NEW APPROACH OF THE AC ELECTRODE POLARIZATION
DURING THE MEASUREMENTS OF IMPEDANCE SPECTRA

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A mathematical approach for describing the influence of the ions dissolved in a liquid crystal on the impedance measurements is presented. New independent variables allow re-formulating the basic coupled differential equations of continuity and Poisson equation as well. The obtained forms are simpler than those used up to now. Illustrative examples are analyzed.

Key words: electrode polarization, impedance spectroscopy, liquid crystal.

1. INTRODUCTION

Nematic liquid crystals are mostly insulating media. Their electrical conduction has an ionic origin. The ions present in the liquid crystals are due either to chemical decomposition of the molecules forming the liquid crystal itself, or to some impurities. When an external field is applied to a liquid crystal cell, the ionic impurities move close to the electrode of opposite sign [1 and the references cited herein]. The accumulation of the ions at the electrode interface leads to reduction of the electric field inside the bulk and to changes of the optical and the electrical properties of the system (cell).

If the motion of ions under the electric field is blocked at electrodes, compensation charges are supplied from the external power source and thus polarization is generated [2, 3]. The polarization effects at electrodes induced by charge carriers in liquids are so called space-charge polarization and have been extensively investigated both experimentally and theoretically [4-7].

Electrode polarization (EP) has been studied experimentally by impedance spectroscopy [8, 9]. In a typical experiment, a capacitor filled with the fluid to be analyzed, is subjected to a sinusoidal external voltage. The real $R$ part and the imaginary part $X$ of the impedance $Z$ are measured as a function of the frequency of the applied voltage. As a response, the ions in the liquid migrate towards the electrodes, contributing to the electric current in the external circuit. It is well known
that $R$ presents an anomalous increase in the low frequency limit. Different mechanisms could account for this behavior. Among them, we mention the Ohmic characteristic of the electrodes [10, 11] and the dissociation recombination effect [12-15]. Another possible mechanism responsible for this behavior of EP is the adsorption/desorption of ions at/from the electrode surfaces.

The equations describing the influence of the ions on the effective dielectric constant of an insulating liquid have been discussed long time ago by MacDonald [16], and applied to several situations of practical interest [13,17,18]. They are equations of continuity for the positive and negative ions, and Poisson equation for the actual potential across the cell. Unfortunately, the final expressions for the real and imaginary parts of the dielectric constant are rather complicated, and their use to interpret experimental data not straightforward.

More recently, simple theoretical versions of the MacDonald model, relevant to the case in which the impurities solved in the liquid crystals are completely dissociated, have been analyzed for several cases [1, 11, 19-25]. Even in these situations, the final formulas have a relatively complicated expression. Sometimes they refer to the same physical system the formulas do not have a unitary character making it difficult to interpret the results.

The reason for a new mathematical model is then to eliminate the shortcomings pointed out and to obtain in a simpler way compact analytical formulas that include the effect of the electrode polarization. In addition, reconsidering the mentioned situations might use a smaller number of calculations.

2. ELECTRODE POLARIZATION-FUNDAMENTAL EQUATIONS

Let us consider an insulating liquid of dielectric constant $\varepsilon (\varepsilon = \varepsilon_0 \varepsilon_r)$. The sample is assumed in the shape of a slab of thickness $L$ and surface area $S$. The Cartesian reference frame has the $x$-axis perpendicular to the limiting surfaces, at $x = \pm L/2$, coinciding with the electrodes, connected to an external power supply with a potential difference $u_a(x,t)$:

$$u_a(x,t) = U_a + u_\delta(t) = U_a + U_A \exp(i\omega t)$$

where $U_a$ is external bias voltage (under dc regime), $u_\delta(t)$ is external alternative voltage (ac regime), $U_A$ is the amplitude and $\omega$ the circular frequency (Fig. 1). In the linear response approximation $U_A$ should be much smaller than thermal potential $V_f = k_B T / q$.

A liquid containing two types of positive charge carriers (cations) and negative (anions) with concentrations $n$ and $p$, is characterized by different values of the associated physical quantities: the mobility $\mu_n$, $\mu_p$, the diffusion coefficient $D_n$, $D_p$, the lifetime $\tau_n$, $\tau_p$. The electric charge of ions is the same except the sign; $q$ is the modulus of electric charge.
In the volume the processes of generation/ recombination for the mobile charge carriers can take place with certain rate. The transport of mobile carriers is described by the equations of continuity for their concentrations and the Poisson equation for the electric field. In the equations of continuity the expressions of the current density contain the field and the diffusion components. Physical quantities associated with these processes are the mobility and the diffusion coefficient.

Fig. 1 – Sketch of the measuring cell.
Ac voltage is applied to a dilute, symmetric, binary electrolyte between parallel plate blocking electrodes separated by $L$.

With the hypothesis that ionic charges are point-like the evolution equations have the form [16, 16, 26]:

$$
\frac{\partial p}{\partial t} + \frac{\partial J_p}{\partial x} = G_p - R_p = -r_p, \\
\frac{\partial n}{\partial t} + \frac{\partial J_n}{\partial x} = G_n - R_n = -r_n, \\
\frac{\partial E}{\partial x} = \frac{q}{\varepsilon} (N + p - n).
$$

where $G_p, G_n$ are the generation rates, $R_p, R_n$ are recombination rates, $r_p, r_n$ are the net recombination rates for the cations and the anions respectively, $J_p, J_n$ are the electric current densities for individual carriers:

$$
J_p = qJ_p = q \left( \mu_p p E - D_p \frac{\partial p}{\partial t} \right) \\
J_n = -qJ_n = q \left( \mu_n n E + D_n \frac{\partial n}{\partial t} \right)
$$

where $J_p, J_n$ are the ion (particle) current densities.
Dissociation of the neutral impurity produces negative and positive mobile charge carriers. The thermal equilibrium of dissociation and recombination of univalent electrolyte $C$ in a solution is given by the reaction: $C \leftrightarrow A^+ + B^-$. 

The generation-recombination rates $r$ in the liquid are given by the equations:

$$-r_p = -r_n = r_C = C_1 n_C - C_2 p n$$

where $p(x, t)$ is the concentration of ions $A^+$, $n(x, t)$ is the concentration of the ions $B^-$ resulted from neutral dissociation centers $C$, with $n_C(x, t)$ concentration; $C_1$ is the dissociation rate, and $C_2$ is the recombination rate [2,16, 27].

The general system of equations must be supplemented with the equation of the evolution for the concentration of the mobile neutral centers [26]:

$$\frac{\partial n_C}{\partial t} = -C_1 n_C + C_2 n_A n_B - D_C \frac{\partial^2 n_C}{\partial x^2}$$

A complete solution of differential equations of the system containing the equations (2), (3) and (5) is obtained with specified boundary conditions imposed by the nature of the electrodes and by the adsorption-desorption processes.

In the following we use the intensity of electric current:

$$I = S j = S \left( J_p + J_n + e \frac{\partial E}{\partial t} \right) = S \left[ q(J_p - J_n) + e \frac{\partial E}{\partial t} \right]$$

$j$, is the total electric current density resulted from Maxwell equations [15, 28, 29].

Since the equations (3) are nonlinear, the variables will contain all harmonics of ac voltage frequency. The complete (accurate) solution for $p$, $n$ and $E$ would involve static component (zero frequency) together with the fundamental and all its higher harmonics components. If the $U_A$ is sufficiently small all harmonics above fundamental may be neglected. The system response to the external voltage can be separated in the part due to stationary dc voltage ($U_a$) and the part due to time-dependent voltage ($u_A$).

In the approximation of small ac signal the concentrations of the charge carriers are:

$$p(x, t) = p_0(x) + \delta p(x, t) = p_0(x) + p_1(x) \exp(i \omega t)$$

$$n(x, t) = n_0(x) + \delta n(x, t) = n_0(x) + n_1(x) \exp(i \omega t)$$

We assume that the expressions of the other variables contain two terms as well. For example the ion current densities (particle current densities) have the following form:

$$J_{m,0}(x) = \pm \mu_m m_0(x) E_0(x) - D_m \frac{dm_m}{dx}$$

$$J_{m,1}(x) = \pm \mu_m [m_1(x) E_0(x) + m_0(x) E_1(x)] - D_m \frac{dm_m}{dx}$$

(8)
where 0 refers to the stationary case and the index 1 is for time-dependent case, \( m \) is either \( n \) or \( p \).

The equations of the static case are independent of the alternative voltage:

\[
\frac{d}{dx} \left[ \pm \mu_m m_0(x) E_0(x) - D_m \frac{dm_0(x)}{dx} \right] = -\frac{m_0(x)}{\tau_m}
\]

(9)

In the ac case the equations system for the variables \( n_1(x) \), \( p_1(x) \) and \( E_1(x) \), contain imaginary terms from the derivative with the time variable:

\[
\left( i \omega + \frac{1}{\tau_m} \right) m_t(x) \pm \frac{d}{dx} \left[ \mu_m m_0(x) E_1(x) + \mu_m m_t(x) E_0(x) \mp D_m \frac{dm_t(x)}{dx} \right] = 0
\]

(10)

The electric field \( E_1 \) is subjected to the following condition:

\[-U_a = \int_{-L/2}^{L/2} E_1(x) dx \]

(11)

Provided with adequate boundary condition the fundamental equations (10) and (11) determine the variables \( p_1, n_1, E_1 \).

In the approximation of small signal the equations are linear and it makes sense to define the impedance \( Z(\omega; U_a) \) as function of the frequency and dc voltage as it is known [19, 22]:

\[
Z(\omega, U_a) = \frac{U_a}{I} = \frac{U_a}{S_{\phi} \left( L / 2 \right)}
\]

(12)

3. PROPOSED APPROACH

A mathematical model developed here permits determination of mobile ion concentration and the electric field distributions in a way even simpler than that already described [1, 11, 18-24].

We define the “common value”; and “differential value” concentration by the arithmetic average and the difference of the two types of carriers concentration. The concentration difference, is, up to a constant factor equal to the elementary charge, the local net charge [29, 30]:

\[
n_c = \frac{p_i + n_i}{2} \quad ; \quad n_d = p_i - n_i
\]

(13)
The choice of new variables is suggested by that the net charge density depends on the concentration difference between positive and negative charge carriers. Charge density occurs both in the expression of the continuity equation and the Poisson equation.

All other physical parameters associated with the charge carriers can be reformulated by means of corresponding of the “common” and the “differential” value.

The linear combinations can get some other equation systems, equivalent to the system (10) given above, according to the new variables \((n_C, n_D, E_0)\). For example, the equation for \(p_1\) is divided by \(D_p\) and the equation for \(n_1\) is divided by \(D_n\) then the obtained equations are added and subtracted. After collecting (grouping) terms according to new variables the results can be written:

\[
\begin{align*}
-d^2n_D + \frac{q}{k_BT}\frac{d}{dx}\left[\left(p_0 + n_0\right)E_1 + \left(p_1 + n_1\right)E_0\right] + \frac{n_C}{\lambda_D^2} + \frac{n_D}{\lambda_C^2} &= 0 \\
-2d^2n_C + \frac{q}{k_BT}\frac{d}{dx}\left[\left(p_0 - n_0\right)E_1 + \left(p_1 - n_1\right)E_0\right] + 2\frac{n_C}{\lambda_C^2} + \frac{n_D}{2\lambda_D^2} &= 0
\end{align*}
\] (14)

\[
\frac{dE(x)}{dx} = qn_D(x)
\]

where

\[
2 \lambda_C^2 = \frac{1 + i\omega\tau_p}{D_p\tau_p} + \frac{1 + i\omega\tau_n}{D_n\tau_n}, \quad \frac{1}{\lambda_D^2} = \frac{1 + i\omega\tau_p}{D_p\tau_p} - \frac{1 + i\omega\tau_n}{D_n\tau_n}
\] (15)

If we assume that there is no dc voltage applied and no internal electric field \((U_0, E_0 = 0)\), as considered in most cases reported in the literature [1,11,18-24], the equilibrium concentrations of carriers are uniformly distributed and equal to each other: \(p_0 = n_0 = N_0\). Thus the equations system is simplified and we can eliminate the static case.

In the situation of net recombination rate and of different mobility and diffusion coefficients for the carriers we have:

\[
\begin{align*}
\frac{d^2n_D}{dx^2} + \left(\frac{q^2(p_0 + n_0)}{k_BT\varepsilon} + \frac{1}{\lambda_C^2}\right)n_D + \frac{1}{\lambda_D^2}n_C &= 0 \\
\frac{d^2n_C}{dx^2} + \frac{1}{\lambda_C^2}n_C + \left(\frac{q^2(p_0 - n_0)}{2k_BT\varepsilon} + \frac{1}{4\lambda_D^2}\right)n_D &= 0
\end{align*}
\] (16)

The above assumptions allow the analysis of several cases: the ions have different physical properties; there are generation-recombination processes, there are several pairs of carriers, the different types of the blocking electrodes.

Thus the obtained system (16) describe a physical model most commonly used for the ac electrode polarization [1, 11, 19–23, 31, 32]. The system can be solved relatively easily if the two equations can be decoupled. For this, we can
neglect the last term of the left sides. There are certain situations in which the system can be decoupled into two sub-systems, which will be presented below. On the other hand, electrode polarization in solid samples is also important [16, 33].

4. ILLUSTRATIVE EXAMPLES

We consider now the situations met in a liquid crystal cell in which the concentration of impurities is small. For this limit case the dissociation can be considered complete and the generation-recombination processes of ions can be neglected [1, 7, 11, 19–23]. We assume that positive and negative ions have the same mobility.

The theoretical analysis of the problem is usually performed by assuming that the nematic liquid crystal contains only a cation-anion pair with diffusion coefficients equal [1, 7, 19, 20] or different [11, 22, 23].

Depending on the nature of the electrodes the cases presented here refers to the complete blocking electrodes or the blocking electrode with the adsorption. First we find the ion distribution and the potential across the sample, when the external voltage has sinusoidal variation in time. The ionic contribution to the current in the external circuit is then evaluated and the equivalent impedance of the cell is deduced. Finally, the equivalent electrical conductivity and the equivalent dielectric constant of the cell filled with the liquid under investigation are presented.

4.1. CASE I

This case start from following assumptions: \( D_p = D_n \), \( \mu_p = \mu_n \), \( r_p = r_n = 0 \), \( n_0 = p_0 = N_0 \), completely blocking electrodes [1, 7, 19]. The boundary conditions for the fundamental equations of the problem depend on the electrodes character. If they can be considered perfectly blocking, the densities of current have to vanish on them: \( J_p (\pm L/2) = J_n (\pm L/2) = 0 \).

In the case of no carrier recombination the system (16) simplifies to:

\[
-\frac{d^2 n_p}{dx^2} + \left( \frac{1}{L_D} + i\omega \frac{D_p + D_n}{2D_pD_n} \right) n_p + i\omega \frac{D_n - D_p}{D_pD_n} n_c = 0
\]

\[
-\frac{d^2 n_p}{dx^2} + \left( \frac{1}{l_d^2} + i\omega \frac{D_p - D_n}{2D_pD_n} \right) n_p + i\omega \frac{D_n + D_p}{2D_pD_n} n_c = 0
\]

\[
\frac{dE_i(x)}{dx} = \frac{q}{\varepsilon} n_p(x)
\]
where \( L_D \) is the Debye length: 
\[
L_D = \sqrt[2]{\frac{k_B T \varepsilon \rho}{2N_0 q^2}}.
\]

With the new variables the boundary conditions (\( x = \pm L / 2 \)) become:
\[
\frac{q(p_0 + n_0)}{k_B T} E_i - \frac{dn_D}{dx} = 0; \quad \frac{q(p_0 - n_0)}{k_B T} E_i - 2 \frac{dn_C}{dx} = 0
\]

Now the equations and the boundary conditions for \( n_D \) and \( E_i \) can be then separated from those for \( n_C \).

Let consider the sub-system with the variables \( n_D \) and \( E_i \):
\[
\frac{d^2 n_D}{dx^2} + \left( \frac{1}{L_D} + i \omega \frac{1}{D} \right) n_D = 0
\]
\[
\frac{dE_i(x)}{dx} = \frac{q}{\varepsilon} n_D(x)
\]

The linear differential equations with constant coefficients (19) have the general solution:
\[
n_D = A e^{\alpha x} + A_2 e^{-\alpha x}; E_i(x) = \frac{q}{\varepsilon} \left( A e^{\alpha x} + A_2 e^{-\alpha x} + B \right)
\]

where
\[
\alpha_{1,2} = \pm \frac{1}{L_D} + i \omega \frac{1}{D} = \pm \frac{1}{L_D} \sqrt{1 + i \omega \frac{L_D^2}{D}} = \pm \alpha
\]

and \( \alpha_1, \alpha_2 \) are the roots of the characteristic equation. From the boundary conditions (18) we obtain: \( A_1 = -A_2 = A / 2 \). So the form of the solution is:
\[
n_D(x) = A \sinh(\alpha x); E_i(x) = \frac{q}{\varepsilon} \left[ A \cosh(\alpha x) + B \right]
\]

In fact the same expression of \( n_D \) and \( E_i \) can be obtained by admitting that the solutions have symmetry properties [16]: \( n_D \) is an odd function and \( E_i \) is an even function of \( x \).

The form of \( A \) and \( B \) constants is determined by solving the system made from eq. (18.a) completed with (11) re-written as:
\[
\frac{q(p_0 + n_0)}{k_B T} \frac{q}{\varepsilon} \left[ A \cosh\left( \frac{\alpha L}{2} \right) + B \right] = \alpha A \cosh\left( \frac{\alpha L}{2} \right)
\]
\[
- U_A = \frac{q}{\varepsilon} \left[ \frac{2 A}{\alpha^2} \sinh\left( \frac{\alpha L}{2} \right) + BL \right]
\]
The constants are:

\[ A = \frac{a}{\cosh(Y)}; \quad B = a \frac{\alpha^2 L_d^2 - 1}{\alpha} \]  \hspace{1cm} (24)

where \( Y = \alpha L / 2 \) and

\[ a = -\frac{\varepsilon \alpha^2 U_q}{2q \left( \tanh(Y) + Y \left( \alpha^2 L_b^2 - 1 \right) \right)} \]  \hspace{1cm} (25)

At the surface of the completely blocking electrodes the total electric current density is \( j = \pm \omega \varepsilon E_1 \left( \pm L / 2 \right) \). Then the expression of the cell impedance is:

\[ Z(\omega) = \frac{2 \tanh(Y) + Y \left( \alpha^2 L_b^2 - 1 \right)}{i \omega \alpha S \left( \alpha L_b \right)^2} \]  \hspace{1cm} (26)

This is an expression similar to that presented in [1, 16, 19] thus confirming the goodness of our results.

The electric equivalent parameters \( \sigma_{ech} \) and \( \varepsilon_{ech} \) of the whole measured system are easily obtained from the impedance and further the permittivity components of the investigated liquid are easily deduced.

4.2. CASE II

The assumptions are now: small signal approximation, \( D_p = D_n \), \( \mu_p = \mu_n \), \( r_p = r_n = 0 \), \( n_0 = p_0 = N_0 \), the blocking electrodes with adsorption [20, 34].

If the electrodes are blocking but they adsorb the ions, the densities of current at the electrodes have to be equal to the time variation of the surface densities of adsorbed ions. The boundary conditions at the electrode blocking surface, identical in the adsorption/desorption process are [11, 20, 34]:

\[ J_m \left( \pm L / 2, t \right) = \pm \frac{d\sigma_m}{dt} \left( \pm L / 2, t \right) \]  \hspace{1cm} (27)

For small adsorption/desorption rates we can consider the equation of Langmuir to describe the surface density of ions, \( \sigma_p, \sigma_n \), at the electrodes. The kinetic equation describing the time variation of the surface density of adsorbed ions contains two phenomenological parameters: one connected to the adsorption phenomenon, and another connected with the desorption:

\[ \frac{d\sigma_m}{dt} = K_m m - \frac{1}{\gamma_m} \sigma_m \]  \hspace{1cm} (28)
where $\gamma_p, \gamma_n$ is the desorption time and $K_p, K_n$ a constant proportional to the adsorption rate of the ions at the electrodes [11, 20, 34].

If the physical parameters of adsorption ($K_p, K_n$) and desorption ($\gamma_p, \gamma_n$) are considered equal the equilibrium concentrations are uniform and equal between them and there is no internal electric field [11].

In the ac mode the boundary conditions equations are:

$$J_{m1}(\pm L/2) = \pm \frac{\text{i} \omega K \gamma}{1 + \text{i} \omega \gamma} m_1(\pm L/2) = \pm K^* m_1$$

which become:

$$x = +L/2: \pm \mu_m m_0 E_1 - D_n \frac{dm_n}{dx} = +K^* m_1$$

$$x = -L/2: \pm \mu_m m_0 E_1 - D_n \frac{dm_n}{dx} = -K^* m_1$$

The above boundary conditions are met if $p_1, n_1$ are odd functions of $x$, and $E_1$ is an even function of $x$ (similar to the case presented above).

In relation to the new variables ($n_D, n_C, E_1$) the boundary conditions have the expressions:

$$\frac{q(p_0 + n_0)}{k_B T} E_1(+L/2) - \frac{dn_D}{dx}(+L/2) = \frac{K^*}{D} n_D$$

$$\frac{q(p_0 - n_0)}{k_B T} E_1(+L/2) - 2 \frac{dn_C}{dx}(+L/2) = 2 \frac{K^*}{D} n_C$$

The form of all the differential equations system and the boundary conditions allows the system separation into sub-systems.

The general solution expression for the variables $n_D, E_i$:

$$n_D(x) = A \sinh(\alpha x); E_i(x) = \frac{q}{\alpha} \left[ A \cosh(\alpha x) + B \right]$$

$A$ and $B$ constants are determined from the equations system:

$$\frac{1}{L_D^2} \left[ \frac{A}{\alpha} \cosh(Y) + B \right] = \alpha A \cosh(Y) + \frac{K^*}{D} A \sinh(Y)$$

$$\frac{q}{\alpha} \left[ 2 \frac{A}{\alpha^2} \sinh(Y) + BL \right] = -U_A$$

Then the expressions of these constants are:
\[ A = \frac{a}{\cosh(Y)}; B = \frac{a}{\alpha} \left[ \left( \alpha^2 L_D^2 - 1 \right) + \alpha L_D^2 \frac{K^*}{D} \tanh(Y) \right] \]  

(34)

where

\[ a = -\frac{\varepsilon \alpha^2 U_A}{2q \left[ (1 + \alpha L_D^2 Y K^*/D) \tanh(Y) + Y \left( \alpha^2 L_D^2 - 1 \right) \right]} \]  

(35)

The electric current density at the electrode surfaces \((x=\pm L/2)\) is:

\[ j_x = \pm q \left( \frac{d\sigma_p}{dt} - \frac{d\sigma_n}{dt} \right) + \pm \omega q K^* n_p + \pm \omega E_i \]  

(36)

In the case of the blocking electrodes with the adsorption/desorption process the impedance \(Z\) has the expression:

\[ Z(\omega) = \frac{2}{\varepsilon S} \frac{1}{\alpha^2} \left[ i \omega \alpha L_D^2 + K^* \left( 1 + \frac{i \omega L_D^2}{D} \right) \tanh(Y) \right] \]  

(37)

In the limit for which \(K^*\) is zero (completely blocking electrode) the above impedance expression reduces to the expression of the previously studied case. Further the equivalent parameters of the cell \(\sigma_{ech}, \varepsilon_{ech}, \varepsilon, \varepsilon\) can be obtained easily.

5. CONCLUSIONS

In this paper we presented a simple mathematical approach describing the influence of the ions dissolved in a liquid crystal on the impedance system.

By introducing new independent variables we obtained a reformulation of the basic coupled differential equations of continuity for the ions and of the Poisson equation for the electric potential.

The new variables have a clear and simple physical meaning. In a simple way the model allows the theoretical analysis for some cases in which the electrode polarization occurs due to the possibility of decoupling the equations system into two simpler sub-systems with fewer variable quantities. For the analyzed cases the number and the complexity of the calculations is lower than other versions of the MacDonald model. In addition certain properties of the system solutions can be deduced directly without additional assumptions.

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