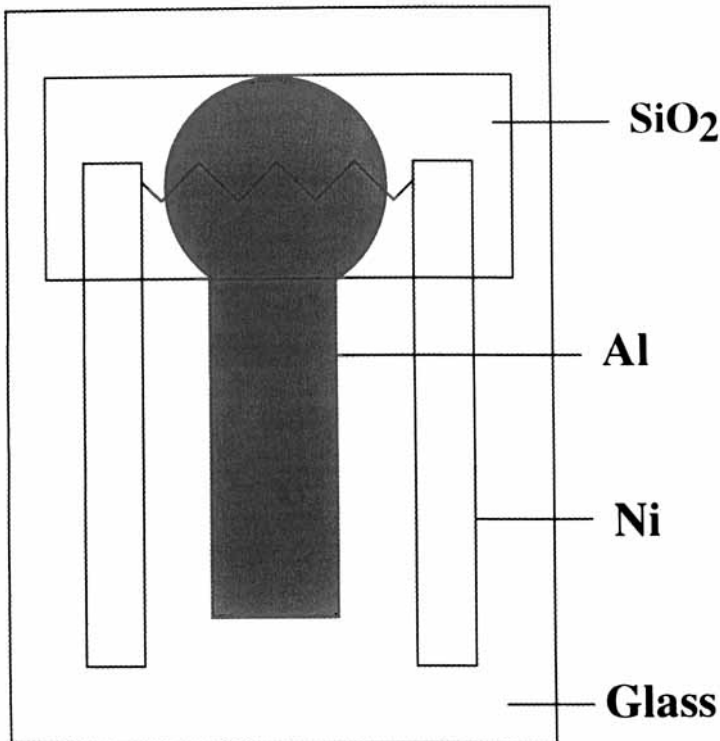

FIGURE 1 Schematic diagram of the patterned coatings on one of the glass plates of the liquid crystal cell. The Ni thermometer and Al electrode are insulated from each other by an SiO_2 layer.
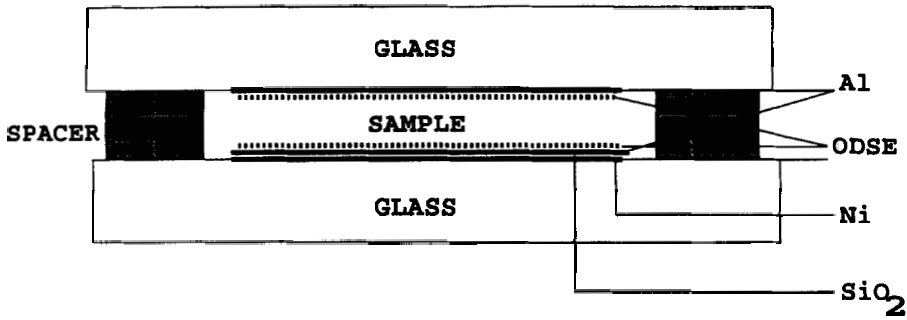
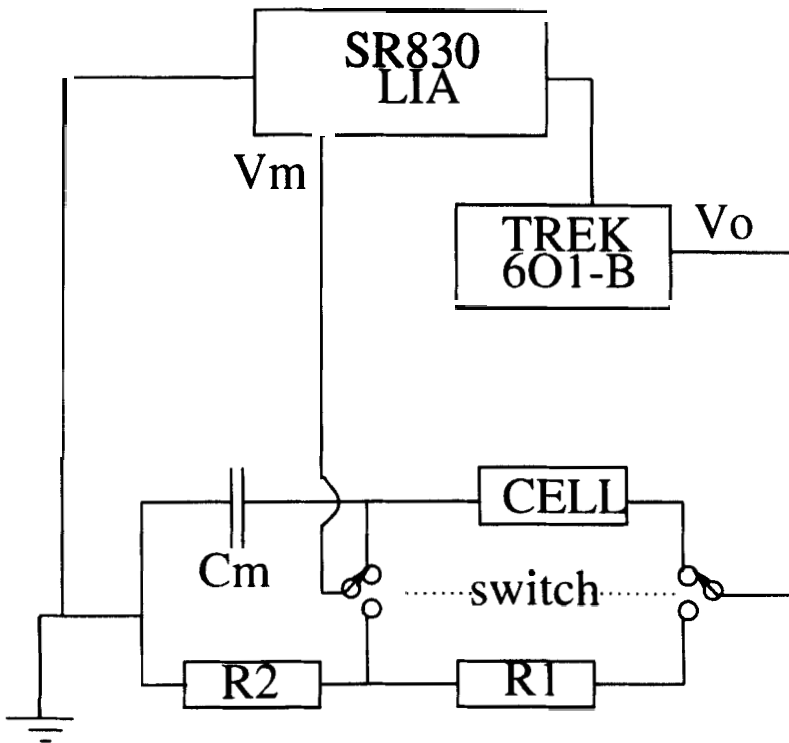FIGURE 2   Cross sectional view of the liquid crystal cell used in the experiment.

FIGURE 3   Block diagram of the experimental set up used for the impedance analysis of the liquid crystal cell.

sample. The amplitude and phase of the amplifier output are calculated by measuring the AC signal across a resistance R_2 which is in series with a large resistance R_1. At any given frequency, the phase of the amplifier output depends on the voltage. The current flowing through the sample is measured by noting the amplitude and phase of the voltage developed across a capacitance C_m (~ 1 μFarad) which is connected in series with the cell. If V_o and ϕ_m are the amplitude and phase of the output of the amplifier, and V_m and ψ_m are the same quantities measured across the capacitor C_m, it is easy to show that the sample resistance (R_S) and capacitance (C_S) are given by:

$$R_S = Y/2\pi\nu \sin\alpha \tag{1}$$

$$C_S = X/Y \tag{2}$$

where $X = \cos\alpha$ - Q, $Y = (\sin^2\alpha + X^2)/$ $C_m Q$, $Q = V_m/V_o$ and $\alpha = \phi_m$ - ψ_m. The dielectric constant of the sample is given by the ratio C_S/C_o where C_o is the capacitance of the empty cell measured before filling it. We use a standard capacitor and resistor connected in parallel in place of the sample cell to measure the stray capacitance added to the circuit by the cables used. It is found to be ~ 4 pF. The cell is mounted in a Mettler FP 82 hot stage which maintains its temperature to an accuracy of $\pm$ 0.1°C. However, we can use the nickel thermometer to measure the sample temperature to a much higher accuracy. By monitoring the resistances of both the nickel thermometer and a sample of 8OCB we have verified that the resistance of 8OCB which is itself senstive to temperature, varies systematically with the local temperature as determined by the nickel thermometer. We estimate that the local temperature is measured to an accuracy of $\sim \pm$ 0.01°C by the nickel thermometer.

We choose the frequency of the AC voltage to be a few kHz so that (a) the ionic heating effect is not excessive, (b) electrohydrodynamic effects are prevented (c) the amplifier output is sufficiently large and (d) electrochemical effects are avoided. At any given Mettler temperature, a few preset voltages are applied to the cell and at each voltage, the electrical parameters of the cell as well as its temperature are measured . At higher voltages, the temperature of the cell is higher. All the measurements that are reported in the present communication were made while cooling the sample from the isotropic phase. The experiment is controlled by a computer using an appropriate software (Spectrum Interface).

RESULTS AND DISCUSSION

We have conducted the experiments on homeotropically aligned samples of octyloxy cyanobiphenyl (8OCB) and pentyl cyanobiphenyl (5CB). In 5CB the highest field used was $\sim 1.47 \times 10^5$ V/cm which is slightly above the critical field reported by Lelidis and Durand.[13] $\epsilon_{//}$ is shown in Figure 4 as a function of the local temperature for some of the applied voltages for which data were collected.
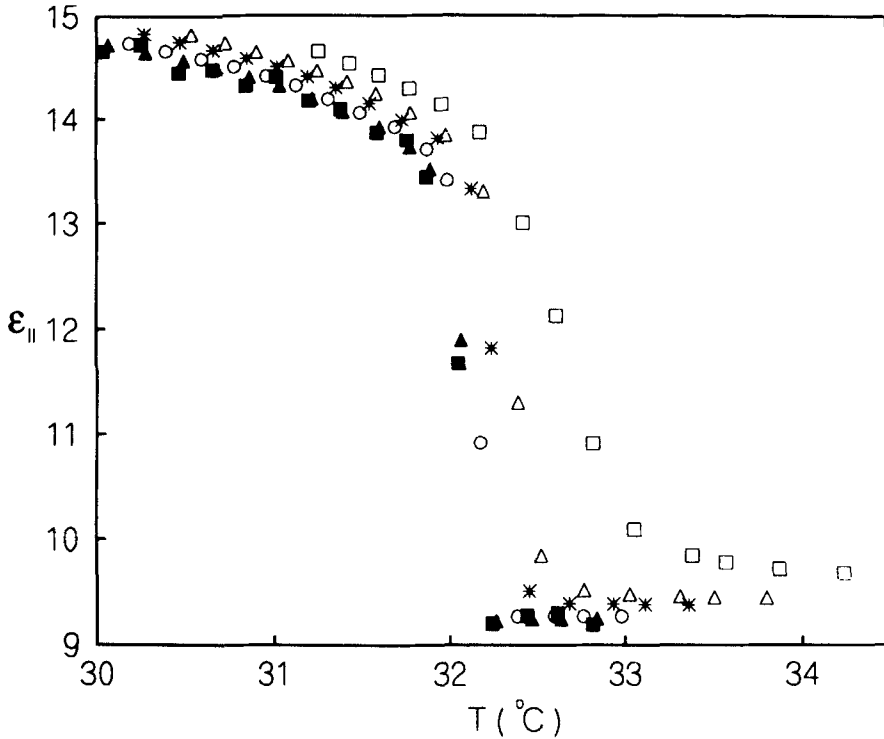

FIGURE 4   Dielectric constant ($\epsilon_{//}$) of 5CB as functions of temperature and voltage across NI transition; frequency of the applied voltage is 2317 Hz. ■ (1.05 V), ▲ (31.8 V), ○ (77.0 V), * (137.0 V), △ (182.8 V), □ (285.5 V).

To a good approximation the relationship between $\epsilon_{//}$ and the orientational order parameter S can be assumed to be of the form.

$$\epsilon_{//} = \bar{\epsilon} + \frac{2}{3}\Delta\epsilon S \tag{3}$$

where $\Delta\epsilon$ is the anisotropy for a medium with $S=1$ and $\bar{\epsilon}$ is the average dielectric constant. It is well known[17] that in materials with highly polar end groups, the stronger antiparallel near neighbour correlations lead to a slightly lower value of $\bar{\epsilon}$ in the nematic phase compared to that of the isotropic phase at T_{NI}. We have taken $\bar{\epsilon}$ to be 1.5% smaller than the value measured in the isotropic phase at low applied

voltages to take account of this fact. We have used the orientational order parameter measured by an optical technique[18] at T_{NI} - 2° to evaluate $\Delta\epsilon$ to be equal to 18.1 in 5CB. The nematic order parameter variation with field can now be compared with the prediction of the Landau theory.[13] Using only the essential terms the Landau-de Gennes free energy density of a nematic subjected to an electric field E is given by

$$F_E = \frac{a(T - T^*)}{2}S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4 - \frac{\Delta\epsilon E^2}{12\pi}S \tag{4}$$

where a, T^*, B and C are the usual Landau coefficients. Some remarks on this free energy are in order:

(i) The low frequency electric field changes the symmetry of the nematic phase as it induces a polarization in the medium. However it can be shown that the polar order parameter can be eliminated in favour of S and equation 4 is then a good approximation.

(ii) Apart from causing local heating, the ionic flow could in principle lead to a change in the order parameter directly. If v is the velocity of ions under the field, and n is the number density of ions, there could be velocity gradients $\sim v\, n^{1/3}$ in the medium. Using the known conductvity of the sample and a simple model for the flow of ions[1], it can be shown that at the highest field applied the velocity gradient is $\sim 10^4$ /sec. This can result in an induced order parameter due to flow alignment $\Delta S \sim 10^{-3}$ near the isotropic-nematic transition temperature,[19] which is much smaller than the dielectric alignment effect. Hence, following all earlier papers,[11-14] we ignore this factor in further discussion. The equilibrium value of S satisfies the condition.

$$\frac{dF_E}{dS} = a(T - T^*)S - BS^2 + CS^3 - \frac{\Delta\epsilon}{12\pi}E^2 = 0 \tag{5}$$

As the NI transition has a first order character the 4-parameter Landau theory can be expected to be inadequate especially at temperatures below T_{NI}. Hence we have used only the data measured close to the critical temperature in the analysis using equation 5. Figure 5 shows the experimental points as well as the calculated variation. The best overall fit was obtained for the following parameters:

T_{NI} - T^* = 1.3 ± 0.06 in °C

B/a = 11.0 ± 0.1 in cgs units

C/a = 21.4 ± 0.15 in cgs units

$a = (1.0 \pm 0.04\,)\times 10^6$ in cgs units

These parameters are broadly consistent with the values given by Lelidis and Durand.[13] We should note that the calculated temperature variation of S in the nematic phase is steeper than that of the experimental data. On the basis of a

number of earlier studies on nematic liquid crystals it has been suggested that the order parameter variation indicates a tricritical rather than a critical behaviour.[5]

The measured values of the dielectric constants of 8OCB are shown in Figure 6. The order parameters calculated as before, and the variations of S given by the Landau model are shown in Figure 7, for temperatures close to the NI transition. The Landau parameters in this case are listed below:

T_{NI} - T^* = 1.2 ± 0.2 in $°C$

B/a = 13.5 ± 0.1 in cgs units

C/a = 29.2 ± 0.2 in cgs units

a = $(0.87 ± 0.1) \times 10^6$ in cgs units

The estimated error in $T_{NI} - T^*$ is larger in 8OCB compared to that in the case of 5CB. This is almost certainly caused by the fact that T_{NI} of 8OCB is 79.6°C which is considerably higher than that of 5CB. This leads to a slow deterioration of the sample and a spread in the transition temperature, as a large number of data points were collected in 8OCB which required a long period of time.
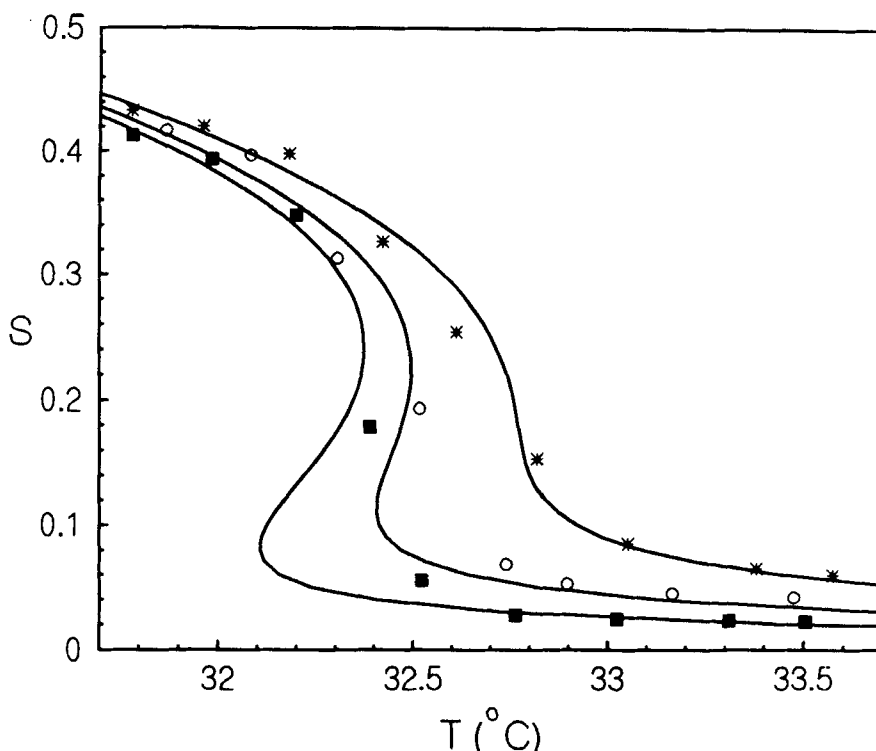

FIGURE 5   Variation of the order parameter S in 5CB as a function of temperature at different voltages. Solid curves are theoretical variations given by the Landau model. ■ (182.8 V), ○ (226.0 V), * (285.5 V).

8OCB also exhibits a transition from the nematic (N) to the smectic A (A) phase. As the smectic order parameter which is the amplitude of the density wave is coupled to the orientational order, the external field indirectly influences the former. This can be seen as an enhancement in the AN transition temperature with the field. The dielectric constant shows a relatively smooth variation around T_{AN} and using this data it is difficult to locate the transition point clearly. On the other hand, the resistance (R) of the sample shows a negative jump as the sample is cooled across the transition temperature (Figure 8). This might seem unusual as the permeative process can be normally expected to decrease the mobility of ions along the layer normal in the smectic phase and hence to an increase in the resistance of the sample. However one should note that 8OCB has a partial bilayer structure and in this case, $\sigma_{\parallel}$ remains larger than $\sigma_{\perp}$ even well within the smectic range.[20]

On the other hand, $\epsilon_{\prime\prime}$ relaxes at a few MHz and even at ~ 2000Hz which is the frequency of measurement, there is a significant contribution of this relaxation to
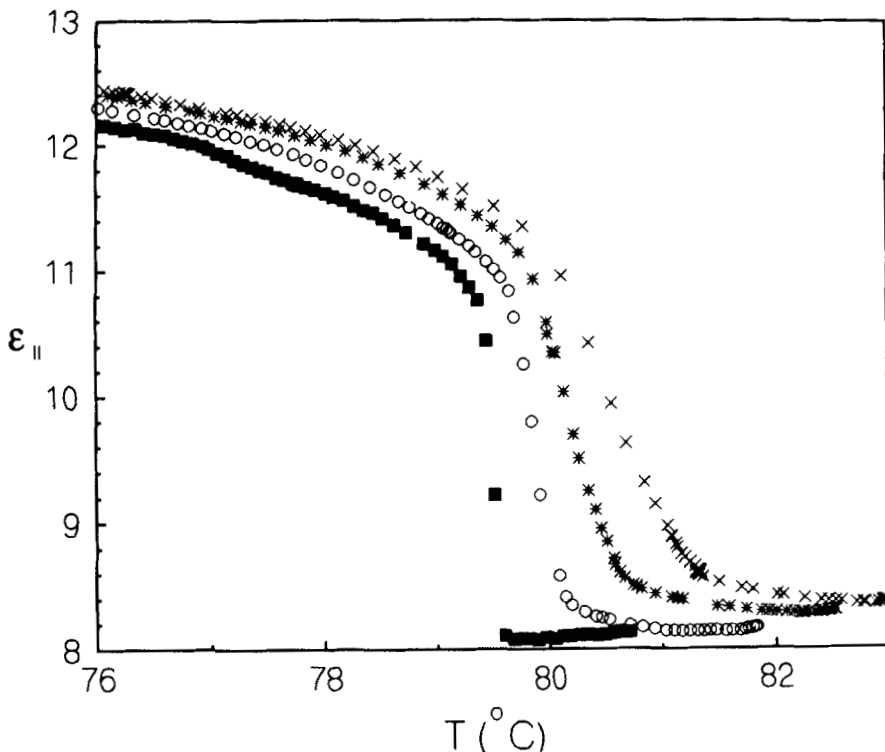

FIGURE 6   Dielectric constant of 8OCB as a function of temperature across NI transition ■ (14.95 V), ○ (195.4 V), * (264.8 V), × (334.5 V).

the effective conductivity of the sample. The total conductivity is given by

$$\sigma(\omega) = \sigma(ion) + \frac{\epsilon_o(\epsilon - 1)}{1 + \omega^2\tau^2}\tau\omega^2 \tag{6}$$

where τ is the relaxation time. The relaxation frequency of 8OCB close to T_{AN} is $\sim$ 6MHz, and further it decreases sharply when the smectic order sets in.[21] The contributions of the relaxation to $\sigma(\omega)$ is $\sim$ 10 % at 2000 Hz and the negative jump in the resistance can be understood as arising from that in the relaxation frequency.

As seen in Fig. 8, in the nematic phase above $\sim$ 67.5°C the resistance of the sample increases with applied voltage at any given temperature. The effect is known in weak electrolytes as the phenomenon of limiting current.[22] As the AN transition point is approached, the resistance decreases between 14.3V and 70.4V and increases at higher voltages. This initial decrease implies a slight misalignment of the sample in the smectic phase, which increases the effective resistance as $\sigma_{\parallel} > \sigma_{\perp}$ [20]. As the voltage is increased, the alignment improves producing the normal trend above 70V.
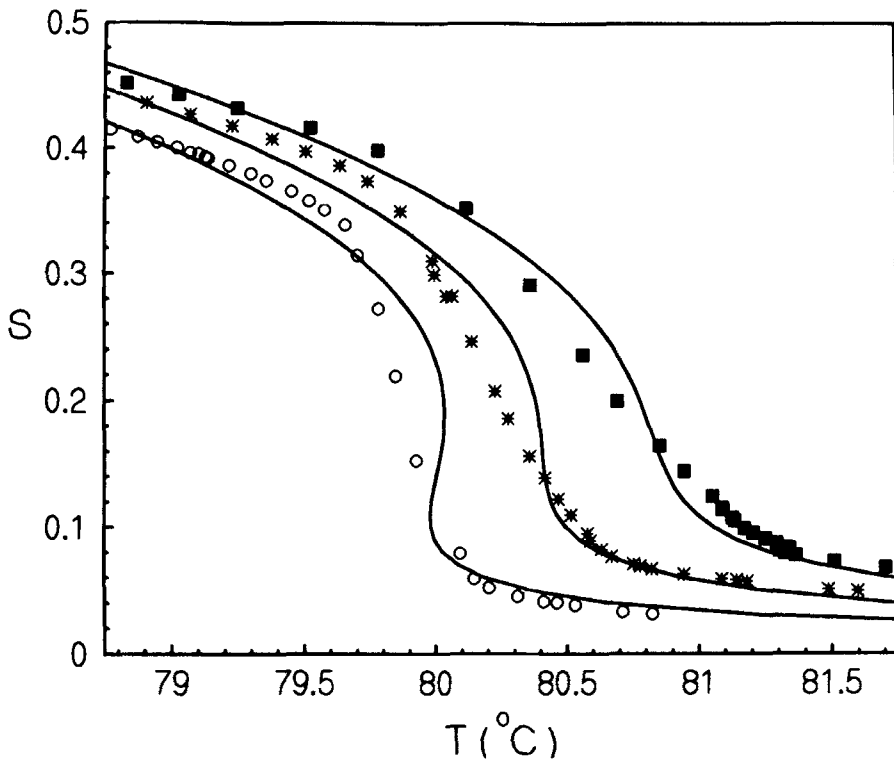

FIGURE 7   Variation of order parameter as a function of temperature and voltage in 8OCB across NI transition. $\bigcirc$ (284.5 V), $*$ (306.7 V), $\blacksquare$ (334.5 V).

By identifying the temperature at which R has a minimum as T_{AN}, we have plotted the latter as a function of the applied voltage in Figure 9. The data can be fitted quite well to a function of the form:

$$T_{AN}^E - T_{AN}^o \ \alpha \ E^2 \tag{7}$$

The quadratic dependence on E of the shift in T_{AN} can be easily understood on the basis of the Landau-de Gennes theory of A-N transition[1]. Adding the electric field dependence to the free energy density in this model, we get

$$F^A = \frac{\alpha(T - T_{NA}^*)}{2} |\psi|^2 + \frac{\beta}{4} |\psi|^4 - \gamma |\psi|^2 (S - S_o)$$
$$+ \frac{(S - S_o)^2}{2\chi} + F(N)_{s_o} - \frac{\Delta\epsilon}{12\pi} E^2 S \tag{8}$$

where α and β are the coefficients of the Landau theory of the A-N transition, T_{NA}^* is the second order AN transition temperature, γ the coefficient which couples the smectic order $|\psi|^2$ to the orientational order, which is enhanced by (S-S$_o$) in the A phase compared to its value (S_o) in the nematic phase at the same temperature, and χ is a susceptibility which minimises the nematic free energy $F(N)_{s_o}$ when the
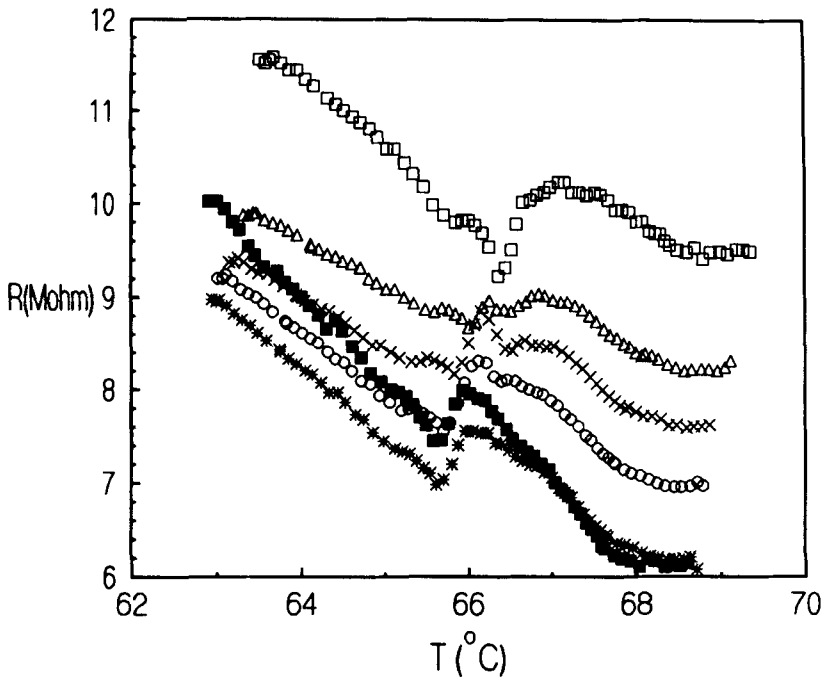

FIGURE 8   Variation of the resistance of 8OCB as a function of temperature at different values of the applied voltage across T_{AN} . The frequency used is 2170 Hz. ■ (14.3 V),* (70.4 V), ○ (127.0 V), × (199.5 V), △ (273.0 V), □ (348.0 V).

order parameter is S_o. As was argued by de Gennes, χ is small when T_{AN} is far below T_{NI}, and AN transition remains second order in character. Minimising the above free energy with respect to S we get

$$S = S_o + \chi\gamma \mid \psi \mid^2 + \frac{\chi\Delta\epsilon}{12\pi}E^2 \tag{9}$$

and substituting this value in equation 8, we get

$$F^A = \frac{\alpha}{2}(T - (T_{NA}^* + \frac{\gamma\chi\Delta\epsilon}{6\alpha\pi}E^2)) \mid \psi \mid^2 + (\frac{\beta}{4} - \gamma\chi^2/2) \mid \psi \mid^4 \tag{10}$$

The above equation leads to an enhancement of T_{NA}^* which is quadratic in the electric field consistent with the experimental result. The calculated variation shown in Figure 9 corresponds to $\gamma\chi/\alpha = 2.71 \times 10^{-5}$ cgs units.
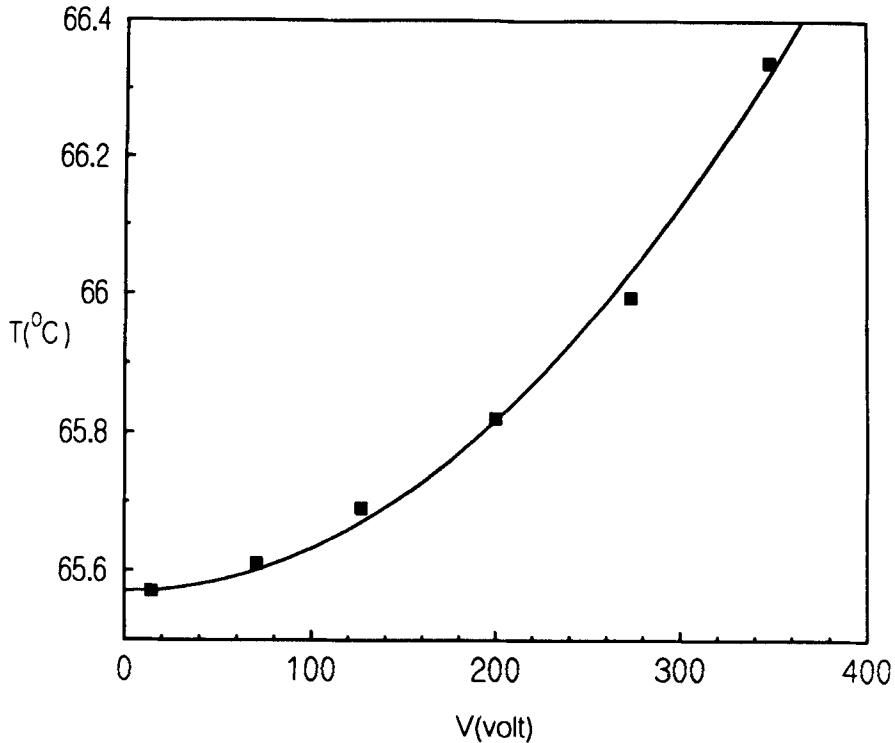

FIGURE 9   AN transition temperature as a function of applied voltage in 8OCB. The solid squares represent values derived from the experimental data given in Figure 8. The line gives the theoretical variation predicted by the Landau model.

Thus our experimental technique can be conveniently used to study the effect of a strong electric field on both the NI and AN transitions. As we stated earlier, the variation of the order parameter with temperature cannot be described well by the simple Landau theory with the minimal set of coefficients that were used

in Equation (4). In addition, in this model, the quenching of the long wavelength thermal fluctuations of the director by the external field is also ignored. As was shown by de Gennes[1], this effect produces an enhancement in the order parameter given by

$$\Delta S \sim \frac{K_B T (\Delta \epsilon S)^{1/2}}{K^{3/2}} \mid E \mid \tag{11}$$

where K is the curvature elastic constant of the nematic (in the one constant approximation). This contribution to the enhancement in S is linear in E and becomes quite important when S is small, as was shown by Lelidis et al.[14]

From the experimental point of view, it is likely that near the periphery of the electrode, the temperature is slightly lower than that in the center. From the dependence of the width of AN transition on field (See Figure 8) this gradient does not appear to be very serious. We are now redesigning the electrode pattern to further reduce this effect. As the order parameter response time is quite fast compared to the frequencies used in our experiments the system can be expected to be inherently non-linear. However, the amplitudes of the higher harmonics are quite small and have been ignored in the present analysis.

In conclusion, we have described a technique of measuring the local temperature of liquid crystal samples subjected to strong electric fields. An electric impedance analysis of the cell allows us to measure both the dielectric constant related with the orientational order parameter and the conductivity which is sensitive to the translational order parameter in the medium. We are now improving the experimental technique to reduce possible temperature gradients and to incorporate optical measurements. We intend to take up systematic studies on the influence of electric fields on the phase transitions of several liquid crystalline compounds.

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