Dielectric Characterization of Doped M5

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We analyze the dielectric properties of the liquid crystal M5 used to investigate the electrohydrodynamics instability in nematic liquid crystals. We show that the spectra of the electrical impedance of doped samples of M5 with several concentrations of salt and of acid can be interpreted by assuming the doped liquid crystal as a dispersion of ions in a dielectric liquid. The analysis has been performed by considering the electrodes as blocking. From the best fit of the experimental data relevant to the real and imaginary parts of the electrical impedance of the cells, we derive the diffusion coefficients for the positive and negative ions and their bulk density. According to our analysis, in the limit of small concentrations of doping substance, the effective dielectric constant of the resulting liquid is, practically, independent of the doping.

I. Introduction

Electrohydrodynamic (EHD) instabilities in nematic liquid crystals are observed when an electric field is applied to a thin layer of nematic with negative dielectric anisotropy, and sufficient electrical conductivity. This instability is characterized by a well-defined threshold. When the applied voltage is larger than the critical one, a pattern formed by parallel straight lines of wavelength approximatively equal to the thickness of the sample, appears in the sample. This pattern is stable only for a small voltage range, close to the threshold value. At higher voltage, the dynamics scattering mode takes place.[1] The origin of the instability was discussed by Helfrich[2] for the dc case, and extended by Dubois et al.[3] and by Penz and Ford[4] to the ac case. The appearance of the instability described above is connected with a relatively large conductivity of the liquid crystal. Liquid crystals are formed by organic molecules and can be considered as dielectric liquids. The electrical conduction is of ionic origin, and it is proportional to the bulk density of ions.

A large part of investigations on the EHD instability have been performed on the liquid crystal known as MBBA (methoxybenzilidenebutylaniline), which possesses values for the dielectric constant and electrical conductivity such to observe, easily, this instability.[5] However, this liquid crystal degrades when it is irradiated with light, or when it is used in measurements relevant to EHD instabilities. Consequently, the experiments on EHD instability in MBBA are not fully reproducible. For this reason, recently, it has been produced the nematic liquid crystal Mischung V (M5) that seems an excellent material for experiments on EDH for its chemical stability.[6] This material has not been yet completely characterized from the electrical point of view, and the description of the influence of the ions on its dielectric constant and electrical conductivity has not been discussed. This is the goal of our paper.

In section II, we describe our experimental set up, by means of which we have measured the frequency dependence of the impedance of the nematic cells. The applied voltage, by means of which the impedance is measured,[7] is so small that the system under investigation can be considered linear.[8]

The nematic sample is assumed oriented in a planar manner, and no reorientation related to the external field is present. In this framework, the nematic liquid crystal can be considered as an isotropic medium with physical parameters corresponding to the ones perpendicular to the director ($\perp$). In section III, the drift-diffusion problem of the ions in the presence of an external field is presented, and the fundamental equations discussed. In section IV, we show that a simple description of the sample based on an electrical circuit formed by a resistance, describing the presence of the electrodes, and a parallel of a resistance and of a capacitance, describing the liquid crystal, works only for frequency larger than few hertz. In the same section we present the best fit of the experimental data performed by means of a model based on the drift-diffusion of the ions in the liquid crystal. From the best fit of the experimental data, we derive the bulk density of ions for several doping of the liquid crystal and the diffusion coefficients for the positive and negative ions.

II. Experiment

M5 is a mixture of four compounds: 4-hexyloxyphenyl-4′-methoxybenzoate(22.0 wt %) + 4-octyloxyphenyl-4′-pentyloxybenzoate(30.3 wt %) + 4-heptyloxyphenyl-4′-hexyloxybenzoate (13.3 wt %) + 4-butyloxyphenyl-4′-hexylbenzoate(34.4 wt %), whose molecular formulas are shown in Figure 1. To increase the M5 conductivity, it has been doped with different percentage of its precursors, 4-(n-octyloxy)phenol and 4-n-heptylbenzoic acid, which act as proton donor impurities.[6]

The investigated cells, bought from EHC Ltd. Japan, are in the shape of a slab of thickness $d \sim 25 \ \mu$m and surface area $S \sim 1 \ \text{cm}^2$. The electrodes of the cells were covered by rubbed polyimide to induce planar alignment.[5] The surface treatment allows to assume that there is not charge injection into the liquid crystal, and that the electrodes can be considered blocking. We investigated the electrical impedance of the cells by means of

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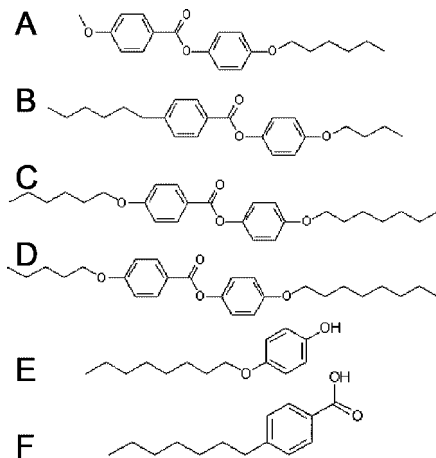
Figure 1. Components of the nematogen M5: (A) 4-hexyloxyphenyl-4′-methoxybenzoate + (B) 4-octyloxyphenyl-4′-pentyloxybenzoate + (C) 4-heptyloxyphenyl-4′-hexyloxybenzoate + (D) 4-butyloxyphenyl-4′-hexylbenzoate. Dopants used in the present work: (E) the alcohol 4-(*n*-octyloxy)phenol and (F) the acid 4-*n*-heptylbenzoic acid.
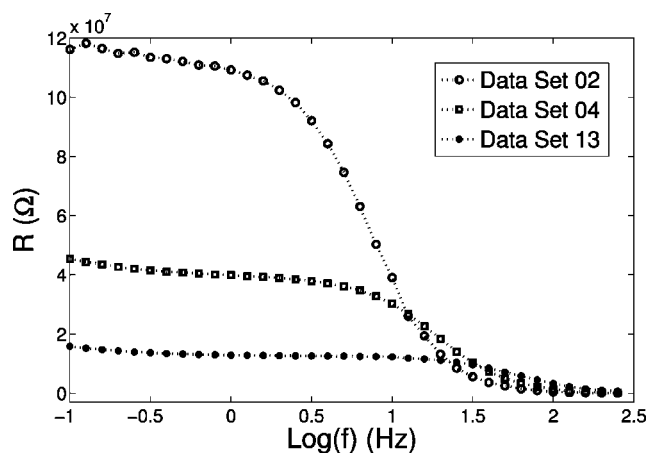

Figure 2. Real part, *R*, of the electrical impedance, *Z*, versus the frequency, *f*, of the applied voltage, for different doping concentrations. The plateaus present a small negative slope. For large frequency, $R \to 0$. The values of *R* corresponding to the plateaus strongly depend on the doping concentrations. Set 02: 6% of acid. Set 04: 10% of salt. Set 13: 12% of salt and 5% of acid.

EG & G model 348 impedance analyzer. The amplitude of the applied voltage was of the order of 10 mV, in such a manner that, from the electrical point of view, the sample behaves as a linear element in the explored frequency range.[9] Since the applied voltage is very small with respect to the threshold voltage for the Freedericksz transitions,[10] reorienting effects connected with the external electric field on the nematic liquid crystal are absent.

The real (*R*) and imaginary (*X*) parts of the electrical impedance (*Z*) versus the angular frequency $\omega = 2\pi f$ of the applied voltage $V(t) = V_0 \exp(i\omega t)$ are shown in Figure 2 and Figure 3, for different doping. As is evident from Figure 2, $R = R(\omega)$ presents a large plateau and tends to zero for large ω. From Figure 3, it follows that $X = X(\omega)$ tends to zero in the limit of $\omega \to \infty$, and for $\omega \to 0$, the effective reactance of the cell tends to $-\infty$, indicating that in this limit the sample is equivalent to a pure condenser. In the limit of $\omega \to 0$, *X* is independent of the doping, in agreement with the theoretical prediction reported in.[11] The minimum of *X* is in correspondence of the maximum slope of *R*, as expected.
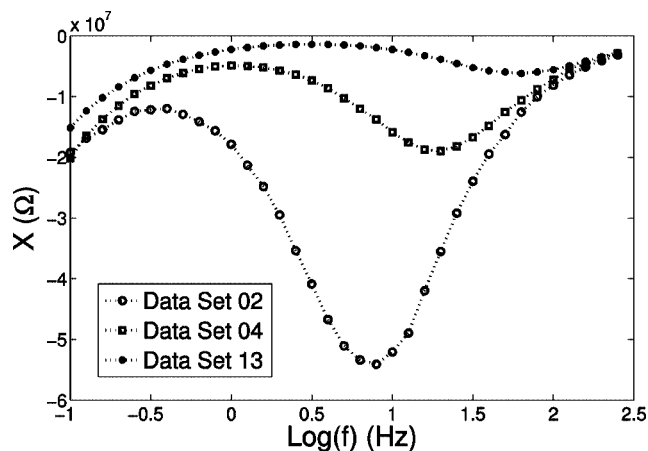

Figure 3. Imaginary part, *X*, of the electrical impedance, *Z*, versus the frequency, *f*, of the applied voltage, for different doping concentrations. For large frequency, $X \to 0$. In the dc limit, $X \to \infty$, indicating that in this limit the equivalent circuit of the cell behaves as a pure condenser. The value of the minimum of *X* at the higher relaxation frequency depends on the doping concentrations. Set 02: 6% of acid. Set 04: 10% of salt. Set 13: 12% of salt and 5% of acid.

III. Electrical Impedance of Doped Liquid Crystals

Let us consider a doped nematic liquid crystal. In the limit of small concentration of doping substance, we assume that the doped nematic can be considered as a dispersion of ions in the liquid crystal. In the absence of an external electric field and of selective adsorption from the limiting surfaces, the medium is locally and globally neutral. When the sample, in the shape of a slab, is submitted to an external electric field, the ions move under the effect of the electric field in the sample, and the gradient of concentrations. In this situation, the nematic liquid crystal is locally charged, but globally neutral. The effective currents of the positive (*p*) and negative (*m*) ions are given by

$$\vec{j}_p = -D_p\left(\nabla n_p - \frac{q}{k_B T} n_p \vec{E}\right)$$

$$\vec{j}_m = -D_m\left(\nabla n_m + \frac{q}{k_B T} n_m \vec{E}\right) \tag{1}$$

where n_p and n_m are the bulk densities of positive and negative ions, D_p and D_m their diffusion coefficients, and **E** the effective electric field in the sample. In eq 1, we have used the Einstein−Smoluchowski equation relating the ionic mobility (μ) with the diffusion constant (*D*), according to which $\mu/D = q/k_B T$, where *q* is the electrical charge of the ions (supposed to differ just for the sign), and $k_B T$ is the thermal energy.[12] The time evolution of the densities of ions in the presence of the external electrical field are governed by the continuity equations, that are

$$\frac{\partial n_p}{\partial t} + \nabla \cdot \vec{j}_p = 0$$

$$\frac{\partial n_m}{\partial t} + \nabla \cdot \vec{j}_m = 0 \tag{2}$$

and the effective electric field across the sample is obtained by solving the equation of Poisson

$$\nabla \cdot \vec{E} = \frac{q}{\varepsilon}(n_p - n_m) \tag{3}$$

with the proper boundary conditions.

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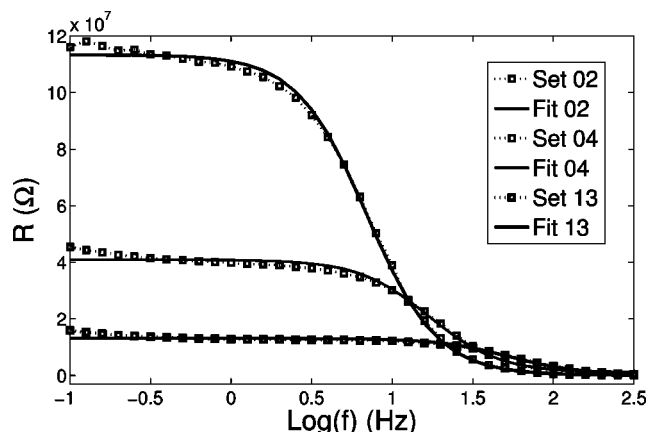*J. Phys. Chem. B, Vol. 112, No. 35, 2008* **11051**

Figure 4. Frequency dependence of the real part, R, of the electrical impedance, Z, of the sample and best fit obtained by approximating the sample with a parallel of a resistance and a condenser in series with a resistance R_s. Set 02: 6% of acid; set 04: 10% of salt; set 13: 12% of salt and 5% of acid.

Figure 5. Frequency dependence of the imaginary part, X, of the electrical impedance, Z, of the sample and best fit obtained by approximating the sample with a parallel of a resistance and a condenser in series with a resistance R_s. Note that for the equivalent circuit used for the description of the sample, in the dc limit, $X \to 0$, contrary to the experimental observations. Set 02: 6% of acid; set 04: 10% of salt; set 13: 12% of salt and 5% of acid.

The influence of the ions on the impedance spectroscopy of a dielectric liquid has been discussed long ago by Macdonald by assuming that the electrodes are perfectly blocking.[13−16] Recently the role of the ions has been reconsidered mainly for its importance in display technology.[17−21] The analysis of Macdonald has been generalized by taking into account the absorption from the surfaces,[22] and the ohmic character of the electrodes.[23] The effect of the difference of the diffusion coefficients on the impedance spectra has also been considered.[24,25]

IV. Fit of the Experimental Data

The experimental data relevant to samples of M5 with different concentrations of dopant are reported in Figure 2 and Figure 3. From these figures, it is evident that in the dc limit the samples behave as pure condensers. In the high frequency limit, the real and imaginary parts of the electrical impedance tend to zero. From these observations it follows that to approximate the sample by means of a parallel of a resistance and a condenser in series with a resistance taking into account the electrodes and the cables, as proposed in,[5] is a rather rough approximation. In fact, a circuit of this type reduces to a pure resistance for $\omega \to 0$ and for $\omega \to \infty$, contrary to our experimental data, reported in Figure 2 and in Figure 3. A description of the system by means of a circuit of this type can work just in a small frequency range.[26] In Figure 4 and Figure 5, we show the best fits of the experimental data relevant to $Z = Z(\omega)$ with the equivalent electrical circuit composed by a resistance R'_s due to the electrodes, with the parallel of a resistance $R_{eq} = \rho_{eq}d/S$ and a capacitance $C_{eq} = \varepsilon_{eq}S/d$. From the best fits, by assuming $S = 10^{-4}$ m², we derive:

for the set 02, $R_s = 186$ K Ω, $\rho_{eq} = 450$ M$\Omega \cdot$m and $\varepsilon_{eq} = 5.7 \times \varepsilon_0$;

for the set 04, $R_s = 170$ K Ω, $\rho_{eq} = 163$ M$\Omega \cdot$m and $\varepsilon_{eq} = 6.4 \times \varepsilon_0$;

for the set 13, $R_s = 620$ K Ω, $\rho_{eq} = 50$ M$\Omega \cdot$m and $\varepsilon_{eq} = 7.2 \times \varepsilon_0$.

Since R_s is very small with respect to the real part of the impedance of the cells under investigation, from now on it will be neglected. As it is evident from Figure 4 and Figure 5 the agreement between the experimental data and equivalent electrical circuit is rather good in the region $f \geq 10$ Hz. However, in the limit of small frequency ($f \leq 10$ Hz), the agreement is poor. These results indicate that it is not possible to describe, in the complet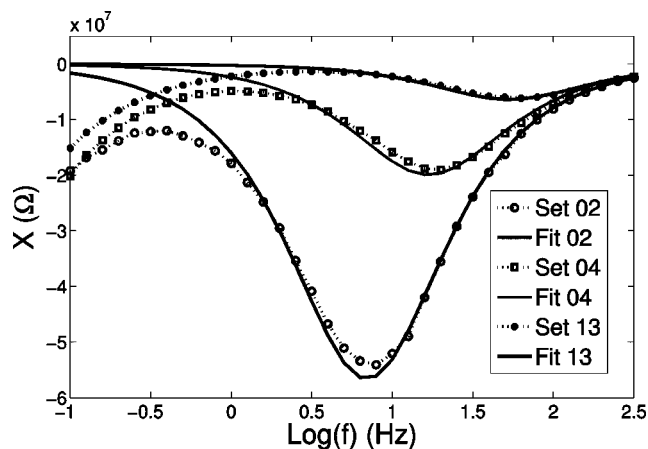e frequency range, the sample by means of resistivity and dielectric constant, frequency independent. It is also a clear indication that the role of the ions on the electrical impedance of the cell depends on the frequency.[11] For this reason, we analyze the experimental data using a model based on the solution of the drift-diffusion of the ions in the liquid crystal, in the presence of an external voltage. As discussed in the previous section, the fundamental equations for the problem under consideration are eq 2, connected with the conservation of the number of ions, and eq 3, relating the divergence of the effective electric field in the sample with the bulk density of ions. These equations have to be solved with the boundary conditions associated to the problem under investigation. In our case, where the sample is in the shape of a slab of thickness d the equations can be simplified. We use a Cartesian reference frame having the z-axis normal to the surfaces limiting the cell, located at $z = \pm d/2$. In this framework, all physical quantities entering in the physical description of the system depend just on z and t. Furthermore, in the limit of small amplitude of the applied voltage (V_0), the variation of the bulk density of ions (δn), with respect to the one in thermodynamical equilibrium (N), due to the presence of the external field, is such that $\delta n \ll N$ and it is also linear in V_0. In this linear limit, the fundamental equations governing the ionic distribution in the presence of an external field are

$$\frac{\partial \delta n_p}{\partial t} = D_p \left\{ \frac{\partial^2 \delta n_p}{\partial z^2} + \frac{qN}{k_B T} \frac{\partial^2 V}{\partial z^2} \right\}$$

$$\frac{\partial \delta n_m}{\partial t} = D_m \left\{ \frac{\partial^2 \delta n_m}{\partial z^2} - \frac{qN}{k_B T} \frac{\partial^2 V}{\partial z^2} \right\} \quad (4)$$

and

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(\delta n_p - \delta n_m) \quad (5)$$

where we have put $n_p = N + \delta n_p$, $n_m = N + \delta n_m$, and introduced the electrical potential $V = V(z, t)$, connected to the electrical field by $\mathbf{E} = -\nabla V$. The boundary conditions for the problem are $j_p(\pm d/2, t) = j_m(\pm d/2, t) = 0$ related to the hypothesis of
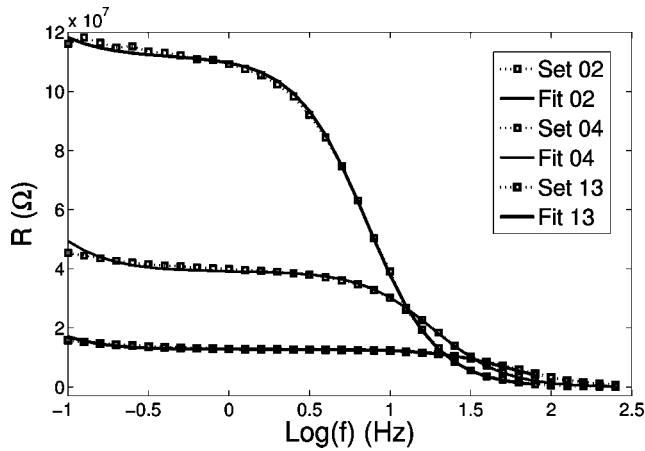
Figure 6. Frequency dependence of the real part, R, of the electrical impedance, Z, of the sample and best fit obtained by taking into account the influence of the ions on the electrical impedance of the cell. Set 02: 6% of acid. Set 04: 10% of salt. Set 13: 12% of salt and 5% of acid.

Figure 7. Frequency dependence of the imaginary part, X, of the electrical impedance, Z, of the sample and best fit obtained by taking into account the influence of the ions on the electrical impedance of the cell. Set 02: 6% of acid. Set 04: 10% of salt. Set 13: 12% of salt and 5% of acid.

blocking electrodes, and $V(\pm d/2, t) = \pm(V_0/2) \exp(i\omega t)$, due to the presence of the external power supply.

The formulas relating the electrical impedance of a cell in the shape of a slab and its frequency dependence (impedance spectroscopy) to the diffusions constants are reported in refs 24 and 25. The main results concerning the low and average frequency ranges are the following. In the limit $\omega \to 0$, $R \to \lambda^2 d/(\varepsilon D_a S)$, and $C \to \varepsilon S/(2\lambda)$, where $\lambda = (\varepsilon k_B T/(2Nq^2))^{1/2}$ is the Debye length, $k_B T$ the thermal energy, and $D_a = 2D_p D_m/(D_p + D_m)$ the ambipolar diffusion coefficient. It follows that, in the limit of small ω, $X(\omega) \sim 2\lambda/(\omega \varepsilon S)$; i.e., it depends only on λ. From the frequency dependence of $X(\omega)$, in the limit of $\omega \to 0$, we obtain λ, and hence N, assuming for ε the one reported in ref 5. Increasing the frequency, the resistance decreases and then presents a new plateau, characterized by a resistance $R' \sim \lambda^2 d/(\varepsilon D_f S)$, where $D_f = (D_p + D_m)/2$ is the diffusion coefficient for the free diffusion. From the numerical value of R' the diffusion coefficient D_f is deduced. The second plateau for R ends at $\omega_h \sim D_f/\lambda^2$, known as Debye's relaxation frequency for the free diffusion. From the numerical values obtained for λ and D_f, we evaluate ω_h and compare it with the experimental value. The ambipolar diffusion coefficient, D_a, is related to the increasing of R, in the low frequency range.

We analyze the impedance spectroscopy of the samples of M5 with several concentration of doping[5] using the models described in refs 24 and 25, according to which the difference in the diffusion coefficients is responsible for a new plateau in the limit for $\omega \to 0$, connected to the ambipolar diffusion,[27] not present in our spectra, where just a tendency to increase for the real part of the impedance has been observed. We assume that there is a pure resistance in parallel to the sample, R_p.

The best fit of the experimental data have been done by means of a Genetic Algorithm (GA),[28,29] using as starting values the ones obtained from the limit for $f \to 0$ and from R' as discussed above, and for ε and d the ones reported in ref 5.

In our case, we analyze the experimental data relevant to the real (R) and imaginary (X) parts of the electrical impedance of the cell, and the best fit of the two quantities is made simultaneously. The best fits, based on the theoretical model,[24,25] are reported in the Figure 6 and Figure 7.

For all sets of the experimental data the fixed parameters are as follows: $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m; $k_B = 1.38 \times 10^{-23}$ J/K; $T = (273.15 + 35)$K; $q = 1.6 \times 10^{-19}$ A·s; $S = 1 \times 10^{-4}$ m^2.
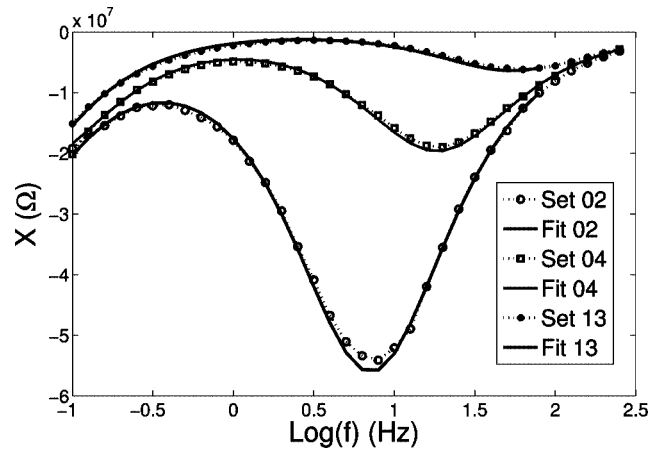
The best fit values are as follows: for **set 02**, $D_m = 1.12 \times 10^{-12}$ m^2/s, $D_p = 0.21 \times 10^{-12}$ m^2/s, $\varepsilon = 5.3 \times \varepsilon_0$, $N = 1 \times 10^{20}$ m^{-3}, $R_p = 180$ MΩ, and $d = 24$ μm; for **set 04**, $D_m = 1.81 \times 10^{-12}$ m^2/s, $D_p = 1.01 \times 10^{-12}$ m^2/s, $\varepsilon = 6.3 \times \varepsilon_0$, $N = 2 \times 10^{20}$ m^{-3}, $R_p = 82$ MΩ, and $d = 26$ μm; for **set 13**, $D_m = 0.52 \times 10^{-12}$ m^2/s, $D_p = 0.61 \times 10^{-12}$ m^2/s, $\varepsilon = 6.6 \times \varepsilon_0$, $N = 24 \times 10^{20}$ m^{-3}, $R_p = 72$ MΩ, and $d = 23.6$ μm.

From the values of the parameters for the best fits, the dielectric constant of the liquid is, approximately, $\varepsilon \sim 6 \times \varepsilon_0$, and $R_p \sim 100$ MΩ for all doping concentrations. The thickness is found to be in the range 24 μm, 26 μm, in good agreement with the nominal value of 25 μm.

We have also analyzed the temperature dependence of the electrical impedance of the cell, performing measurements at 35°, 50°, and 60°. From the best fit, we deduce that the bulk density of ions is sensible to the temperature variations, as expected.

From the good agreement between the theoretical model and the experimental data shown in Figure 6 and Figure 7, we infer that the system under investigation is well described by an insulating liquid containing one group of positive and one group of negative ions, with different mobilities. The resistance R_p introduced in the model could be connected with the presence of the spacers. Another origin of R_p could be a nonionic conduction in the liquid crystal under consideration. Further investigations are necessary to understand the origin of this parameter of the model. According to our experimental results and theoretical interpretation, the dielectric constant of the liquid is, practically, independent of the doping, in the limit of small concentration of doping material. To relate the effective ionic diffusion coefficients to the doping concentration, a systematic investigation of the impedance spectroscopy of cells doped with several concentrations of salt or of acid is necessary. The work is in progress, and will be published elsewhere.

V. Conclusion

We have analyzed the impedance spectra of samples of nematic liquid crystal M5, with different doping concentrations. Our experimental data refer to samples in the shape of a slab, with electrodes covered with polymide, to induce planar alignment, that we assume as blocking. The applied voltage is smaller than 25 mV (thermal voltage), in such a manner than the fundamental equations for the drift-diffusion of the ions in

the liquid crystal can be linearized, and the nematic cell can be described by an electrical impedance, whose conductivity and dielectric constant are renormalized by the presence of the ions. We have shown that the experimental data are in agreement with the predictions of a theoretical model based on the drift-diffusion equations, where the positive and negative ions have different diffusion coefficients. From the best fits we deduce the bulk density of ions and their diffusion coefficients in M5. As expected, the bulk density of ions strongly depends on the concentration of the doping and on the temperature.

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(8) As is well known, the concept of electrical impedance can be defined for all systems subjected to a sinusoidal external voltage. However, for non-linear systems, the impedance depends on the amplitude of the applied voltage, and its utility in the description of a sample is limited. For this reason, for non-linear systems from the current-voltage characteristic is derived the differential impedance, relating the variation of the amplitude of applied voltage with the corresponding variation of the electrical current. Only in the case in which the fundamental equations of the problem are linear, the electrical current is proportional to the applied voltage, as in Ohm's law, and the constant of proportionality between current and voltage is independent of the amplitude of the applied voltage. In this case, from a measurement of the impedance for a given amplitude of the applied voltage, it is easy to evaluate the parameters of the model. If the system is non-linear, to obtain information on the parameters of the model it is necessary to know all current−voltage characteristic. Since the equations relevant to the drift-diffusion problem can be linearized in the limit of amplitude of the applied voltage smaller than the thermal voltage 25 mV, as it will be discussed in the following, we worked in this limit in order to avoid non-linear effects. For a discussion on the concept of the electrical impedance for electrolytic cell, see: Freire, F. C. M.; Barbero, G.; Scalerandi, M. *Phys. Rev. E* **2006**, *73*, 051202.

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