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Role of the diffuse layer of the ionic charge on the impedance spectroscopy of a cell of liquid

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We investigate the role of the diffuse layer of the ionic cloud on impedance spectroscopy measurements. The analysis is performed assuming that the ions have equal mobility, the electrodes are perfectly blocking and adsorption phenomenon can be neglected. We find that the dielectric permittivity, in the limit of high frequency ω, tends to the dielectric permittivity of the pure liquid as $\omega^{-3/2}$. The relationship between the detected equivalent permittivity and conductivity of the cell with the real and imaginary part of the complex dielectric constant is discussed. We show also that the presence of the ions is responsible for a distribution of relaxation times. An application to nematic liquid crystals is presented.

1. Introduction

The impedance spectroscopy technique is used to characterize liquids electrically [1]. In this technique a condenser having the shape of a slab is filled with the material to be investigated. The condenser is then submitted to an a.c. voltage, and the impedance of the sample is measured as a function of the frequency of the applied voltage. The analysis is performed in the limit of small amplitude of the applied voltage, in such a manner that the response of the sample to the external signal is linear. The meaning of *small voltage* is that the applied voltage is small with respect to the thermal voltage $V_T = kT/q$, where kT is the thermal energy and q the electric charge of the ion. In the limit of low frequency of the signal, the ions present in the liquid contribute to the electrical current, and so to the detected impedance. Several models have been proposed to take into account the effect of the ions on the electric response of a liquid [2]. In this paper we present a simple model to describe the influence of the ions on the impedance spectra. We assume that the ions, monovalent of charge q, are dimensionless and dispersed in a homogeneous medium of dielectric constant ε and have the same mobility, and that they are not adsorbed by the electrodes. According to this last hypothesis, the ζ-potential vanishes, and the analysis of the impedance spectroscopy is greatly simplified [3, 4]. The electrodes are supposed perfectly blocking, in such a manner that there is no charge injection into the liquid. First we find the distribution of ions, when the external voltage depends sinusoidally on the time. The ionic contribution to the current in the external circuit is then evaluated; finally, the equivalent impedance of the cell is deduced. Our paper is organized as follows. The physical system and basic hypotheses are presented in § 2; the fundamental equations of the problem are discussed in § 3; the distribution of the ionic charge and the potential across the sample are reported in § 4. The impedance of the cell is evaluated in § 5, where we also present the frequency dependence of the equivalent resistance and equivalent admittance of the sample. In this section are also presented the frequency dependence of the equivalent electrical conductivity and of the equivalent dielectric constant of the cell filled with the liquid under investigation. The relationship between the equivalent conductivity and of the equivalent dielectric permittivity with the imaginary and real parts of the complex dielectric constant is discussed in § 6; § 7 is devoted to the conclusion.

2. The physical system and basic hypotheses

Let us consider a slab of thickness d filled with an isotropic liquid. The z-axis of the cartesian reference frame used in the description is normal to the bounding surfaces at $z = \pm d/2$. We assume that in thermodynamical equilibrium the liquid contains a density N of ions of positive and negative sign, uniformly distributed. The ions are assumed to be identical in all respects, except

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for the sign of the electrical charge. In particular they have the same mobility $\mu_+=\mu_-=\mu$. In this situation, in the absence of selective adsorption, the liquid is globally and locally neutral. The presence of an external electric voltage produces a perturbation of the distribution of the ions in the liquid, in the sense that it remains globally neutral, but it is now locally charged. In the following we suppose the sample to be submitted to an external sinusoidal voltage of amplitude V_0 and frequency $f=\omega/(2\pi)$. By indicating with n_+ and n_- the density of the two kinds of ions we have $n_+(z, t)=n_-(z, t)=N$, for $V_0=0$, and $n_+(z, t)\neq n_-(z, t)$, for $V_0\neq 0$. The conservation of the number of particles implies that

$$\int_{-d/2}^{d/2} n_+(z, t)\mathrm{d}z=\int_{-d/2}^{d/2} n_-(z, t)\mathrm{d}z=N\,d \tag{1}$$

under the assumption that there is no recombination and the electrodes are perfectly blocking, as we suppose in our analysis. We assume that the amplitude of the external voltage V_0 is such that the actual densities of ions differ only slightly from N. By putting

$$n_\pm=N+\delta n_\pm(z, t) \tag{2}$$

the previous hypothesis implies that $\delta n_\pm(z, t)\ll N$. We suppose furthermore that $V(\pm d/2, t)=\pm(V_0/2)\exp(\mathrm{i}\omega t)$. In this case, since $\mu_+=\mu_-=\mu$, we have $n_+(z, t)=n_-(-z, t)$. Equation (1), taking into account equation (2), implies that

$$\int_{-d/2}^{d/2} \delta n_+(z, t)\mathrm{d}z=\int_{-d/2}^{d/2} \delta n_-(z, t)\mathrm{d}z=0 \tag{3}$$

thus stating the global neutrality.

3. Fundamental equations of the problem

The fundamental equations of the problem are [5] the equation of continuity

$$\frac{\partial n_\pm}{\partial t}=-\frac{\partial j_\pm}{\partial z} \tag{4}$$

and the Poisson equation

$$\frac{\partial^2 V}{\partial z^2}=-\frac{q}{\varepsilon}(n_+-n_-) \tag{5}$$

where q is the electrical charge of the ions, and $j_\pm$ the density of currents of positive and negative ions given by

$$j_\pm=-D\left(\frac{\partial n_\pm}{\partial z}\pm\frac{q}{KT}n_\pm\frac{\partial V}{\partial z}\right). \tag{6}$$

In equation (6) the first term in the r.h.s. is the diffusion current, while the second is the drift current. In equation (6) we have used the Einstein–Smolukowsky relation relating the mobility μ to the diffusion coefficient D, $\mu/D=q/(kT)$ where k is the Boltzmann constant and T the absolute temperature [6]. Since the electrodes are supposed perfectly blocking we have the following boundary conditions on $j_\pm$

$$j_\pm(\pm d/2, t)=0. \tag{7}$$

The others boundary conditions of the problem are connected with the imposed difference of potential $V(\pm d/2, t)=\pm(V_0/2)\exp(\mathrm{i}\omega t)$. To find the influence of the diffuse layers of ions on the impedance spectroscopy we have to evaluate first the total current in the external circuit, taking into account the presence of the ions. After that it is necessary to evaluate the electrical impedance of the cell under investigation.

4. Solution of the problem

From Equation (6), by taking into account that $\delta n_\pm(z, t)\ll N$, we get

$$j_\pm=-D\left\{\frac{\partial(\delta n_\pm)}{\partial z}\pm\frac{Nq}{kT}\frac{\partial V}{\partial z}\right\}. \tag{8}$$

Substituting equation (8) into (4) we obtain

$$\frac{\partial(\delta n_\pm)}{\partial t}=D\left\{\frac{\partial^2(\delta n_\pm)}{\partial z^2}\pm\frac{Nq}{kT}\frac{\partial^2 V}{\partial z^2}\right\}. \tag{9}$$

Furthermore, by substituting equation (2) in (5) we have

$$\frac{\partial^2 V}{\partial z^2}=-\frac{q}{\varepsilon}(\delta n_+-\delta n_-). \tag{10}$$

Equations (9) and (10) show that if $V(\pm d/2, t)=\pm(V_0/2)\exp(\mathrm{i}\omega t)$, in the steady state $\delta n_\pm(z, t)=\eta_\pm(z)\exp(\mathrm{i}\omega t)$ and $V(z, t)=\phi(z)\exp(\mathrm{i}\omega t)$, where, in particular

$$\phi(\pm d/2)=\pm V_0/2 \tag{11}$$

for the boundary conditions imposed on the applied potential. It follows that in the steady state equation (10) can be rewritten as

$$\phi''(z)=-(q/\varepsilon)\left[\eta_+(z)-\eta_-(z)\right] \tag{12}$$

where the prime means derivative with respect to the z-coordinate.

The functions $\eta_\pm(z)$ are solutions of the differential equations

$$\eta''_\pm(z)-\frac{1}{2\lambda^2}\left(1+2\mathrm{i}\frac{\omega}{D}\lambda^2\right)\eta_\pm(z)+\frac{1}{2\lambda^2}\eta_\mp(z)=0 \tag{13}$$

obtained by equation (9), where $\lambda=\left[\varepsilon kT/\left(2Nq^2\right)\right]^{\frac{1}{2}}$ is the Debye length [7]. From the condition $n_+(z)=n_-(-zt)$, related to the hypothesis that the positive and negative ions have the same mobility, taking into account (2) it follows that $\eta_+(z)=\eta_-(-z)$. The solutions of equation (13) satisfying this symmetry condition are

$$\eta_\pm(z)=m_0\cosh(\alpha z)\pm p_0\sinh(\beta z) \tag{14}$$

where

$$\alpha^2=\mathrm{i}\frac{\omega}{D}, \quad \text{and} \quad \beta^2=\frac{1}{\lambda^2}\left(1+\mathrm{i}\frac{\omega}{D}\lambda^2\right). \tag{15}$$

From the definition of β^2 it follows that for $\omega\ll\omega_r=D/\lambda^2$, its real part is large with respect to its imaginary part. *Vice versa* for $\omega\gg\omega_r$. It follows that for $\omega\sim\omega_r$ we expect a change in the frequency behaviour of the system.

The conservation of the number of particles is contained in equation (3), which can be rewritten in the form

$$\int_{-d/2}^{d/2}\eta_\pm(z)\mathrm{d}z=0. \tag{16}$$

Condition (16), taking into account (14) implies $m_0=0$. Hence $\eta_\pm(z)=\pm p_0\sinh(\beta z)$, where p_0 is an integration constant to be determined by means of the boundary conditions (7) and (11).

The profile of the electric potential is given by equation (12), which in the case under consideration reads

$$\phi''(z)=-2(q/\varepsilon)p_0\sinh(\beta z) \tag{17}$$

from which, by taking into account that in our framework $\phi(z)=-\phi(-z)$, we get

$$\phi(z)=-2\left(q/\varepsilon\beta^2\right)p_0\sinh(\beta z)+cz. \tag{18}$$

The integration constant c is determined by the boundary conditions (7) and (11).

The current densities are, according to equation (8), given by

$$j_\pm=-D\left[\eta'_\pm\pm(qN/kT)\phi'(z)\right]\exp(\mathrm{i}\omega t) \tag{19}$$

which for the results reported above can be rewritten in the form

$$j_\pm=\mp D[\mathrm{i}(\omega/D\beta)p_0\cosh(\beta z)+(Nq/kT)c]\exp(\mathrm{i}\omega t). \tag{20}$$

By means of equations (18) and (20) the boundary conditions of the problem become

$$\begin{gathered}-2\left(q/\varepsilon\beta^2\right)p_0\sinh(\beta d/2)+cd/2=V_0/2\\ \mathrm{i}(\omega/D\beta)p_0\cosh(\beta d/2)+(Nq/kT)c=0.\end{gathered} \tag{21}$$

By solving equation (21) with respect to p_0 and c we get

$$\begin{gathered}p_0=-\frac{Nq\beta}{2kT}\frac{1}{(1/\lambda^2\beta)\sinh(\beta d/2)+\mathrm{i}(\omega d/2D)\cosh(\beta d/2)}V_0\\ c=\mathrm{i}\frac{\omega}{2D}\frac{\cosh(\beta d/2)}{(1/\lambda^2\beta)\sinh(\beta d/2)+\mathrm{i}(\omega d/2D)\cosh(\beta d/2)}V_0.\end{gathered} \tag{22}$$

The electrical problem is then solved.

5. Impedance of the cell

We can now evaluate the charge sent by the power supply on the electrodes. Since $V(z, t)=\phi(z)\exp(\mathrm{i}\omega t)$ the electric field is

$$E(z, t)=-\frac{\partial V}{\partial z}=-\phi'(z)\exp(\mathrm{i}\omega t) \tag{23}$$

From the theorem of Coulomb $E(d/2, t)=-\Sigma(t)/\varepsilon$, where Σ is the surface charge density on the electrode at $z=d/2$. Consequently, $\Sigma(t)=\varepsilon\phi'(d/2)\exp(\mathrm{i}\omega t)$, and for the discussion reported above,

$$\Sigma(t)=\frac{1}{2}\varepsilon\beta^2\frac{\cosh(\beta d/2)}{(1/\lambda^2\beta)\sinh(\beta d/2)+\mathrm{i}(\omega d/2D)\cosh(\beta d/2)}V_0\exp(\mathrm{i}\omega t). \tag{24}$$

The current $I=S\mathrm{d}\Sigma/\mathrm{d}t$, where S is the surface area of the electrodes, is then

$$I=S\frac{\mathrm{i}\omega}{2}\varepsilon\beta^2\frac{\cosh(\beta d/2)}{(1/\lambda^2\beta)\sinh(\beta d/2)+\mathrm{i}(\omega d/2D)\cosh(\beta d/2)}V. \tag{25}$$

The impedance of the cell defined by $\mathcal{Z}=V/I$ is found to be

$$\mathcal{Z}=-\mathrm{i}\frac{2}{\omega\varepsilon\beta^2S}\left\{\frac{1}{\lambda^2\beta}\tanh(\beta d/2)+\mathrm{i}\frac{\omega d}{2D}\right\}. \tag{26}$$

If a true dielectric is considered, $N=0$, and hence $\lambda\to\infty$. In this case equation (26) gives

$$\mathcal{Z}=\frac{1}{\mathrm{i}\omega\varepsilon S/d} \tag{27}$$

as expected.

From equation (26) one can obtain $\mathcal{R}=\Re\mathcal{Z}$ and $\mathcal{X}=\Im\mathcal{Z}$, which are the quantities experimentally detectable. The phenomenological parameters characterizing the physical properties of the cell are the equivalent conductivity σ_{eq}, and the equivalent dielectric constant $\varepsilon_{\mathrm{eq}}$, defined by

$$\sigma_{\mathrm{eq}}=\frac{1}{\mathcal{R}}\frac{d}{S}, \quad \text{and} \quad \varepsilon_{\mathrm{eq}}=-\frac{1}{\omega\mathcal{X}}\frac{d}{S}. \tag{28}$$

Before entering into a detailed analysis of the impedance of the cell given by equation (26) we consider the special cases of $\omega\to0$ and $\omega\to\infty$, limiting our investigations to the case in which $\lambda \ll d$[†]. In the first case, from (26) we obtain $\mathcal{Z}(\omega\rightarrow 0)=\mathcal{R}(\omega\rightarrow 0)+\mathrm{i}\mathcal{X}(\omega\rightarrow 0)$, where

$$\begin{aligned}\mathcal{R}(\omega\rightarrow 0)&=\frac{\lambda^2 d}{D\varepsilon S}\left(1-\frac{\lambda^4}{D^2}\omega^2\right)\\ \mathcal{X}(\omega\rightarrow 0)&=-2\frac{\lambda}{\omega\varepsilon S}\left(1+\frac{\lambda^3 d}{2D^2}\omega^2\right).\end{aligned} \tag{29}$$

From equation (29), taking into account (28), we get for $\sigma_{\mathrm{eq}}(\omega\rightarrow 0)$ and $\varepsilon_{\mathrm{eq}}(\omega\rightarrow 0)$ the expressions

$$\begin{aligned}\sigma_{\mathrm{eq}}(\omega\rightarrow 0)&=\frac{\varepsilon D}{\lambda^2}\left(1+\frac{\lambda^4}{D^2}\omega^2\right)\\ \varepsilon_{\mathrm{eq}}(\omega\rightarrow 0)&=\frac{1}{2}\varepsilon\frac{d}{\lambda}\left(1-\frac{\lambda^3 d}{2D^2}\omega^2\right).\end{aligned} \tag{30}$$

In particular, in the d.c. limit, $\sigma_{\mathrm{eq}}(0)=\varepsilon D/\lambda^2=2Nq\mu$, as expected because we have two identical carriers of charge [8]. Furthermore, $\varepsilon_{\mathrm{eq}}(0)=(1/2)\varepsilon(d/\lambda)$, since in this limit the equivalent capacity of the cell is the one of two equal condensers of thickness λ in series. Note that $\sigma_{\mathrm{eq}}(0)$ is d-independent, whereas $\varepsilon_{\mathrm{eq}}(0)$ is proportional to d[9].

In the limit of high frequency ($\omega\rightarrow\infty$) from equation (26) we obtain $\mathcal{Z}(\omega\rightarrow\infty)=\mathcal{R}(\omega\rightarrow\infty)+\mathrm{i}\mathcal{X}(\omega\rightarrow\infty)$, where

$$\begin{aligned}\mathcal{R}(\omega\rightarrow\infty)&=\frac{Dd}{\omega^2\lambda^2\varepsilon S}\left[1-\frac{1}{d}\left(\frac{2D}{\omega}\right)^{\frac{1}{2}}\right]\\ \mathcal{X}(\omega\rightarrow\infty)&=-\frac{d}{\omega\varepsilon S}\left[1-\frac{D}{\lambda^2 d\omega}\left(\frac{2D}{\omega}\right)^{\frac{1}{2}}\right].\end{aligned} \tag{31}$$

In this case $\sigma_{\mathrm{eq}}(\omega\rightarrow\infty)$ and $\varepsilon_{\mathrm{eq}}(\omega\rightarrow\infty)$ are found to be

$$\begin{aligned}\sigma_{\mathrm{eq}}(\omega\rightarrow\infty)&=\frac{\varepsilon\lambda^2}{D}\omega^2\left[1+\frac{1}{d}\left(\frac{2D}{\omega}\right)^{\frac{1}{2}}\right]\\ \varepsilon_{\mathrm{eq}}(\omega\rightarrow\infty)&=\varepsilon\left[1+\frac{D}{\lambda^2 d\omega}\left(\frac{2D}{\omega}\right)^{\frac{1}{2}}\right].\end{aligned} \tag{32}$$

From equation (32) it follows that for $\omega\rightarrow\infty$, the equivalent conductivity is $\sigma_{\mathrm{eq}}=(\varepsilon\lambda^2/D)\omega^2=\sigma_{\mathrm{eq}}(0)(\lambda^2\omega/D)^2$. The equivalent capacitance of the cell at high frequency is $C_{\mathrm{eq}}=\varepsilon_{\mathrm{eq}}(S/d)$, showing that $\lim_{\omega\rightarrow\infty}\varepsilon_{\mathrm{eq}}=\varepsilon$, as expected because in this limit the ions give no contribution to the electrical response of the cell. The leading terms for $\sigma_{\mathrm{eq}}(\omega\rightarrow\infty)$ and $\varepsilon_{\mathrm{eq}}(\omega\rightarrow\infty)$ are independent of the thickness of the cell. We note, finally, that in this limit $\varepsilon_{\mathrm{eq}}(\omega\rightarrow\infty)$ tends to ε as $\omega^{-3/2}$, as has been experimentally observed [10].

We can now investigate the frequency dependence of the real and imaginary parts of the impedance of the cell. In order to obtain an explicit expression for $\mathcal{R}$ and $\mathcal{X}$ we write $\beta=\beta_{\mathrm{r}}+\mathrm{i}\beta_{\mathrm{i}}$. Simple calculations give $\beta_{\mathrm{r}}=(1/\lambda)[(M+1)/2]^{\frac{1}{2}}$ and $\beta_{\mathrm{i}}=(1/\lambda)[(M-1)/2]^{\frac{1}{2}}$, where $M=\left[1+\left(\omega\lambda^2/D\right)^2\right]^{\frac{1}{2}}$. By using the definition of $\omega_{\mathrm{r}}=D/\lambda^2$ introduced previously, we have $M=\left[1+(\omega/\omega_{\mathrm{r}})^2\right]^{\frac{1}{2}}$. We now put $A=\tanh(\beta_{\mathrm{r}}d/2)$, $B=\tan(\beta_{\mathrm{i}}d/2)$ and $m=A(1+B^2)/[1+(AB)^2]$, $n=B(1-A^2)/[1+(AB)^2]$. With these positions the explicit expression for the real and imaginary parts of the impedance of the cell are found to be

$$\begin{aligned}\mathcal{R}&=\frac{2\lambda^2}{\omega\varepsilon M^2 S}\left\{\left(\frac{n\beta_{\mathrm{r}}-m\beta_{\mathrm{i}}}{M}+\frac{\omega d}{2D}\right)-\frac{\omega\lambda^2}{D}\frac{m\beta_{\mathrm{r}}+n\beta_{\mathrm{i}}}{M}\right\}\\ \mathcal{X}&=-\frac{2\lambda^2}{\omega\varepsilon M^2 S}\left\{\frac{m\beta_{\mathrm{r}}+n\beta_{\mathrm{i}}}{M}+\frac{\omega\lambda^2}{D}\left(\frac{n\beta_{\mathrm{r}}-m\beta_{\mathrm{i}}}{M}+\frac{\omega d}{2D}\right)\right\}.\end{aligned} \tag{33}$$

For $\omega\ll\omega_{\mathrm{r}}$, $M\rightarrow 1$, and for $\omega\gg\omega_{\mathrm{r}}$, $M\rightarrow(\omega/\omega_{\mathrm{r}})$. Hence a change in the frequency dependence of $\mathcal{R}$ and $\mathcal{X}$ is expected for $\omega\sim\omega_{\mathrm{r}}$.

We suppose that the cell is a slab of thickness $d_1=25\,\mu\mathrm{m}$ or $d_2=50\,\mu\mathrm{m}$, filled with the nematic liquid crystal 5CB (4-cyano-4′-*n*-pentylbiphenyl), planarly oriented by the surface treatment, as considered by Murakami *et al.* [9]. Since the applied voltage is very small with respect to the threshold voltage for the Freedericksz transition, there is no reorientation of the nematic liquid crystal induced by the external voltage. In this case $\varepsilon=\varepsilon_{\perp}=6.7\varepsilon_0$, where ε_0 is the dielectric permittivity of free space. We assume furthermore that the density of ions is $N\sim 4.2\times 10^{20}\,\mathrm{m}^{-3}$ and $D\sim 8.2\times 10^{-12}\,\mathrm{m}^{-2}/\mathrm{s}$ [11, 12]. By using these values we get $\lambda\sim 10^{-7}\,\mathrm{m}$ and $\omega_{\mathrm{r}}\sim 740\,\mathrm{rad\,s}^{-1}$.

In figure 1 we show $\mathcal{R}(\omega)$. It tends to a constant value for $\omega\rightarrow 0$, and to zero for $\omega\rightarrow\infty$; and presents a large plateau until $\omega\sim\omega_{\mathrm{r}}$. In figure 2 $\mathcal{X}(\omega)$ is reported. It tends to $-\infty$ for $\omega\rightarrow 0$, and to 0, from the negative side, for $\omega\rightarrow\infty$. In between it has first a maximum and then a minimum for $\omega\sim\omega_{\mathrm{r}}$. The equivalent conductivity of the cell $\sigma_{\mathrm{eq}}(\omega)$ is shown in figure 3. As discussed above, $\lim_{\omega\rightarrow 0}\sigma_{\mathrm{eq}}(\omega)=\varepsilon D/\lambda^2$, and $\sigma_{\mathrm{eq}}(\omega\rightarrow\infty)=(\varepsilon\lambda^2/D)\omega^2$. From figure 3 it follows that σ_{eq} is practically independent of the thickness of the sample. Finally, in figure 4

[†] In this case $u=d/\lambda\gg 1$. Consequently $\tanh u\sim 1$ and $\cosh u\sim\sinh u\sim e^u/2$.

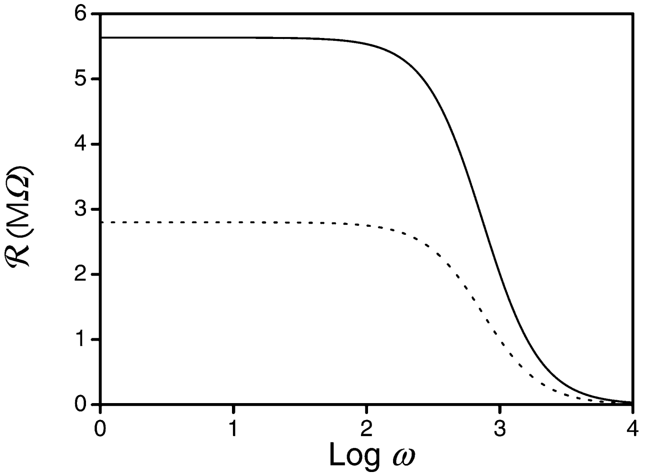

Figure 1. Real part of the impedance of the cell $\mathcal{R}$ vs. ω, in semi-logaritmic scale. Dotted line $d_1=25\,\mu$m, full line $d_2=50\,\mu$m.

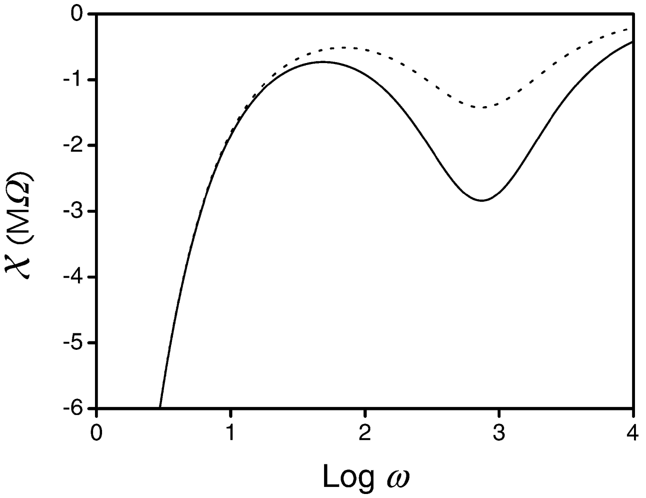

Figure 2. Imaginary part of the impedance of the cell $\mathcal{X}$ vs. ω, in semi-logaritmic scale. Dotted line $d_1=25\,\mu$m, full line $d_2=50\,\mu$m.

we report $\varepsilon_{eq}(\omega)$. In this case $\lim_{\omega\rightarrow 0}\varepsilon(\omega)=\varepsilon(d/2\lambda)$, and $\lim_{\omega\rightarrow 0}\varepsilon_{eq}(\omega)=\varepsilon$.

6. Real and imaginary parts of the dielectric constant

In the previous sections we have investigated the influence of ions on the dielectric spectroscopy of a nematic cell. According to our scheme this influence is described by the equivalent conductivity σ_{eq} and equivalent dielectric permittivity ε_{eq} of the cell. Usually, the dielectric properties of a cell are described by introducing a complex dielectric constant $\epsilon=\epsilon'-i\epsilon''$. The real part ϵ' is connected with the usual dielectric properties of the medium, whereas the imaginary part ϵ'' is related to the relative dielectric loss factor. The

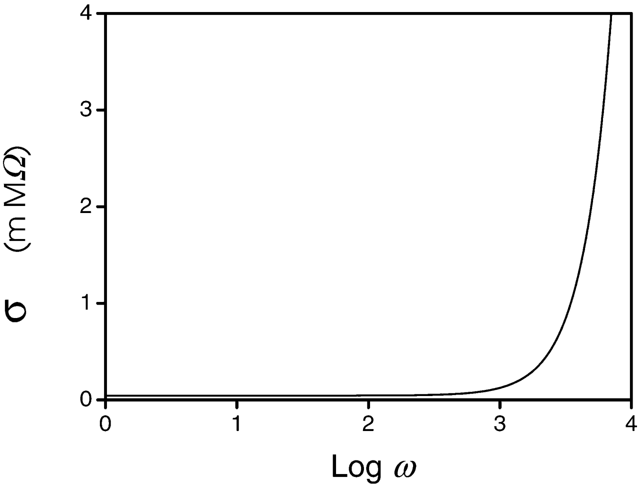

Figure 3. Equivalent conductivity of the cell σ_{eq} vs. ω, in semi-logaritmic scale. Dotted line $d_1=25\,\mu$m, full line $d_2=50\,\mu$m. Note that σ_{eq} is practically independent of the thickness of the sample.

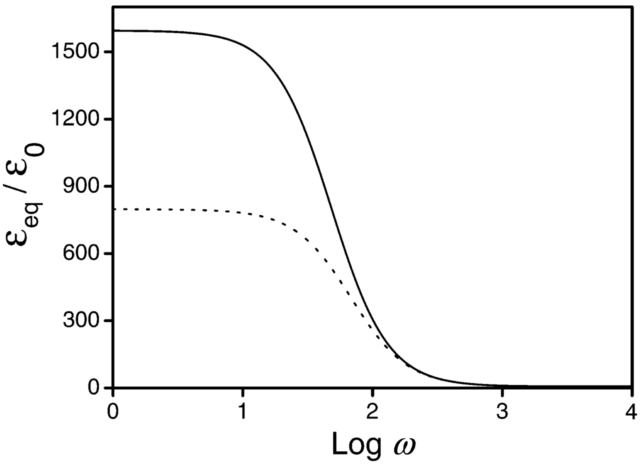

Figure 4. Equivalent relative dielectric permittivity of the cell ε_{eq} vs. ω, in semi-logaritmic scale. Dotted line $d_1=25\,\mu$m, full line $d_2=50\,\mu$m.

relationship between σ_{eq}, ε_{eq} and ϵ', ϵ'' can be easily determined. If the dielectric permittivity is a complex quantity, the impedance of the cell is

$$\mathcal{Z}=-i\frac{1}{\omega(\epsilon'-i\epsilon'')}\frac{d}{S}. \qquad (34)$$

From equation (34) it follows that the real, $\mathcal{R}$, and imaginary, $\mathcal{X}$, parts of the impedance $\mathcal{Z}$ are

$$\begin{aligned}\mathcal{R}&=\frac{\epsilon''}{\omega\left(\epsilon'^2+\epsilon''^2\right)}\frac{d}{S}\\ \mathcal{X}&=-\frac{\epsilon'}{\omega\left(\epsilon'^2+\epsilon''^2\right)}\frac{d}{S}.\end{aligned} \qquad (35)$$

From equations (35) and (28) we get

$$\sigma_{\mathrm{eq}} = \omega \frac{\epsilon'^2 + \epsilon''^2}{\epsilon''}, \qquad \varepsilon_{\mathrm{eq}} = \frac{\epsilon'^2 + \epsilon''^2}{\epsilon'}. \tag{36}$$

Consequently ε' and ε'' can be expressed in terms of σ_{eq} and $\varepsilon_{\mathrm{eq}}$ as follows

$$\epsilon' = \frac{\varepsilon_{\mathrm{eq}}}{1 + \omega^2 \left(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}}\right)^2}, \qquad \epsilon'' = \frac{\omega\left(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}}\right)}{1 + \omega^2 \left(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}}\right)^2}\varepsilon_{\mathrm{eq}}. \tag{37}$$

Equations (37) are similar to Debye equations for relaxation phenomena in dielectrics [13]. In the present case the relaxation time is given by $\tau = \varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}}$. In our case $\sigma_{\mathrm{eq}} = \sigma_{\mathrm{eq}}(\omega)$ and $\varepsilon_{\mathrm{eq}} = \varepsilon_{\mathrm{eq}}(\omega)$, due to the presence of the ions. It follows that when ions are present, they give rise to a distribution of relaxation times.

By means of equations (37) and (30) we get in the limit of $\omega \to 0$, when $d \gg \lambda$,

$$\epsilon' = \frac{1}{2}\varepsilon\frac{d}{\lambda}\left(1 - \frac{1}{4}\frac{d^2\lambda^2}{D^2}\omega^2\right), \qquad \epsilon'' = \frac{1}{4}\varepsilon\frac{d^2}{D}\omega\left(1 - \frac{1}{4}\frac{d^2\lambda^2}{D^2}\omega^2\right). \tag{38}$$

The relationship for ϵ'', in the limit of $\omega \to 0$, shows that in the low frequency region ϵ'' presents a maximum for $\omega_{\mathrm{M}} \sim D/(\lambda d)$. Furthermore, in the d.c. limit, the relaxation time tends to $\tau(0) = d\lambda/(2D)$.

In the opposite limit of high frequency ($\omega \to \infty$), from equations (36) and (32), by again assuming $d \gg \lambda$, we obtain

$$\epsilon' = \varepsilon\left[1 + \frac{D}{\lambda^2 d\omega}\left(\frac{2D}{\omega}\right)^{\frac{1}{2}}\right], \qquad \epsilon'' = \frac{D}{\omega\lambda^2}\varepsilon. \tag{39}$$

In this limit the relaxation time tends to zero as $\tau = D/(\omega^2\lambda^2)$.

In figure 5 the dependence of $\log(\epsilon''/\varepsilon_0)$ on $\log\omega$ is shown. Again we note that ϵ'' is independent of the thickness of the sample, as σ_{eq}. In figure 6 we show $\log(\epsilon'/\varepsilon_0)$ vs. $\log\omega$, which has the usual trend. In figure 7 we compare $\log(\epsilon'/\varepsilon_0)$ with $\log(\epsilon''/\varepsilon_0)$ vs. $\log\omega$. Finally, in figure 8 the frequency dependence of the relaxation time of ionic origin is shown.

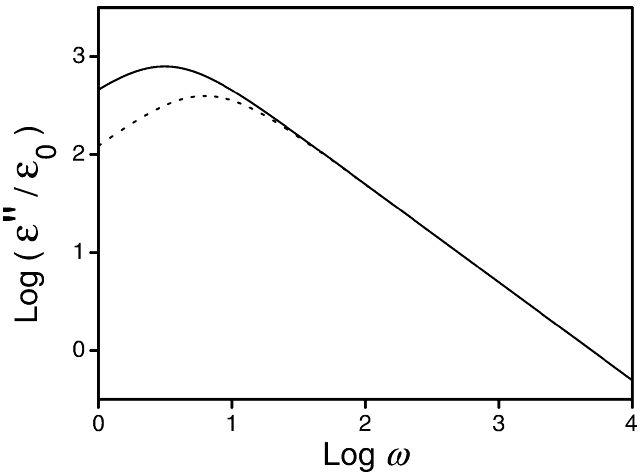

Figure 5. Imaginary part of the relative complex dielectric permittivity of the cell $\varepsilon''/\varepsilon_0$ vs. ω. Dotted line $d_1 = 25\,\mu\mathrm{m}$, full line $d_2 = 50\,\mu\mathrm{m}$.

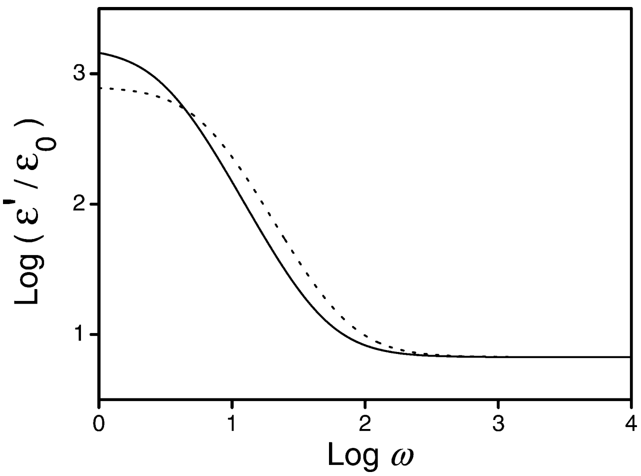

Figure 6. Real part of the relative complex dielectric permittivity of the cell $\varepsilon'/\varepsilon_0$ vs. ω. Dotted line $d_1 = 25\,\mu\mathrm{m}$, full line $d_2 = 50\,\mu\mathrm{m}$.

7. Conclusion

We have analysed the influence of the diffuse layer of charge of ionic origin on the impedance spectroscopy of a cell. In this study we have assumed that the electrodes are ideally polarizable, so that neither charge transfer, nor adsorption takes place. We have determined the density profiles of positive and negative ions across the sample, the current in the external circuit, and the impedance of the cell. The equivalent conductivity σ_{eq} and dielectric constant $\varepsilon_{\mathrm{eq}}$ of the sample have been

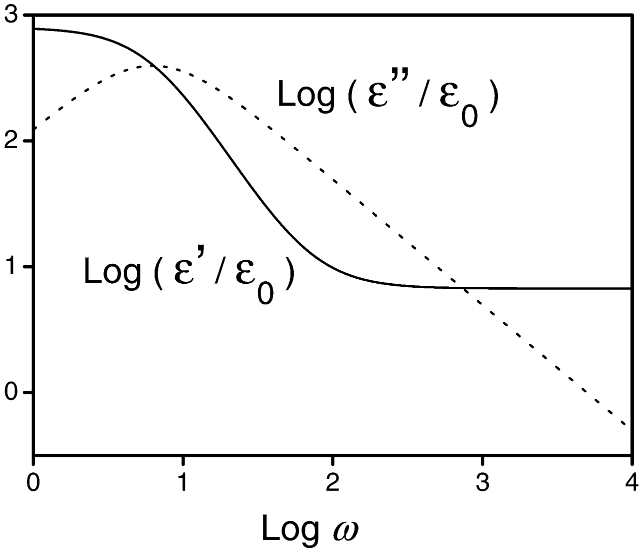

Figure 7. Real, $\varepsilon'/\varepsilon_0$, and imaginary, $\varepsilon''/\varepsilon_0$, part of the relative complex dielectric permittivity of the cell relevant to $d=25\,\mu\text{m}$.

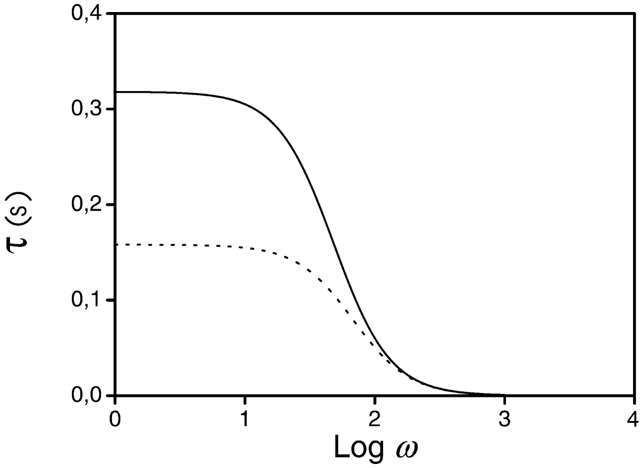

Figure 8. Relaxation time τ vs. ω, in semi-logaritmic scale. Dotted line $d_1=25\,\mu\text{m}$, full line $d_2=50\,\mu\text{m}$.

obtained from the impedance of the system, and their frequency dependence investigated. In particular we have analysed the limits of $\omega \to 0$ and $\omega \to \infty$. In the first case $\sigma_{eq} \to \varepsilon D/\lambda^2$ and $\varepsilon_{eq} \to \varepsilon(d/\lambda)$, whereas in the other limit $\sigma_{eq} \to (\varepsilon\lambda^2/D)\omega^2$ and $\varepsilon_{eq} \to \varepsilon$ with $\omega^{-3/2}$. We have also evaluated the real ϵ' and imaginary ϵ'' parts of the complex dielectric constant ϵ. According to our model, the presence of ions is responsible for a distribution of relaxation times, ranging from $d\lambda/(2D)$ for $\omega \to 0$, to zero for $\omega \to \infty$. Finally, we have shown that in the low frequency region ϵ' has a non-monotonic behaviour.

References

[1] J. Ross Macdonald, W.B. Johnson. in *Impedance Spectroscopy*. John Wiley, New York, Chap. 1 (1987).

[2] I.D. Raistrick, J. Ross Macdonald, D.R. Franceschetti. in *Impedance Spectroscopy*. John Wiley, New York, Chap. 2 (1987).

[3] M. Scott, R. Paul, K.V.I.S. Kalert. *J. colloid interface Sci.*, **230**, 377 (2000).

[4] M. Scott, R. Paul, K.V.I.S. Kalert. *J. colloid interface Sci.*, **230**, 388 (2000).

[5] P.A. Cirkel, J.P.M. van der Ploeg, G.J.M. Koper. *Physica A*, **235**, 269 (1997).

[6] J. Lyklema. *Fundamentals of Interface and Colloid Sciences*. Academic Press, London (1993).

[7] J. Israelachvili. *Intermolecular Forces*. Academic Press, London, Chap. 12 (1985).

[8] J.O. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry: Ionics*.

[9] S. Murakami, H. Iga, H. Naito. *J. appl. Phys.*, **80**, 6396 (1996).

[10] S.L. Srivastava, R. Dhar, Indian . *J. pure appl. phys.*, **29**, 745 (1991).

[11] A. Sawada, K. Tarumi, S. Naemura. *Jpn. J. appl. Phys.*, **38**, 1418 (1999).

[12] A. Sawada, K. Tarumi, S. Naemura. *Jpn. J. appl. Phys.*, **38**, 1423 (1999).

[13] H. Frohlich. *Theory of Dielectrics*. Oxford University Press, London (1958).