5-22-2006

Electric Field Dependence of the Electric Conductivity in Liquid Crystals Made of Bent-Core Molecules

O. G. Martins

G. Barbero

A. M. Pedreira

Antal Jakli
Kent State University - Kent Campus, ajakli@kent.edu

H. Sawade

See next page for additional authors

Authors

O. G. Martins, G. Barbero, A. M. Pedreira, Antal Jakli, H. Sawade, and A. M. F. Neto

Electric field dependence of the electric conductivity in liquid crystals made of bent-core molecules

O. G. Martins, G. Barbero, and A. M. Pedreira
Instituto de Física, Universidade de São Paulo, P.O. Box 66318, São Paulo, São Paulo 05389-970, Brazil

A. Jákli
Liquid Crystal Institute, Kent State University, P.O.Box 5190, Kent, Ohio 44242-0001

H. Sawade
TU Berlin, I.N. Stranski Institute, Sekretariat ER 11, Strasse des 17, Juni 135, D-10623, Germany

A. M. Figueiredo Neto[a]
Instituto de Física, Universidade de São Paulo, P.O. Box 66318, São Paulo, São Paulo 05389-970, Brazil

We investigate the influence of the electric field on the conductivity of an antiferroelectric liquid crystal formed by bananalike molecules. Our experimental analysis shows that large deviations of the current from a pure Ohmic behavior are observed for applied voltage of the order of the ones used for the determination of the spontaneous polarization in these types of materials. The measurements are performed in the isotropic and B_2 phases. In the isotropic phase these deviations are interpreted in terms of the model proposed by Onsager, according to which, for weak electrolyte, the conductivity depends on the actual electric field present in the liquid. In the ordered phase we show that they are partially due to the external field induced reorientation of the director structure. A good agreement between the model and the experimental data is obtained, and an estimate of the coefficients taking into account the effect of the electric field on the conductivity is deduced. The relevance of this effect on the experimental determination of the spontaneous polarization is found to be of the order of 10%. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2206684]

The spontaneous polarization of ferro- and antiferroelectric liquid crystals is usually calculated by measuring the electrical current in a sample cell, as a function of the applied voltage. This voltage can be a sinusoidal,[1,2] triangular,[3] or square[4] function of time. In all these methods, however, it is commonly assumed that the conductivity of the sample does not depend on the applied electric field (**E**). Among these methods, the one employing the triangular wave is, by far, the most widely used by experimentalists. One of its advantages is the straightforward subtraction of the components of the electric current, one proportional to the field and the other to the time derivative of the field. The measurements are performed by applying to the sample external voltages of the order of several $V/\mu m$. Since the electric field in the sample is rather large, a possible influence of the electric field on the sample's conductivity is expected. This fact contrasts with the usual assumption of a pure Ohmic behavior of the material under investigation.[5] A source of the dependence of the conductivity on **E** is the presence of dissociable impurities in the sample, or even an eventual molecular dissociation in the pure material.[6] In fact, the dissociation constant for ionization depends on **E** when its amplitude is of the order of several $V/\mu m$. In the ordered B_2 phase (made of bent-core or banana-shaped molecules) the director reorientation induced by **E** can also give a contribution to the field dependence of the electrical conductivity. Let us consider, for example, a measurement of the spontaneous electrical polarization (**P**) of an antiferroelectric liquid crystal. If there exists an electric field dependence of the electrical conductivity, σ, it can drastically affect the base line of the mea-

sured response, e.g., of the drop of potential on the sample, or on the Ohmic resistance over which is measured the response of the cell to an external electric excitation. As known, this quantity has to be subtracted from the total sample-cell response to calculate the spontaneous polarization. An error in this subtraction causes immediately an error in the calculated polarization. The aim of this letter is to investigate the behavior of the electrical conductivity of a liquid crystalline sample in the isotropic and ordered phase. We consider a slab-type cell with the liquid crystal 1,3-phenyilen bis4-(4-tetradecylphenyliminomethyl) benzoate (Ref. 7) formed by bananalike molecules and impurities, in the paraelectric isotropic (ISO) phase and the switched B_2 (antiferroelectric at $E=0$) phase.[8–10] The phase sequence as a function of the (decreasing) temperature is ISO (151.8 °C) B_2 (124.7 °C). We do not observe any changes in the transition temperatures, within our accuracy, due to the external electric field application. The sample is placed in a cell composed by two parallel glass plates (slab geometry, surface area: $S=1$ cm^2, cell thickness: $d=22$ μm), where there are semitransparent ITO deposits in order to apply the triangular wave electrical voltage (Fig. 1). The sample cell is connected to the external power supply by means of a resistance R_o. By measuring the drop of potential on R_o, the current $I(t)$ in the circuit is determined. The temperatures of the sample are set at 139 and 154.3 °C in the B_2 and ISO phases, respectively. Figure 1 shows the electrical voltage $V_o(t)$ measured on R_o as a function of the time (ISO phase): a large deviation from the linear behavior is observed. It follows that, without a model, it is very difficult to extract this nonlinear contribution from the data $I(t)$, in order to obtain the spontaneous polarization in the B_2 phase. To analyze the data we take into account that
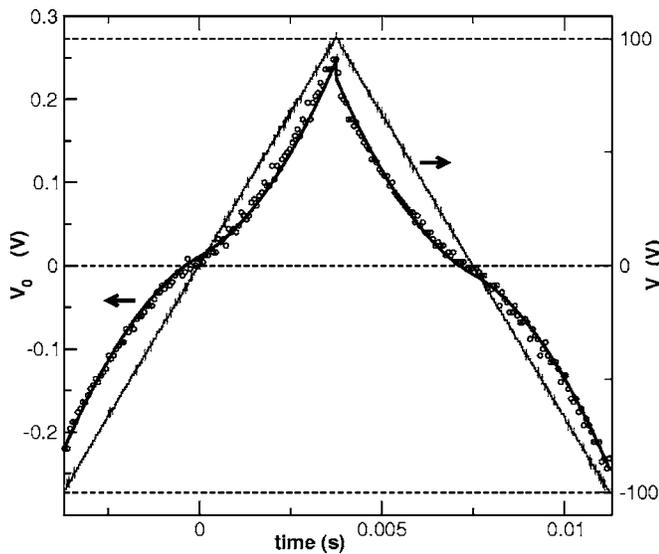
[a]Electronic mail: afigueiredo@if.usp.br

FIG. 1. External voltage $V(t)$, with amplitude of the emf 100 V, and $T = 7.5 \times 10^{-2}$ s. Drop of potential measured over the resistance R_o. The points represent the experimental data. The sample is in paraelectric ISO phase (temperature 153.4 °C). The continuous curve is the best fit obtained taking into account the influence of the electric field on the electrical conductivity. The triangular wave excitation is also represented.

the total electrical current in the circuit coincides with the one in the sample. Denoting the electrical field along the geometrical normal to the electrodes by E and the electrical displacement across the electrodes by $D = \varepsilon E + P$, the density of the conductive current is $J_C = \sigma E$, whereas the one of displacement is $J_D = dD/dt$. The total current in the circuit is then $I = [\sigma E + \varepsilon^*(dE/dt)]S$, where S is the surface area of the

electrodes and $\varepsilon^* = \varepsilon + \chi$, being $\chi = dP/dE$ the electrical susceptibility of ferroelectric origin. The total current and the electric field have to satisfy the equation $V = Ed + R_oI$. By using the relations reported above we get

$$\frac{dq}{dt} + \frac{1}{C}\left(\frac{1}{R_o} + \frac{1}{R}\right)q = \frac{V}{R_o}, \tag{1}$$

where $q = \varepsilon^* SE$ is the total charge on the surface of the sample and $R = (1/\sigma)(d/S)$ its electrical resistance. Equation (1) is the fundamental equation of our problem. If R were independent of the actual field, the solution of Eq. (1) is the usual one relevant to the charge of a condenser, with relaxation time $\tau_o = CRR_o/(R + R_o)$, and nothing new is expected.[3] However, when the applied voltage is of the order of several V/μm, the conductivity, σ, is expected to depend on the actual electric field in the liquid crystal. Let us consider first the data relevant to the isotropic phase. In this case $\varepsilon^* = \varepsilon$. According to the model proposed by Onsager, $\sigma = \sigma_o + r|E|$, where σ_o is the electrical conductivity for vanishing small external electric field, and r is the coefficient introduced by Onsager.[6] In this case Eq. (1) can be rewritten in the form

$$\frac{dq}{dt} + (a + b|q|)q = \frac{V}{R_o}, \tag{2}$$

where $a = (R_oC)^{-1} + \sigma_o/\varepsilon$, and $b = r/(\varepsilon Cd)$. The homogeneous part of Eq. (2) has the solution $q_{\text{hom}} = -ae^{ah}/b(e^{ah} - e^{at})$, where h is an integration constant to be determined by the boundary conditions. Taking into account the definitions of a and b, it follows that the relaxation time depends on R_o. Note that, if σ is field independent, $a = 1/\tau_o$, where the relaxation time τ_o has been introduced above. The solution of Eq. (2), when $V(t) = m + nt$, where m and n are constants is

$$q(t) = -\frac{a[\text{Bi}(\eta) + k\,\text{Ai}(\eta)] - 2(bn/R_o)^{1/3}[\text{Bi}'(\eta) + k\,\text{Ai}'(\eta)]}{2b[\text{Bi}(\eta) + k\,\text{Ai}(\eta)]}, \tag{3}$$

where k is an integration constant, and

$$\eta = \frac{a^2R_o + 4b(m + nt)}{4R_o(bn/R_o)^{2/3}}. \tag{4}$$

In Eq. (3) Ai and Bi are Airy's functions, and Ai$'$ and Bi$'$ their derivatives.[13] When the function $q(t)$ has been determined, the total current in the circuit is given by $I(t) = (1/R_o)(V - q/C)$. The parameters of the best fit shown in Fig. 1 are $\varepsilon = \varepsilon_0$, $\sigma_o = 2 \times 10^{-8}$ (m Ω)$^{-1}$, and $r = 7.5 \times 10^{-15}$ (V Ω)$^{-1}$. Using the value of r determined above, we can evaluate the variation of the density of electrical charge carriers due to the presence of the external electric field. According to elementary electrodynamics, $\sigma \propto \mu q n$, where μ is the mobility of the ion, q its charge, and n the bulk density of ions. Assuming that the mobility μ is independent of the electric field (that is a good assumption in the absence of the hydratation phenomenon) and that $n = n(E)$, we have

$$\frac{n(E) - n(0)}{n(0)} = \frac{\sigma - \sigma_o}{\sigma_o} = \frac{rE}{\sigma_o}. \tag{5}$$

It follows that, for the sample investigated by us, where the maximum field is $E \sim U/d \sim 4 \times 10^6$ V/m, the relative variation of the density of ions induced by the external field is of the order of 10^{-2}, i.e., rather modest. However, it is clearly visible on our experimental data. Let us consider now the sample in the ordered B_2 phase, where $\varepsilon^* = \varepsilon + \chi$. In Fig. 2 we report the same type of measurements described above, on the same material, at the temperature of 139 °C in the B_2 phase. In this case to interpret the experimental data, we have to take into account that in the ordered phase the system is an anisotropic two-dimensional (2D) liquid. SmCPA is a biaxial material and the eigenvectors of the conductivity are along the layers and normal to the smectic layers. We are interested in the conductivity in the layer, along the geometrical normal to the limiting surfaces. We assume, in a first approximation that, in the layer, the medium behaves as a uniaxial crystal, along the average molecular direction coinciding with the director, **n**. In this framework the electrical conductivity, in
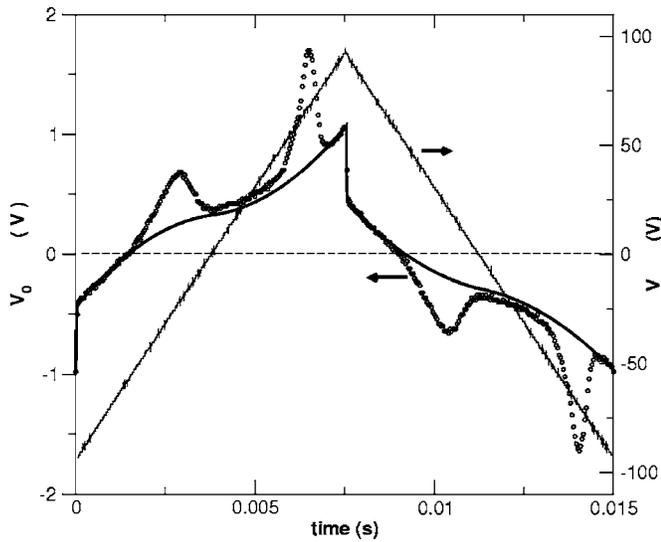
FIG. 2. Drop of potential measured over the resistance R_o. The points represent the experimental data. The sample is in the B_2 phase (temperature 139 °C). The continuous curve is the best fit obtained taking into account the influence of the electric field on the electrical conductivity. It well describes the basis of V_o when the excitation is a triangular wave of the type described in the text. The triangular wave excitation is also represented.

the layer, is a symmetric tensor whose elements are $\sigma_{ij} = \sigma_\perp \delta_{ij} + \sigma_a n_i n_j$, where $\sigma_a = \sigma_\parallel - \sigma_\perp$ is the anisotropy of the conductivity, and $\parallel$, $\perp$ refer to **n**. To describe the system under investigation, we suppose that the medium is in the bookshelf geometry. We use a Cartesian reference frame with the z axis perpendicular to the electrodes, placed at $z = \pm d/2$, and $\mathbf{n} = (\sin\theta\cos\phi, \cos\theta, \sin\theta\sin\phi)$, where θ is the angle formed by the molecular axis with the normal to the layer, and ϕ the angle describing the rotation of the molecular axis around the normal to the layer.[11] We hypothesize that the surfaces are such to induce strong anchoring condition along a tilted direction for ϕ, such that $\phi(\pm d/2) = \phi_s$. Since the medium has a dielectric anisotropy and we want to analyze the bases of the line of the experimental data, where the sample is in paraelectric phase, the dielectric coupling between the medium and the external electric field is $-(\varepsilon_a/2)E^2 \sin^2\theta\sin^2\phi$, where $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy.[12] By assuming that the distortion induced by the external field on the orientation is small, by operating in a standard manner[12] we get that the reorientation induced by the field, $\delta\phi(z)$, is given by

$$\delta\phi(z) = \frac{\varepsilon_a E^2 d^2}{8K} \sin^2\theta \sin(2\phi_s)[1 - (2z/d)^2], \tag{6}$$

where K is the elastic constant. It follows that its average value is $\langle\delta\phi\rangle = \varepsilon_a E^2 d^2 \sin^2\theta \sin(2\phi_s)/(12\,K)$. The effective conductivity, along the z axis, is then given by

$$\sigma_{zz} = \sigma_\perp(E) + \sigma_a(E)\sin^2\theta\sin^2\phi_s + \mathcal{R}E^2. \tag{7}$$

In Eq. (7) $\sigma_\perp(E) = \sigma_\perp(0) + rE$ and $\sigma_a(E) = \sigma_a(0)$, where r is the coefficient of Onsager introduced above, assumed to be the same for $\sigma_\perp$ and $\sigma_\parallel$, and

$$\mathcal{R} = \frac{1}{12}\sigma_a \frac{\varepsilon_a d^2}{K} \sin^2\theta \sin^2(2\phi_s), \tag{8}$$

takes into account the influence of the orientation induced by the electric field on the conductivity. By assuming $\sigma_a \sim 10^{-9}$, $\varepsilon_a \sim 5 \times \varepsilon_0$, $d = 20 \times 10^{-6}$, and $K \sim 5 \times 10^{-11}$, we get $\mathcal{R} \sim 10^{-21}$, in *Systéme International* (SI). In Fig. 2 the points are the experimental data in the B_2 phase, whereas the continuous curve is obtained by taking into account the variation of the electrical conductivity with the electric field. For the fit we have assumed that the parameter r is nearly the same in the isotropic and ordered phase, because, as predicted by Onsager,[6] $r \propto (1/T^2)$, where T is the absolute temperature. The other parameters of the best fit shown in Fig. 2 are $\varepsilon^* = 30 \times \varepsilon_o$, $\sigma_o = 7.8 \times 10^{-8}$ (m Ω)$^{-1}$, $\mathcal{R} \sim 4.5 \times 10^{-21}$ (SI). The electrical conductivity in the (ordered) B_2 phase is expected to be larger than the one in the ISO phase not only because $T_{B_2} < T_{\text{ISO}}$ but also mainly for the ordered structure which is present in the B_2 phase. From ε^* we can evaluate $\chi \sim 25 \times \varepsilon_o$, in agreement with the one reported in Ref. 5. As it is evident from Fig. 2, the basis of the drop of potential, V_o, on the resistance of measurement, R_o, when the existing voltage is the one reported in Fig. 1, is very well described by the effect of E on σ. The spontaneous polarization of the antiferroelectric sample is usually calculated measuring the surface area of one of the peaks present in Fig. 2, after removing the linear contribution. This means that by neglecting the effect described here, the relative error on P is proportional to the integral of $(rE + \mathcal{R}E^2)/\sigma_o$. For the experimental results shown in Fig. 2, this relative error is larger than 10%.

[1]H. Diamant and K. Drenk, Rev. Sci. Instrum. **28**, 30 (1957).
[2]O. G. Martins and A. M. Figueiredo, Rev. Sci. Instrum. **71**, 2161 (2000).
[3]K. M. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys., Part 2 **22**, L661 (1983).
[4]Ph. Martinot-Lagarde, J. Phys. (France) Lett. **38**, L37 (1977).
[5]M. I. Barnik, L. M. Blinov, N. M. Shtykov, S. P. Palto, G. Pelzl, and W. Weissflog, Liq. Cryst. **29**, 597 (2002).
[6]L. Onsager, J. Chem. Phys. **2**, 599 (1934).
[7]G. Heppke, A. Jakli, and H. Sawade, Phys. Rev. E **60**, 5575 (1999).
[8]T. Niori, T. Sekine, J. Watanabe, T. Fukurawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996).
[9]W. Weissflog, Ch. Lischka, T. Benne, T. Scharf, G. Pelzl, S. Diele, and H. Kruth, Proc. SPIE **3319**, 14 (1997).
[10]D. M. Walba, E. Korblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser, and N. A. Clark, Science **288**, 2181 (2000).
[11]Tiezheng Qian and P. L. Taylor, Phys. Rev. E **60**, 2978 (1999).
[12]P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
[13]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972).