Complex Dielectric Constant of a Nematic Liquid Crystal Containing Two Types of Ions: Limit of Validity of the Superposition Principle

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We investigate the influence of two groups of ions on the complex dielectric constant of a nematic liquid crystal limited by perfectly blocking electrodes. The analysis is performed by solving the equations of continuity for the two groups of cations and anions, and the equation of Poisson relating the actual electric field to the net density of charge. We consider a typical experiment of impedance spectroscopy, and evaluate the equivalent resistance and reactance of the cell, in the series representation, versus the frequency of the applied voltage to the cell. We show that the presence of two groups of ions gives rise to two plateaux in the spectrum of the resistance, similar to those related to the ambipolar and free diffusion in the case where there is only one type of ions, but for which the cations and anions have different diffusion coefficients. The correspondence between the usual ambipolar and free diffusion coefficients and those related to the presence of two groups of ions is discussed. The spectra of the real and imaginary parts of the complex dielectric constant are obtained, and their dependence on the bulk densities of the two types of ions is investigated. The nonvalidity of the superposition principle is discussed.

I. Introduction

The contribution of ions in the electric properties of semiconductors, electrolytes, and dielectric materials has been extensively investigated in the past both theoretically and experimentally.[1-6] The dielectric characterization of a sample is usually done by applying a single-frequency voltage (or current) to the electrodes and measuring the phase shift and amplitude of the resulting current at that frequency. The sample behaves as a linear system when the amplitude of the measurement voltage is small with respect to the thermal voltage. When more than one type of ions are present and the measurements are done in the linear regime, one uses the superposition principle to add the contributions of each type of ions in the dielectric response of the sample. For a clear introduction to the subject, see the book of Macdonald.[7]

The influence of the ions on the dielectric properties of nematic liquid crystals has been discussed by many authors mainly for its technological importance.[8-12] The theoretical analysis of the problem is usually performed by assuming that the nematic liquid crystal contains only a group of cations and anions, with equal[13] or different[14] diffusion coefficients. The extension of the theory to the case where several groups of ions are dissolved in the nematic liquid crystal is important from the practical point of view, because more than one type of impurities is, usually, present in the nematic liquid crystals. The first attempt to generalize the model to take into account in the analysis different types of ions has been done by Sawada et al.,[15] by assuming the validity of the superposition principle. In

a recent paper, a generalization of the model of Macdonald[3] to the case where two groups of ions are present has been proposed.[16] The aim of our paper is to complete the analysis presented in ref 16, and to compare the predictions with a model based on the superposition principle. Therefore, the model we discuss does not take into account fluctuations and pretransitional effects,[17] ion recombination and adsorption,[7] confinement effects,[18,19] etc. Our paper is organized as follows. In section II, the general equations of the problem are presented, and their solution derived in section III. The frequency dependencies of the real and imaginary parts of the electrical impedance of the cell are discussed in section IV. The real and imaginary parts of the complex dielectric constant are analyzed in section V, where the comparison with those obtained by means of the superposition principle is also presented. Section V is devoted to the conclusions.

II. Fundamental Equations of the Problem

Let us consider an insulating liquid of dielectric constant ε. The sample is assumed in the shape of a slab of thickness d and surface area S. The Cartesian reference frame has the z-axis perpendicular to the limiting surfaces, at $z = \pm d/2$, coinciding with the electrodes, connected to an external power supply fixing a difference of potential $V(d/2, t) - V(-d/2, t) = V_0 \exp(i\omega t)$, where V_0 is the amplitude and ω the circular frequency. We assume that the electrodes are perfectly blocking, and nonadsorbing.[20] Furthermore, we suppose that the ionic recombination can be neglected. This hypothesis works well when the ionic bulk densities are small with respect to the bulk density of nematic liquid crystal molecules, that is, the case of interest. In thermodynamic equilibrium, the bulk densities of the ions of groups 1 and 2 are N_1 and N_2, position independent. In the presence of an electric field imposed by an external power

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supply, the bulk density of the cations and anions of the two groups are indicated by $n_{p1} = N_1 + \delta n_{p1}$, $n_{p2} = N_2 + \delta n_{p2}$, $n_{m1} = N_1 + \delta n_{m1}$, and $n_{m2} = N_2 + \delta n_{m2}$, respectively. The fundamental equations of the problem are the equations of continuity for the cations and anions of the two groups, and the equation of Poisson relating the actual electric field in the sample with the net electrical charge density. We assume that, for each group, the diffusion coefficient for the positive ions equals the one for the negative ions, and that the electrical charges of the ions of the two groups are equal. We indicate the electric field, directed along the z-axis, by E, and by V the electrical potential, related to E by $E = -V_{,z}$, where the notation comma is used for the partial derivatives: $V_{,z} = \partial V/\partial z$.

In our one-dimensional problem, where all functions depend only on the coordinate z and time t, these equations read

$$n_{p1,t} = D_1\{n_{p1,z} + (q/K_BT)n_{p1}V_{,z}\}_{,z}$$
$$n_{m1,t} = D_1\{n_{m1,z} - (q/K_BT)n_{m1}V_{,z}\}_{,z}$$
$$n_{p2,t} = D_2\{n_{p2,z} + (q/K_BT)n_{p2}V_{,z}\}_{,z}$$
$$n_{m2,t} = D_2\{n_{m2,z} - (q/K_BT)n_{m2}V_{,z}\}_{,z}$$
$$V_{,zz} = -(q/\varepsilon)(n_{p1} + n_{p2} - n_{m1} - n_{m2}) \quad (1)$$

respectively. Equation 1 has been written by taking into account the Einstein−Smolucowski relation between the ionic mobilities and the diffusion coefficients.[21] We have indicated by D_1 and D_2 the diffusion coefficients of the two groups of ions, by q the modulus of the electrical charge of the ions, and by T the absolute temperature. K_B is Boltzmann's constant.

Equation 1 has to be solved with the boundary conditions, at $z = \pm d/2$,

$$n_{p1,z} + (q/K_BT)n_{p1}V_{,z} = 0$$
$$n_{m1,z} - (q/K_BT)n_{m1}V_{,z} = 0$$
$$n_{p2,z} + (q/K_BT)n_{p2}V_{,z} = 0$$
$$n_{m2,z} - (q/K_BT)n_{m2}V_{,z} = 0 \quad (2)$$

and $V = \pm(V_0/2)\exp(i\omega t)$, connected with the hypothesis that the electrodes are perfectly blocking, and to the presence of the external power supply.

We limit our analysis to the case where the external difference of potential is so small that the bulk density variation due to the presence of the external field is very small with respect to the bulk density of ions in thermodynamical equilibrium.[22] In this framework, eq 1 can be linearized. We indicate by

$$p_1 = \frac{\delta n_{p1}}{N_1}, \quad m_1 = \frac{\delta n_{m1}}{N_1}, \quad p_2 = \frac{\delta n_{p2}}{N_2}, \quad m_2 = \frac{\delta n_{m2}}{N_2},$$
$$\text{and} \quad u = \frac{q}{K_BT}V \quad (3)$$

the relative variations of the bulk densities of ions and the electrical potential, in thermal units. With these reduced quantities, eq 1 can be rewritten as

$$p_{1,t} = D_1(p_{1,zz} + u_{,zz})$$
$$m_{1,t} = D_1(m_{1,zz} - u_{,zz})$$
$$p_{2,t} = D_2(p_{2,zz} + u_{,zz})$$
$$m_{2,t} = D_2(m_{2,zz} - u_{,zz})$$
$$u_{,zz} = -\frac{1}{2\lambda_1^2}(p_1 - m_1) - \frac{1}{2\lambda_2^2}(p_2 - m_2) \quad (4)$$

that have to be solved with the boundary conditions, at $z = \pm d/2$,

$$p_{1,z} + u_{,z} = 0 \quad \text{and} \quad m_{1,z} - u_{,z} = 0$$
$$p_{2,z} + u_{,z} = 0 \quad \text{and} \quad m_{2,z} - u_{,z} = 0 \quad (5)$$

and $u = \pm(u_0/2)\exp(i\omega t)$, where $u_0 = qV_0/K_BT$. In eq 4, we have introduced the lengths of Debye related to ions 1 and 2 defined by $\lambda_1^2 = (\varepsilon K_BT/2N_1q^2)$ and $\lambda_2^2 = (\varepsilon K_BT/2N_2q^2)$,[23] where ε is the permittivity of the medium. The set of equations in eqs 4 and 5 are the fundamental equations of the problem, in the linear approximation, where the system under investigation behaves in a linear manner, from the electrical point of view.

Since the electrodes are assumed perfectly blocking and the ionic recombination is neglected, the number of ions in the sample remains constant, for each group. This implies that

$$\int_{-d/2}^{d/2} n_{pi}\, dz = \int_{-d/2}^{d/2} n_{mi}\, dz = N_i d \quad (6)$$

where $i = 1, 2$. By taking into account the definition of p_i and m_i, given by eq 3, eq 6 can be rewritten as

$$\int_{-d/2}^{d/2} p_i\, dz = \int_{-d/2}^{d/2} m_i\, dz = 0 \quad (7)$$

for all d. It follows that p_i and m_i, in our framework, have to be odd functions of z.

III. Solution of the Equations of the Problem

The quantities p_1, m_1, p_2, m_2, and u depend on z and t. In the steady state, we look for a solution of the type

$$(p_1, m_1, p_2, m_2, u) = (\psi_{p1}, \psi_{m1}, \psi_{p2}, \psi_{m2}, \psi_u)\exp(i\omega t) \quad (8)$$

where ψ_{p1}, ψ_{m1}, ψ_{p2}, ψ_{m2}, and ψ_u depend only on the spatial coordinate z. From now on, we indicate the z derivatives by $G' = dG/dz$. By substituting ansatz 8 into eqs 4 and 5, we get

$$i\omega\psi_{p1} = D_1(\psi_{p1}'' + \psi_u'')$$
$$i\omega\psi_{m1} = D_1(\psi_{m1}'' - \psi_u'')$$
$$i\omega\psi_{p2} = D_2(\psi_{p2}'' + \psi_u'')$$
$$i\omega\psi_{m2} = D_2(\psi_{m2}'' - \psi_u'') \quad (9)$$

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and

$$\psi_u'' = -\frac{1}{2\lambda_1^2}(\psi_{p1} - \psi_{m1}) - \frac{1}{2\lambda_2^2}(\psi_{p2} - \psi_{m2}) \tag{10}$$

that have to be solved with the boundary conditions at $z = \pm d/2$

$$\psi_{p1}' + \psi_u' = 0 \quad \text{and} \quad \psi_{m1}' - \psi_u' = 0$$
$$\psi_{p2}' + \psi_u' = 0 \quad \text{and} \quad \psi_{m2}' - \psi_u' = 0 \tag{11}$$

and $\psi_u = \pm u_0/2$. From eq 9, we obtain

$$i\omega(\psi_{p1} + \psi_{m1}) = D_1(\psi_{p1} + \psi_{m1})'' \tag{12}$$

and a similar equation for $\psi_{p2} + \psi_{m2}$. By putting $\mathcal{J}_1 = \psi_{p1} + \psi_{m1}$, eq 12 can be rewritten as

$$i\omega \mathcal{J}_1 = D_1 \mathcal{J}_1'' \tag{13}$$

whose solution, odd in z for condition 7, is

$$\mathcal{J}_1 = \mathcal{J}_{10} \sinh(\sqrt{i\omega/D_1}z) \tag{14}$$

From eq 11, we have furthermore $\psi_{p1}' + \psi_{m1}' = 0$ for $z = \pm d/2$, i.e., $\mathcal{J}_1' = 0$ on the limiting surfaces. It follows that for all d we have

$$\sqrt{\frac{i\omega}{D_1}} \mathcal{J}_{10} \cosh\left(\sqrt{\frac{i\omega}{D_1}}\frac{d}{2}\right) = 0 \tag{15}$$

and hence $\mathcal{J}_{10} = 0$, that implies $\mathcal{J}_1 = 0$. Consequently, the distribution of ions is such that $\psi_{m1} = -\psi_{p1}$. In a similar manner, it is possible to show that $\psi_{m2} = -\psi_{p2}$. The set of fundamental equations of the problem is then

$$i\omega\psi_{p1} = D_1(\psi_{p1}'' + \psi_u'')$$
$$i\omega\psi_{p2} = D_2(\psi_{p2}'' + \psi_u'')$$
$$\psi_u'' = -\frac{1}{\lambda_1^2}\psi_{p1} - \frac{1}{\lambda_2^2}\psi_{p2} \tag{16}$$

that have to be solved with the boundary conditions at $z = \pm d/2$

$$\psi_{p1}' + \psi_u' = 0, \quad \psi_{p2}' + \psi_u' = 0, \quad \text{and} \quad \psi_u = \pm u_0/2 \tag{17}$$

By eq 16, we obtain

$$\psi_{p1}'' - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\psi_{p1} - \frac{1}{\lambda_2^2}\psi_{p2} = 0$$

$$\psi_{p2}'' - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)\psi_{p2} - \frac{1}{\lambda_1^2}\psi_{p1} = 0 \tag{18}$$

A solution of eq 18, satisfying eq 7, is of the type

$$(\psi_{p1}, \psi_{p2}) = (C_{p1}, C_{p2}) \sinh(\mu z) \tag{19}$$

where C_{p1} and C_{p2} are constants and $1/\mu$ a characteristic length to be determined. By substituting the trial solution 19 into eq 18, we obtain the homogeneous system

$$\left\{\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\}C_{p1} - \frac{1}{\lambda_2^2}C_{p2} = 0$$

$$-\frac{1}{\lambda_1^2}C_{p1} + \left\{\mu^2 - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)\right\}C_{p2} = 0 \tag{20}$$

Equation 20 has a solution for C_{p1} and C_{p2} different from the trivial one only if μ is a solution of the biquadratic equation

$$\left\{\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\}\left\{\mu^2 - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)\right\} - \frac{1}{\lambda_1^2\lambda_2^2} = 0 \tag{21}$$

Furthermore, from the first eq 20, it follows that $C_{p2} = k(\mu^2)C_{p1}$, where

$$k(\mu^2) = \lambda_2^2\left\{\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\} \tag{22}$$

Therefore, the solutions of eq 18 are

$$\psi_{p1} = C_1 \sinh(\mu_1 z) + C_2 \sinh(\mu_2 z)$$
$$\psi_{p2} = k_1 C_1 \sinh(\mu_1 z) + k_2 C_2 \sinh(\mu_2 z) \tag{23}$$

where μ_1 and μ_2 are the two positive solutions of eq 21, $k_1 = k(\mu_1^2)$ and $k_2 = k(\mu_2^2)$. By substituting eq 23 into the third of eq 16 and integrating, taking into account the symmetry of the problem, we get

$$\psi_u = -\frac{1}{\mu_1^2}\left(\frac{1}{\lambda_1^2} + \frac{k_1}{\lambda_2^2}\right)C_1 \sinh(\mu_1 z) - $$
$$\frac{1}{\mu_2^2}\left(\frac{1}{\lambda_1^2} + \frac{k_2}{\lambda_2^2}\right)C_2 \sinh(\mu_2 z) + C_3 z \tag{24}$$

The integration constants C_1, C_2, and C_3 have to be determined by imposing the boundary conditions eq 17, that by taking into account eqs 23 and 24 can be rewritten as

$$\left\{\mu_1 - \frac{1}{\mu_1^2}\left(\frac{1}{\lambda_1^2} + \frac{k_1}{\lambda_2^2}\right)\right\}C_1 \cosh(\mu_1 d/2) +$$

$$\left\{\mu_2 - \frac{1}{\mu_2^2}\left(\frac{1}{\lambda_1^2} + \frac{k_2}{\lambda_2^2}\right)\right\}C_2 \cosh(\mu_2 d/2) + C_3 = 0$$

$$\left\{k_1\mu_1 - \frac{1}{\mu_1^2}\left(\frac{1}{\lambda_1^2} + \frac{k_1}{\lambda_2^2}\right)\right\}C_1 \cosh(\mu_1 d/2) +$$

$$\left\{k_2\mu_2 - \frac{1}{\mu_2^2}\left(\frac{1}{\lambda_1^2} + \frac{k_2}{\lambda_2^2}\right)\right\}C_2 \cosh(\mu_2 d/2) + C_3 = 0$$

$$-\frac{1}{\mu_1^2}\left(\frac{1}{\lambda_1^2} + \frac{k_1}{\lambda_2^2}\right)C_1 \sinh(\mu_1 d/2) -$$

$$\frac{1}{\mu_2^2}\left(\frac{1}{\lambda_1^2} + \frac{k_2}{\lambda_2^2}\right)C_2 \sinh(\mu_2 d/2) +$$

$$C_3 d/2 = u_0/2$$

The distribution of the ions, as well as the profile of the electric potential across the sample, is then determined.

IV. Electrical Impedance of the Cell

The electric potential in the cell is given by $V(z, t) = (K_B T/q)\psi_u(z) \exp(i\omega t)$, and the electric field by $E(z, t) = -V'(z, t) = -(K_B T/q)\psi_u' \exp(i\omega t)$. The surface density of charge, on the electrode at $z = d/2$, sent by the external power supply to fix the voltage on the sample is then $\sigma(t) = -\varepsilon E(d/2, t)$. The displacement current is

$$I(t) = S\frac{d\sigma}{dt} = i\omega\varepsilon\frac{K_B T}{q}\psi_u'(d/2)e^{i\omega t} \tag{25}$$

The electrical impedance of the cell, defined as the ratio between the applied voltage and the current, $Z = V_0 \exp(i\omega t)/I$, is then given by

$$Z = \frac{1}{i\omega}\frac{q}{\varepsilon K_B T S}\frac{V_0}{\psi_u'(d/2)} \tag{26}$$

As it follows from the system of equations defining the integration constants, C_1, C_2, and C_3 are linear in u_0, and hence in V_0. Consequently, Z is independent of the amplitude of the applied difference of potential V_0, as expected, due to the linearity of the system under consideration. From eq 26, the real and imaginary parts of the impedance can be easily determined. They correspond to the resistance and reactance of the cell, in the series representation.

For the discussion reported in the following, it is useful to define the following effective diffusion coefficients

$$D_I = \frac{N_1}{N_1 + N_2}D_1 + \frac{N_2}{N_1 + N_2}D_2$$

$$\frac{1}{D_{II}} = \frac{N_1}{N_1 + N_2}\frac{1}{D_1} + \frac{N_2}{N_1 + N_2}\frac{1}{D_2} \tag{27}$$

that corresponds, in some manner, to the free and ambipolar diffusion coefficients,[24] and the effective length of Debye

$$\frac{1}{\lambda^2} = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} = \frac{(N_1 + N_2)q^2}{\varepsilon K_B T} \tag{28}$$

that corresponds to the length of Debye of the liquid containing a bulk density of ions $N = N_1 + N_2$. Note that, for $D_1 = D_2$, $D_I = D_{II}$.

For the numerical calculation, we assume for the geometrical parameters of the cell $d = 25$ μm and $S = 1$ cm^2, which correspond to a typical sample used for measurements of impedance spectroscopy. The nematic liquid crystal considered is 5CB, in planar orientation, for which $\varepsilon = \varepsilon_\perp = 6.7 \times \varepsilon_0$, with $N_1 = 10^{20}$ m^{-3} and $N_2 = 3 \times N_1$, having diffusion coefficients $D_1 = 10^{-11}$ m^2/s and $D_2 = 0.1 \times D_1$.[25] The nematic sample is assumed homogeneous. Note that there is no electric field induced reorientation of the nematic molecules, since the measuring voltage is much lower than the threshold for the Freedericksz transition.

In Figure 1, we show the resistance of the cell versus the frequency. The dotted line corresponds to the case in which all of the ions have the diffusion coefficient D_I, whereas the dashed line corresponds to the case in which all of the ions have the diffusion coefficient D_{II}. In these cases, R_I and R_{II} present a plateau, ending at the Debye relaxation frequency, as discussed in ref 26. On the contrary, the presence of two groups is responsible for two plateaux in the spectrum of the resistance of the cell. The plateau in the low frequency region corresponds to the ambipolar diffusion, whereas the one in the intermediate frequency to the free diffusion.[24] In Figure 2, the frequency dependence of the reactance of the cell is reported, as well as the reactances corresponding to D_I and D_{II}. As it is evident from this figure, the reactance does not present an extremum corresponding to the relaxation frequency relevant to the frequency of Debye for R_{II}. In the low frequency region, the reactance is independent of the diffusion coefficients.[13] In Figure 3, we compare the spectrum of R with that of X to show the absence of an extremum in the low frequency region of the imaginary part.
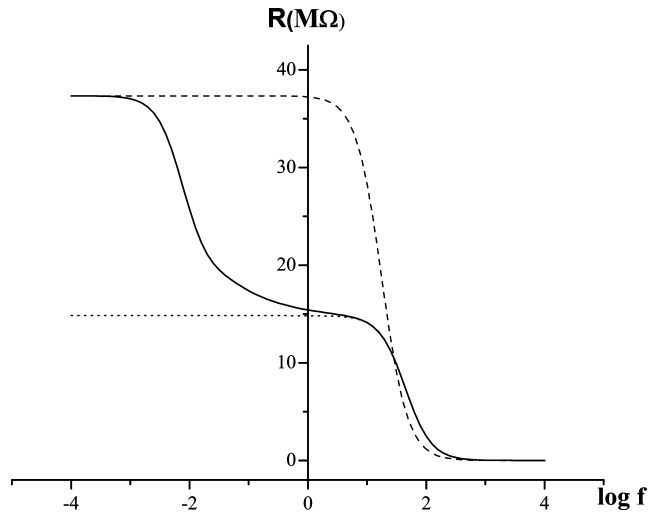
V. Real and Imaginary Parts of the Complex Dielectric Constant

From the electrical impedance of the cell, it is possible to evaluate the equivalent conductivity and equivalent dielectric constant defined by $\sigma_{eq} = (1/R)(d/S)$ and $\varepsilon_{eq} = -(1/\omega X)(d/S)$. By introducing the complex dielectric constant $\varepsilon = \varepsilon_r - i\varepsilon_i$, and the complex capacitance defined by $\mathcal{C} = \varepsilon(S/d)$, the electrical impedance is given by $Z = 1/(i\omega \mathcal{C})$. From this relation, it follows that the relations connecting σ_{eq} and ε_{eq} with ε_r and ε_i are

$$\varepsilon_r = \frac{\varepsilon_{eq}}{1 + \omega^2(\varepsilon_{eq}/\sigma_{eq})^2} \quad \text{and} \quad \varepsilon_i = \frac{\omega(\varepsilon_{eq}/\sigma_{eq})}{1 + \omega^2(\varepsilon_{eq}/\sigma_{eq})^2}\varepsilon_{eq} \tag{29}$$

In the case in which only one group of ions is present, with the same diffusion coefficient D, the analysis reported in ref 13 shows that in the limit $\omega \to 0$

$$\varepsilon_r = \frac{1}{2}\varepsilon\frac{d}{\lambda} + \mathcal{O}(\omega^2) \quad \text{and} \quad \varepsilon_i = \frac{1}{4}\varepsilon\frac{d^2}{D}\omega + \mathcal{O}(\omega^3) \tag{30}$$

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R(MΩ)

Figure 1. Frequency dependence of the real part, R, of the electrical impedance of a cell containing two types of ions. The dotted line corresponds to the situation in which all of the ions have the same diffusion coefficient $D_I = (N_1 D_1 + N_2 D_2)/(N_1 + N_2)$. The dashed line corresponds to the case in which all of the ions have the diffusion coefficient $D_{II} = (N_1 + N_2)D_1 D_2/(N_2 D_1 + N_1 D_2)$. Note the presence of two plateaux in the spectrum of R.

X(MΩ)
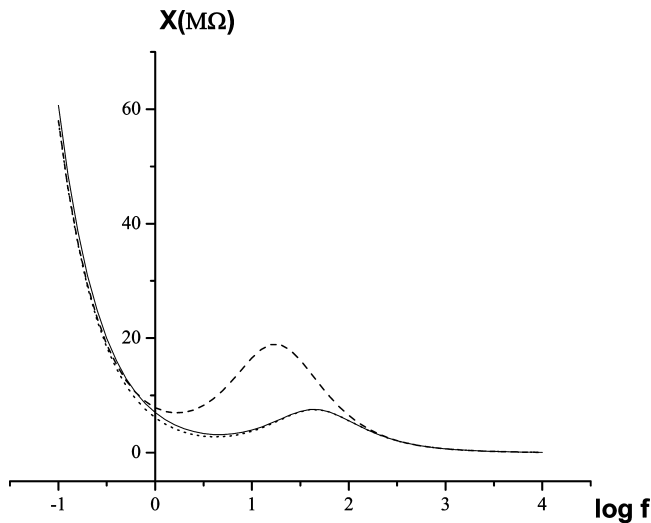
Figure 2. Frequency dependence of the imaginary part, X, of the electrical impedance of a cell containing two types of ions. The dotted line corresponds to the situation in which all of the ions have the same diffusion coefficient $D_I = (N_1 D_1 + N_2 D_2)/(N_1 + N_2)$. The dashed line corresponds to the case in which all of the ions have the diffusion coefficient $D_{II} = (N_1 + N_2)D_1 D_2/(N_2 D_1 + N_1 D_2)$. Note that in the low frequency region the spectra corresponding to the three cases coincide, as expected, because in this part of the spectrum the reactance is independent of the diffusion coefficient, and depends only on the effective length of Debye. The same conclusion holds true in the high frequency region, where the ions do not participate in the conduction.

whereas in the limit $\omega \to \infty$

$$\varepsilon_r = \varepsilon + \mathcal{O}(\omega^{-3/2}) \quad \text{and} \quad \varepsilon_i = \frac{D}{\omega\lambda^2}\varepsilon + \mathcal{O}(\omega^{-2})$$
(31)

where λ is the length of Debye of the liquid. We are now interested in the evaluation of the ionic contribution to the complex dielectric constant of an insulating liquid.

log R(Ω),log(-X(Ω))
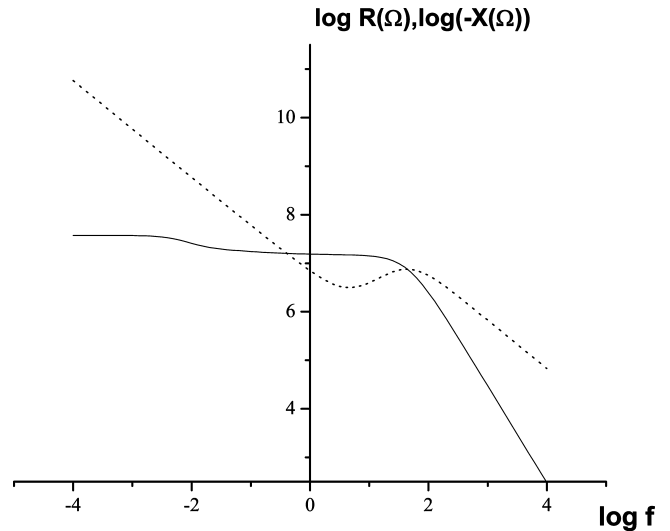
Figure 3. Comparison of the spectra of $\log R$ (continuous curve) and $\log (-X)$ (dotted curve) to show that in the low frequency region the imaginary part does not present an extremum at the relaxation frequency of the first plateau of R.

Since we are considering an insulating liquid containing two groups of ions, the ionic contributions to the components of the complex dielectric constant are $\delta\varepsilon_r = \varepsilon_r - \varepsilon$ for the real part and $\delta\varepsilon_i = \varepsilon_i$ for the imaginary part.

In Figure 4, we show the spectra of $\delta\varepsilon_r$ (a) and $\delta\varepsilon_i$ (b). In the same figure are reported the values of the real and imaginary parts of the ionic contribution to the complex dielectric constant deduced by assuming the validity of the superposition principle. According to this principle, the real and imaginary parts of the complex dielectric constant of the nematic liquid crystal containing the two groups of ions is evaluated by adding the contributions to the real and imaginary parts due to the single group of ions, separately, according to the relations

$$\delta\varepsilon_r(S) = \delta\varepsilon_r(1) + \delta\varepsilon_r(2) \quad \text{and} \quad \delta\varepsilon_i(S) = \delta\varepsilon_i(1) + \delta\varepsilon_i(2)$$
(32)

as assumed in several papers devoted to the dielectric characterization of nematic liquid crystals.[27−31] As is evident from these figures, the agreement between eqs 29 and 32 is rather poor in the low frequency region.

In Figure 5, we show the spectra of ε_r (a) and ε_i (b) and the approximate expressions deduced from eqs 30 and 31 written for the case under consideration, that are
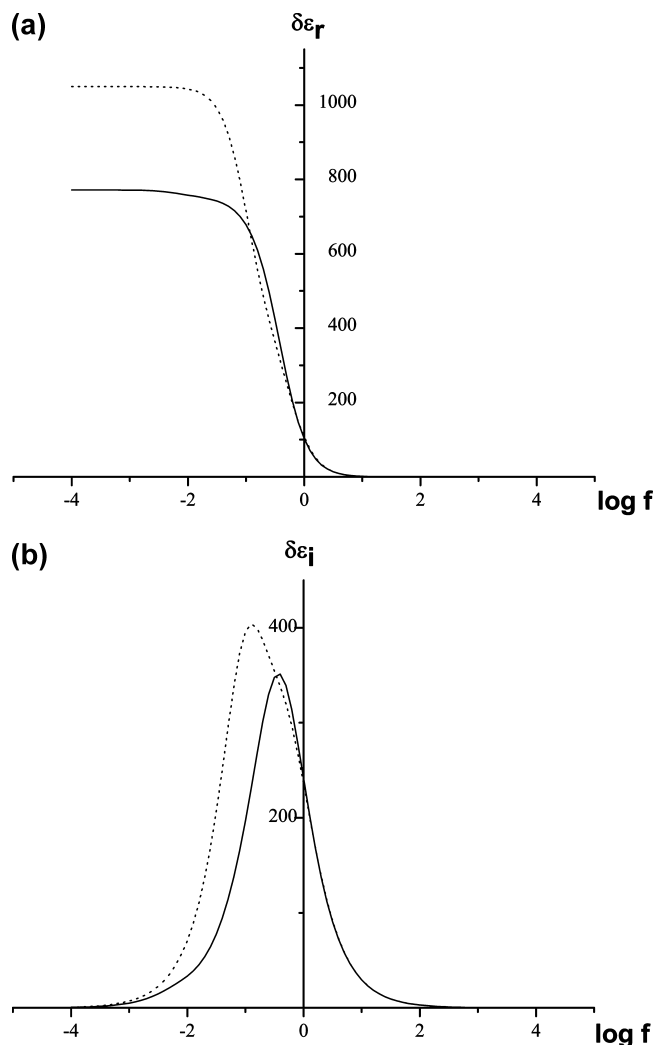
$$\varepsilon_r = \frac{1}{2}\varepsilon\frac{d}{\lambda} + \mathcal{O}(\omega^2) \quad \text{and} \quad \varepsilon_i = \frac{1}{4}\varepsilon\frac{d^2}{D_{II}}\omega + \mathcal{O}(\omega^3)$$
(33)

and

$$\varepsilon_r = \varepsilon + \mathcal{O}(\omega^{-3/2}) \quad \text{and} \quad \varepsilon_i = \frac{D_I}{\omega\lambda^2}\varepsilon + \mathcal{O}(\omega^{-2})$$
(34)

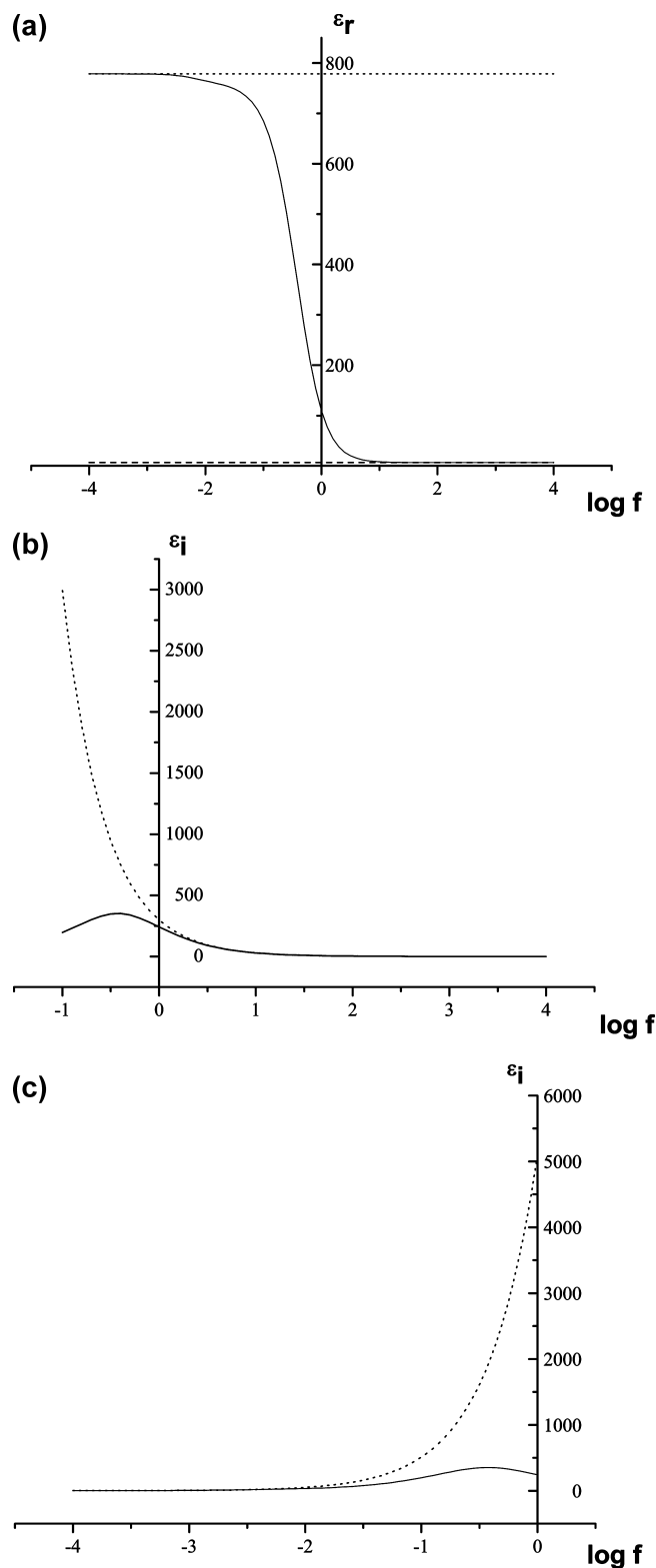The agreement is rather good in the two limits.

(a)

(b)

Figure 4. Spectra of $\delta\varepsilon_r$ (a) and $\delta\varepsilon_i$ (b) deduced by means of the complete solution of the drift-diffusion of the ions in the presence of an external field (continuous curves) and deduced by means of the superposition principle (dotted curves).

VI. Conclusions

We have investigated the dielectric properties of an insulating liquid containing two groups of ions. According to our analysis, when the two groups of ions have different diffusion coefficients, the spectrum of the real part of the impedance of the cell, in the series representation, presents two plateaux. These are related to different diffusion coefficients, that correspond, in some manner, to the ambipolar and free diffusion coefficients. We have also evaluated the ionic contribution to the complex dielectric constant. According to our results, the superposition principle, widely used to determine the ionic properties dispersed in nematic liquid crystals, represents a very rough approximation of the real problem. The result that the superposition principle does not work well in the present case is not surprising. In fact, the drift-diffusion of the ions depends on the actual electric field in the sample; that for the equation of Poisson depends on both types of ions. Only in the case in which the electric field in the sample coincides with the applied one, the superposition principle works well. However, this situation is not realistic, because the electric field due to the ions is

(a)

(b)

(c)

Figure 5. Spectra of ε_r (a) and ε_i (b, c) deduced by means of the complete solution of the drift-diffusion of the ions in the presence of an external field (continuous curves) and approximate expressions (dotted and dashed curves) given by eqs 33 and 34.

not negligible with respect to the external one, when the system behaves in a linear manner.

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