

Influence of adsorption phenomenon on the impedance spectroscopy of a cell of liquid

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We investigate the influence of the adsorption phenomenon on the impedance spectroscopy measurements. The analysis is performed by assuming that the ions have the same mobility and the electrodes are perfectly blocking. We find that in the low frequency range the presence of the adsorption phenomenon is responsible for an increasing of the real part of the impedance of the cell, similar to the one usually described by means of the impedance of the metal-electrolyte interface. The frequency dependencies theoretically predicted by our model for the real and imaginary parts of the complex dielectric constant are in qualitative agreement with the experimental data published by other groups.

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I. INTRODUCTION

The impedance spectroscopy of a cell in the shape of a slab filled with a liquid containing ions can give useful information on the complex dielectric constant of the doped liquid [1]. The sample under investigation is usually described by means of a R - C circuit, if the electrodes of the cell are such to avoid injection of charge into the liquid. In the framework of the standard Debye description [2], in the low frequency range, the real part, \mathcal{R} , of the impedance, \mathcal{Z} , has to tend to a constant value $\mathcal{R}(0)=[1/\sigma_{\text{eq}}(0)]d/S$, where $\sigma_{\text{eq}}(0)$ is the dc conductivity of the medium, d the thickness of the sample, and S the surface of the electrodes. According to elementary electrodynamics $\sigma_{\text{eq}}(0)=2n_0\mu q$, if the ions participating to the phenomenon have the same mobility μ , charge q , and n_0 is their density in thermodynamical equilibrium. However, in real samples \mathcal{R} in the limit of small frequency presents an anomalous increasing. The increasing of \mathcal{R} for $\omega \rightarrow 0$ is usually interpreted by introducing the concept of impedance of the metal-electrolyte interface \mathcal{Z}_i , resulting from a random distribution of local impedances onto the electrode surfaces. According to [3] $\mathcal{Z}_i=w(i\omega)^{-\nu}$, where w and ν are positive constants depending on the metal and the electrolyte, and $\nu < 1$. The impedance of the interface \mathcal{Z}_i contributes to the total resistance of the cell with a term, $\mathcal{R}_i=\text{Re } \mathcal{Z}_i=w\omega^{-\nu} \cos(\nu\pi/2)$, which is frequency dependent. In particular, it diverges for $\omega \rightarrow 0$. In the same manner, it gives a contribution to the total imaginary part of the type $\mathcal{X}_i=\text{Im } \mathcal{Z}_i=-w\omega^{-\nu} \sin(\nu\pi/2)$. Also this contribution diverges for $\omega \rightarrow 0$, as $\omega^{-\nu}$. According to Levie [4], ν depends on the roughness of the electrodes. However, Bates *et al.* [5] have found no correlation between ν and the fractal dimension of the surface of a rough electrode.

Our aim is to investigate the influence of the adsorption phenomenon on the impedance spectroscopy of a cell in the shape of a slab of thickness d , and to show that it gives rise to an increasing of \mathcal{R} in the limit of $\omega \rightarrow 0$, similar to the one predicted by the phenomenological impedance of the interface discussed above. We will show also that by taking into account the adsorption phenomenon it is possible to interpret in a simple manner the frequency dependence of the real and imaginary part of the complex dielectric constant of a nem-

atic liquid crystal reported by Murakami and Naito [6,7].

II. THEORY

The z axis of the Cartesian reference frame used in the description is perpendicular to the limiting surfaces at $z = \pm d/2$. The problem is supposedly one dimensional. We assume that the liquid filling the cell contains, in thermodynamical equilibrium, a density n_0 of positive and negative ions, uniformly distributed. The ions are assumed identical in all the aspects, in particular with the same mobility. The surfaces limiting the sample are also assumed identical, with the same adsorption energy with respect to two types of ions, in order to avoid the problems connected with the selective ions adsorption [8,9]. We neglect the recombination phenomenon [6]. We indicate by $n_p(z,t)$ and $n_m(z,t)$ the bulk densities of positive and negative ions, and with $\sigma_p(t)$ and $\sigma_m(t)$ the surface densities of adsorbed ions of positive and negative charge. The electrical potential will be indicated by $V(z,t)$. The fundamental equations of the problem are [10] the equations of continuity

$$\frac{\partial n_\alpha(z,t)}{\partial t} = - \frac{\partial j_\alpha(z,t)}{\partial z}, \quad (1)$$

where $\alpha=p,m$, and the equation of Poisson

$$\frac{\partial^2 V(z,t)}{\partial z^2} = - \frac{q}{\epsilon} [n_p(z,t) - n_m(z,t)], \quad (2)$$

where q is the electrical charge of the ions, ϵ the dielectric constant of the liquid, and $j_\alpha(z,t)$ the density of currents of positive, p , and negative, m , ions given by

$$j_\alpha(z,t) = -D \left\{ \frac{\partial n_\alpha(z,t)}{\partial z} \pm \frac{q}{KT} n_\alpha(z,t) \frac{\partial V(z,t)}{\partial z} \right\}. \quad (3)$$

In Eq. (3), there is the sign $+$ for $\alpha=p$, and the sign $-$ for $\alpha=m$. In Eq. (3) we used the relation of Einstein-Smoluchowski relating the mobility, μ , to the diffusion coefficient, D , $\mu/D=q/(KT)$ where K is the constant of Boltzmann and T the absolute temperature [11]. Since the electrodes are supposed perfectly blocking we have the following boundary conditions on $j_\alpha(z,t)$:

$$j_\alpha(\pm d/2, t) = \pm \frac{d\sigma_\alpha(\pm d/2, t)}{dt}. \quad (4)$$

The other boundary conditions of the problem are connected with the imposed difference of potential. The evolution of the surface densities of adsorbed charges, at $z = \pm d/2$, is assumed of the type

$$\frac{d\sigma_\alpha(\pm d/2, t)}{dt} = kn_\alpha(\pm d/2, t) - \frac{1}{\tau}\sigma_\alpha(\pm d/2, t), \quad (5)$$

proposed long ago by Langmuir, and works well in the limit of low adsorption, as assumed in our analysis. The parameters k and τ are the adsorption and desorption coefficients, respectively [12]. A large value of k corresponds to a strong adsorption, whereas a large value of τ means that the desorption phenomenon is slow.

In the absence of an external electric field, the boundary conditions on the potential are $V(\pm d/2, t) = 0$. In this case the solution of Eqs. (1) and (2) with the relevant boundary conditions are

$$n_p(V=0) = n_m(V=0) = n^* = \frac{n_0}{1 + 2(k\tau/d)},$$

$$\sigma_p(V=0) = \sigma_m(V=0) = \sigma^* = \frac{k\tau d}{1 + 2(k\tau/d)} n_0 d \quad (6)$$

for the distributions of the ionic charge, and $V(z, t) = 0$ for the electric potential across the cell. In this situation, the sample is locally and globally neutral.

Let us suppose now that the sample is submitted to a sinusoidal external potential of amplitude V_0 and frequency $f = \omega/2\pi$ of the type $V(\pm d/2, t) = \pm (V_0/2)\exp(i\omega t)$. The applied voltage induces a charge separation. We set $n_\alpha(z, t) = n^* + \delta n_\alpha(z, t)$, and $\sigma_\alpha(\pm d/2, t) = \sigma^* + \delta\sigma_\alpha(\pm d/2, t)$ and we assume that the applied voltage is such that $\delta n_\alpha(z, t) \ll n^*$ and $\delta\sigma_\alpha(t) \ll \sigma^*$. In this framework, from Eq. (3) we get

$$j_\alpha(z, t) = -D \left\{ \frac{\partial \delta n_\alpha(z, t)}{\partial z} \pm \frac{n^* q}{KT} \frac{\partial V(z, t)}{\partial z} \right\}. \quad (7)$$

Substituting Eq. (7) into Eq. (1) we obtain

$$\frac{\partial \delta n_\alpha(z, t)}{\partial t} = D \left\{ \frac{\partial^2 \delta n_\alpha(z, t)}{\partial z^2} \pm \frac{n^* q}{KT} \frac{\partial^2 V(z, t)}{\partial z^2} \right\}. \quad (8)$$

Equations (2) and (8) show that in the steady state $\delta n_\alpha(z, t) = \eta_\alpha(z)\exp(i\omega t)$ and $V(z, t) = \phi(z)\exp(i\omega t)$ and from the boundary conditions (4) it follows that $\delta\sigma_\alpha(\pm d/2, t) = s_\alpha(\pm d/2)\exp(i\omega t)$. Finally, from the conditions $V(\pm d/2) = \pm (V_0/2)\exp(i\omega t)$, it follows that

$$\phi(\pm d/2) = \pm V_0/2. \quad (9)$$

In the steady state Eq. (2) can be rewritten as

$$\phi''(z) = -(q/\varepsilon)[\eta_+(z) - \eta_-(z)], \quad (10)$$

where the prime means derivative with respect to the z coordinate. The functions $\eta_\alpha(z)$ are solutions of the differential equations

$$\eta_{p,m}''(z) - \frac{1}{2\lambda^2} \left(1 + 2i \frac{\omega}{D} \lambda^2 \right) \eta_{p,m}(z) + \frac{1}{2\lambda^2} \eta_{m,p}(z) = 0, \quad (11)$$

obtained by Eq. (8), where $\lambda = \sqrt{\varepsilon KT / (2n^* q^2)}$ is the length of Debye [11]. From the conditions $n_p(z, t) = n_m(-z, t)$ and $\sigma_m(\pm d/2, t) = \sigma_p(\mp d/2, t)$, connected with the hypotheses that the positive and negative ions have the same mobility, the limiting surfaces have the same adsorption energies with respect to the two types of ions, and that $V(\pm d/2, t) = \pm (V_0/2)\exp(i\omega t)$, it follows that $\eta_p(z) = \eta_m(-z)$ and $s_m(\pm d/2) = s_p(\mp d/2)$. The solutions of Eq. (11) satisfying these symmetry conditions are

$$\eta_{p,m}(z) = m_0 \cosh(\alpha z) \pm p_0 \sinh(\beta z), \quad (12)$$

where $\alpha^2 = i\omega/D$ and $\beta^2 = (1/\lambda^2) + i\omega/D$. The profile of the electric potential is given by Eq. (10), which in the case under consideration reads

$$\phi''(z) = -2(q/\varepsilon)p_0 \sinh(\beta z), \quad (13)$$

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

$$\phi(z) = -2(q/\varepsilon\beta^2)p_0 \sinh(\beta z) + cz. \quad (14)$$

The integration constants m_0 , p_0 , and c are determined by the boundary conditions (4) and (9). Simple considerations show that $m_0 = 0$, and that p_0 and c are the solutions of the system

$$\left\{ 1 + \beta \frac{k\tau}{1 + i\omega\tau} \tanh\left(\frac{\beta d}{2}\right) \right\} p_0 - i \frac{n^* q / (KT)}{(\omega/D)\beta \cosh(\beta d/2)} c = 0,$$

$$-2 \frac{q}{\varepsilon\beta^2} \sinh\left(\frac{\beta d}{2}\right) p_0 + \frac{d}{2} c = \frac{V_0}{2}. \quad (15)$$

The electrical problem is then solved.

III. ELECTRICAL IMPEDANCE OF THE CELL

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

$$E(z, t) = -\frac{\partial V(z, t)}{\partial z} = -\phi'(z)\exp(i\omega t). \quad (16)$$

From the theorem of Coulomb $E(d/2, t) = -[\Sigma(t) + q\sigma(t)]/\varepsilon$, where Σ is the surface density of charge on the electrode at $z = d/2$ and $\sigma q = (\sigma_p - \sigma_m)q$ the net adsorbed charge at $z = d/2$. From Eqs. (4) and (5) we get

$$\sigma = 2 \frac{k\tau}{1 + i\omega\tau} p_0 \sinh(\beta d/2) \exp(i\omega t). \quad (17)$$

It follows that $\Sigma = -\sigma q + \varepsilon\phi'(z = d/2)\exp(i\omega t)$. The current $I = Sd\Sigma/dt$, where S is the surface of the electrodes, is then

$$I(t) = i\omega S$$

$$\times \left\{ -2 \frac{q}{\beta} \left(\cosh(\beta d/2) + \beta \frac{k\tau}{1 + i\omega\tau} \sinh(\beta d/2) \right) p_0 + \varepsilon c \right\}$$

$$\times \exp(i\omega t). \quad (18)$$

From Eq. (18) it follows that the presence of the adsorption phenomenon is responsible for a pick of the dielectric losses centered at $\omega^* \sim 1/\tau$. The admittance of the cell defined by $\mathcal{Y} = I/V$ is found to be

$$\mathcal{Y} = i \frac{\omega S}{V_0} \times \left\{ -2 \frac{q}{\beta} \left(\cosh(\beta d/2) + \beta \frac{k\tau}{1+i\omega\tau} \sinh(\beta d/2) \right) \rho_0 + \varepsilon c \right\}. \quad (19)$$

Note that, since from Eqs. (15) ρ_0 and c are proportional to V_0 , actually \mathcal{Y} is independent of it, as expected. From Eq. (19) one can obtain the impedance of the cell, defined by $\mathcal{Z} = 1/\mathcal{Y}$, the resistance $\mathcal{R} = \text{Re } \mathcal{Z}$ and the reactance $\mathcal{X} = \text{Im } \mathcal{Z}$, which are the quantities experimentally detectable. In the limit of $\omega \rightarrow 0$, making use of Eq. (19), we get for \mathcal{R} and \mathcal{X} the expressions

$$\mathcal{R} = \frac{\lambda^2 d}{\varepsilon D S} \left\{ 1 + \frac{D}{k d} \left(\frac{\rho}{1+\rho} \right)^2 \right\},$$

$$\mathcal{X} = - \frac{1}{\omega \varepsilon} \frac{2\lambda}{(1+\rho) S}, \quad (20)$$

where $\rho = k\tau/\lambda$ is a typical parameter characterizing the adsorption in the present context, where the intrinsic length connected with the adsorption phenomenon $k\tau$ has to be compared with the Debye's screening length λ . In the case $\rho \gg 1$, relevant to the strong adsorption, from Eqs. (20) we obtain

$$\mathcal{R} = \frac{\lambda^2 d}{\varepsilon D S} \left(1 + \frac{D}{k d} \right), \quad \mathcal{X} = - \frac{1}{\omega \varepsilon} \frac{2\lambda^2}{k \tau S}. \quad (21)$$

In this case the relative increasing of \mathcal{R} and \mathcal{X} due to the adsorption are then $\delta\mathcal{R}/\mathcal{R}(k=0) = D/(kd)$ and $\delta\mathcal{X}/\mathcal{X}(k=0) = -1$.

The phenomenological parameters characterizing the physical properties of the cell are the equivalent conductivity, σ_{eq} , and the equivalent dielectric constant, ε_{eq} , defined by $\sigma_{\text{eq}} = (1/\mathcal{R})(d/S)$, and $\varepsilon_{\text{eq}} = -(1/\omega\mathcal{X})(d/S)$. In the limit of $\omega \rightarrow 0$, by using for \mathcal{R} and \mathcal{X} the expressions (20), we obtain for σ_{eq} and ε_{eq} the relations

$$\sigma_{\text{eq}} = \frac{\varepsilon D / \lambda^2}{1 + (D/k\tau)[\rho/(1+\rho)]^2},$$

$$\varepsilon_{\text{eq}} = \varepsilon \frac{d}{2\lambda} (1+\rho). \quad (22)$$

In the limit of large adsorption from Eq. (22) we obtain

$$\sigma_{\text{eq}} = \frac{\varepsilon D / \lambda^2}{1 + (D/kd)} \quad \text{and} \quad \varepsilon_{\text{eq}} = \varepsilon \frac{k\tau d}{2\lambda^2}. \quad (23)$$

Usually, the dielectric properties of a cell are described by introducing a complex dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$. The real part ε' is connected with the usual dielectric properties of the medium, whereas the imaginary part ε'' is related to the rela-

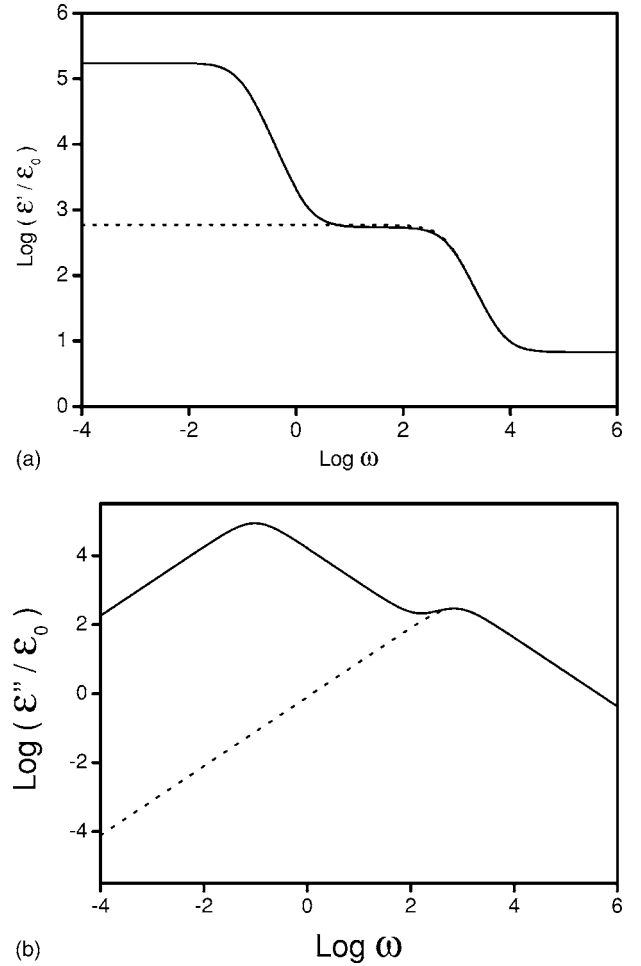


FIG. 1. (a) $(\varepsilon'/\varepsilon_0)$ vs ω and (b) $(\varepsilon''/\varepsilon_0)$ vs ω . Continuous curves $k=10^{-7} \text{ m}^{-1} \text{ s}^{-1}$ and $\tau=10 \text{ s}$, whereas the dotted lines correspond to the case in which the adsorption phenomenon is absent ($k=0$). The logarithms are in base 10.

tive dielectric loss factor. The quantities ε' and ε'' can be expressed in terms of σ_{eq} and ε_{eq} as follows:

$$\varepsilon' = \frac{\varepsilon_{\text{eq}}}{1 + \omega^2 (\varepsilon_{\text{eq}} / \sigma_{\text{eq}})^2},$$

$$\varepsilon'' = \frac{\omega (\varepsilon_{\text{eq}} / \sigma_{\text{eq}})}{1 + \omega^2 (\varepsilon_{\text{eq}} / \sigma_{\text{eq}})^2} \varepsilon_{\text{eq}}. \quad (24)$$

For an estimation of the adsorption phenomenon on the impedance spectroscopy of a cell we assume that the liquid is a nematic liquid crystal of the type considered by Sawada *et al.* [13,14]. In this case $\varepsilon = 6.7\varepsilon_0$, $\mu = 3 \times 10^{-9} \text{ m}^2/\text{V s}$, $n_0 = 4 \times 10^{21} \text{ m}^{-3}$, and $d \sim 6 \mu\text{m}$. For the adsorption parameters we assume $k \sim 10^{-6} \text{ m}^{-1} \text{ s}^{-1}$ and $\tau \sim 10^{-2} \text{ s}$, as reported in [15]. In this case $\delta\mathcal{R}/\mathcal{R}(k=0) \sim 10$. This means that the increase of the real part of the impedance of the cell in the low frequency range due to the adsorption phenomenon is rather important.

In Fig. 1 we show the influence of the adsorption phenomenon on the real and imaginary parts of the complex

dielectric constant of the cell. The full lines correspond to a case of weak adsorption with $k=10^{-7} \text{ m}^{-1} \text{ s}^{-1}$ and $\tau=10 \text{ s}$, whereas the dotted lines to the case in which the adsorption phenomenon is absent ($k=0$). As it follows from Fig. 1(a), showing (ϵ'/ϵ_0) vs ω , the presence of the adsorption is responsible for an increasing of ϵ' in the low frequency region. The deviation of ϵ' from the case in which the adsorption phenomenon is absent takes place at the frequency $\omega^* \sim 1/\tau$, as expected. In Fig. 1(b) is reported (ϵ''/ϵ_0) . As is evident from Fig. 1, in the absence of the adsorption phenomenon, ϵ' presents a large plateau, and tends to ϵ at large frequency. On the contrary, ϵ'' presents a maximum at $\omega_M \sim D/\lambda d$, for which ϵ' is decreasing toward ϵ . The presence of the adsorption phenomenon introduces a new plateau for ϵ' , and a new maximum for ϵ'' at ω^* . In both cases, in the high frequency region, the presence of the adsorption does not play any role.

IV. CONCLUSION

From the results discussed above we can conclude that the experimental observations by Murakami *et al.* [6,7] in the low and ultralow frequency regimes can be interpreted in terms of the adsorption effect of weak adsorbing systems. In particular, the experimental data reported in [6] indicate that the presence of the polyimide layers modify the adsorption properties of the substrate. In the absence of the polyimide $\tau \sim 10^2 \text{ s}$ (see Fig. 1 of Ref. [6] and Fig. 2 of Ref. [7]), whereas when the polyimide is present $\tau \sim 10^{-2} \text{ s}$ (see Fig. 3 of Ref. [6]). These experimental observations indicate that the presence of the polyimide is responsible for the dielectric losses at frequencies between 0 and 100 Hz.

According to this point of view, the impedance spectroscopy technique could be very useful in obtaining a precise determination of the adsorption-desorption coefficients.

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