

Ionic contribution to the electric current in an electrolytic cell submitted to an external voltage

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The ionic contribution to the electrical current in an electrolytic cell submitted to an external voltage linearly increasing with the time is evaluated. The investigation is performed in the limit of small and large electric field, in which the density of ions depends on the actual electric field in the sample. In the analysis, it is assumed that the ionic separation induced by an external field can be described by a surface density of charge. We show that the ions are responsible for a peak in the current, followed by a delay in the application of the external voltage. From the analysis of the peak and its delay, it is possible to obtain information on the density of ions in thermodynamical equilibrium, and on the mobility of the ions in the considered liquid.

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We analyze the influence of the ions present in a liquid on the detectable current, when the cell is submitted to an external voltage linearly increasing with the time. We assume that the sample is in the shape of a slab of thickness d . The Cartesian reference frame used in the description has the z axis normal to the limiting surfaces, placed at $z = \pm d/2$. We suppose that the electrodes are covered by means of an insulating material of thickness L and dielectric constant ϵ_S in such a manner that they can be considered perfectly blocking with respect to the ions present in the liquid. The case in which the surface layer is absent, and hence the electrodes are not blocking, can be treated as proposed in [1]. However, since for technological applications to avoid charge injection the electrodes are usually covered by an insulating material, we limit the analysis to the system described in Fig. 1. We suppose first that the chemical equilibrium for the dissociation of impurity in ions is not perturbed by the external voltage, and that there is no specific ion adsorption on the surfaces. This assumption is valid in the limit of small external field [2]. In the opposite limit of large external field, the chemical equilibrium is perturbed [3], and this case will be analyzed later. In this framework, in the absence of an external electric field, the liquid is locally and globally neutral.

We indicate by n_0 the density of ions in the thermodynamical equilibrium, q the modulus of the electrical ionic charge, ϵ_B the dielectric constant of the liquid in which the ions are dispersed, and μ the mobility of the ions in the liquid.

When an external voltage V_0 is applied to the cell, an electric force pushes the positive ions close to the negative electrode and the negative ions close to the positive electrode. Since the layers where the ions are confined are very thin with respect to d , we consider them as surface distribution of charges. These surface densities of charge are indicated by $\mp q\sigma$, whereas the ones sent by the power supply on the electrodes to fix the applied potential to V_0 are indicated by $\pm q\Sigma$. The bulk density of ions, when the external voltage is present, is indicated by n . We assume that n is constant across the cell, as discussed in [4]. This simple model is in agreement with a more rigorous calculation performed by taking into account the drift and diffusion currents, as has been shown by Scalerandi *et al.* [5]. Since the number of

ions is a constant, $n = n_0 - \sigma/d$. According to elementary electrodynamics, we have that the electric fields in the surface layer, E_S , and in the bulk, E_B , are given by [4]

$$E_S = q \frac{\Sigma}{\epsilon_S} \quad \text{and} \quad E_B = q \frac{\Sigma - \sigma}{\epsilon_B}. \quad (1)$$

By imposing the condition $2E_S L + E_B d = V_0$, we get

$$q\Sigma = \gamma \left(\epsilon_B \frac{V_0}{d} + q\sigma \right), \quad (2)$$

where $\gamma^{-1} = 1 + 2(\epsilon_B L / \epsilon_S d)$. It follows that

$$E_S = \frac{\gamma}{\epsilon_S} \left(\epsilon_B \frac{V_0}{d} + q\sigma \right) \quad \text{and} \quad (3)$$

$$E_B = \gamma^{-1} \left(V_0 - 2q \frac{L}{\epsilon_S} \sigma \right).$$

To find the temporal evolution of σ , we have to take into account that in a time dt the charge collected on the limiting surface is $dQ = qd\sigma A = JAdt$, where A is the surface of the electrodes and J is the density of electrical current. It is given by $J = 2nqv$, where $v = \mu E_B$ is the velocity of drift due to the presence of the field acting on the ions, E_B . By taking into

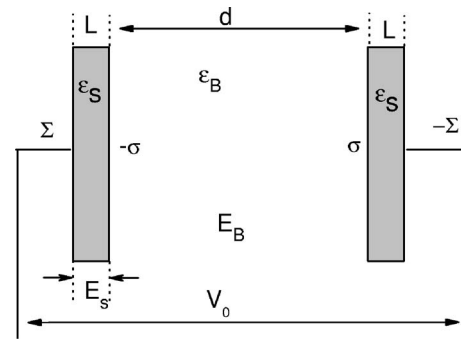


FIG. 1. Cell of thickness d filled with an isotropic fluid of dielectric coefficient ϵ_B . The electrodes are covered with a film of thickness L , having a dielectric coefficient ϵ_S .

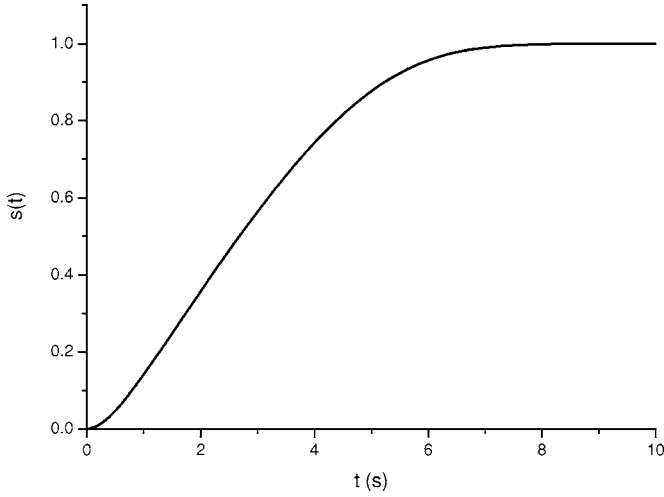


FIG. 2. Dimensionless surface charge density $s = \sigma/\sigma_M$ vs t .

account the expression reported above for n , we obtain for σ the differential equation

$$\frac{d\sigma}{dt} = \frac{\gamma\mu}{d} \left(n_0 - \frac{\sigma}{d} \right) \left(V_0 - 2 \frac{qL}{\varepsilon_S} \sigma \right). \quad (4)$$

By putting

$$\sigma_M = n_0 d \quad \text{and} \quad V_c = 2q \frac{n_0 d L}{\varepsilon_S}, \quad (5)$$

and introducing the dimensionless quantities $s = \sigma/\sigma_M$ and $u = V_0/V_c$, it is possible to rewrite Eq. (4) in the form

$$\frac{ds}{dt} = \gamma\mu \frac{V_c}{d^2} (1-s)(u-s). \quad (6)$$

As is evident from the definition, σ_M is the maximum value of σ . It is attained when all the ions present in the electrolyte are pushed by the electric field to the limiting surface. Hence, $s \leq 1$. The quantity V_c is a counterpotential of ionic origin. In the following, we are interested in the analysis of the case in which $V_0 = Kt$, and hence $u = kt$, where $k = K/V_c$. In this case, since we have the obvious condition $\sigma(0) = 0$, i.e., $s(0) = 0$, from Eq. (6) it follows that $(ds/dt)_0 = 0$. Furthermore, since for $t \rightarrow \infty$, $s \rightarrow 1$, we have also $(ds/dt)_\infty = 0$. The solution of Eq. (6), with the boundary condition $s(0) = 0$ and $u = kt$, is

$$s(t) = 1 + \frac{e^{\alpha t - (\alpha/2)t^2}}{C - \sqrt{\frac{\pi\alpha}{2k}} e^{\alpha/2k} \operatorname{erf}\left(\sqrt{\frac{\alpha}{2k}}(-1 + kt)\right)}, \quad (7)$$

where $\alpha = \gamma\mu V_c/d^2$, and

$$C = - \left(1 + \sqrt{\frac{\pi\alpha}{2k}} e^{\alpha/2k} \operatorname{erf}\left(\sqrt{\frac{\alpha}{2k}}\right) \right). \quad (8)$$

The electrical current in the external circuit is given by $I = Aq d\Sigma/dt$ that, by taking into account Eq. (2), is found to be

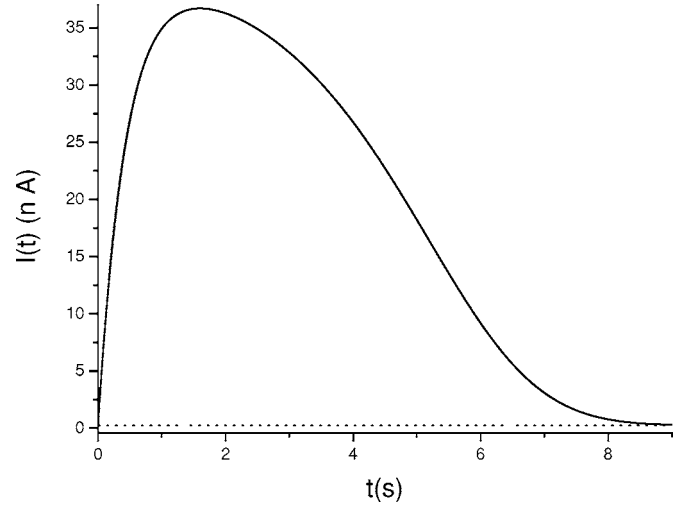


FIG. 3. Current in the external circuit vs t . The area under the curve is $n_0 q d$, given in Eq. (12). The curve was depicted for $K = 1$ V/s. The dotted line indicates the limiting value given by Eq. (11), $I_{\text{lim}} \approx 0.24$ nA.

$$I = \gamma\varepsilon_B \frac{A}{d} \frac{dV_0}{dt} + \gamma A q \frac{d\sigma}{dt}. \quad (9)$$

In Eq. (9) the first contribution to I is the usual one due to an ideal capacitor. In fact, $C_B = \varepsilon_B A/d$ is the capacity of the bulk, and

$$\frac{1}{\gamma C_B} = \frac{d}{\varepsilon_B A} + 2 \frac{L}{\varepsilon_S A} = \frac{1}{C_B} + 2 \frac{1}{C_S} = \frac{1}{C_{\text{eq}}} \quad (10)$$

is just the equivalent capacity of the series of the capacitor corresponding to the bulk, C_B , and of the two corresponding to the surface layers, $C_S/2$. The remaining term in Eq. (9) is the contribution to the current connected with the presence of the ions dissolved in the liquid. From Eq. (9), taking into account that $(d\sigma/dt)_0 = (d\sigma/dt)_\infty = 0$, it follows that for $V_0 = Kt$, $\lim_{t \rightarrow 0} I(t) = \lim_{t \rightarrow \infty} I(t) = K C_{\text{eq}}$ [6].

For a numerical estimation of the predicted effect, we assume $n_0 = 4.2 \times 10^{20} \text{ m}^{-3}$, $\mu = 3.28 \times 10^{-10} \text{ m}^2/\text{V s}$, $\varepsilon_B = 6.7 \times \varepsilon_0$, $d = 25 \times 10^{-6} \text{ m}$, $A = 10^{-4} \text{ m}^2$ as in [7], $L = 40 \times 10^{-9} \text{ m}$, and $\varepsilon_S = 4\varepsilon_0$ [4]. For the ionic concentration reported above, Debye's screening length for the liquid under consideration is $\lambda = \sqrt{\varepsilon_B k_B T / 2n_0 q^2} \sim 0.1 \mu\text{m} \ll d$. Therefore, the assumption of the independence of the ion concentration on the z coordinate in the bulk of the solution, according to which $n = n_0 - \sigma/d$, is justified.

Using the value reported above, if $K = 1$ V/s we have for the evolution of the surface charge, $s(t)$, and of the current in the external circuit, $I(t)$, the trends reported in Fig. 2 and in Fig. 3, respectively. From Fig. 2, it follows that $s(t)$ tends to 1, i.e., $\sigma \rightarrow \sigma_M$, as expected.

From Fig. 3, it is evident that with the set of physical parameters used in our calculations, the current presents a peak, and after that it tends to the charging current

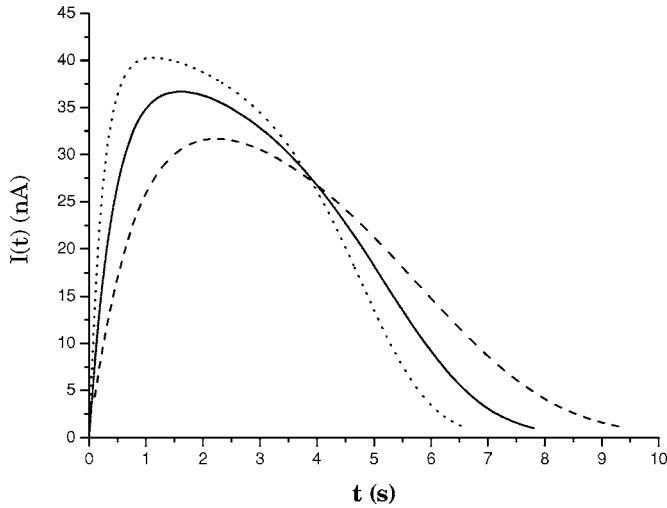


FIG. 4. Current in the external circuit vs t . Solid line corresponds to the reference value $\mu_1 = 3.28 \times 10^{-10} \text{ m}^2/\text{V s}$, dotted line to $\mu = 2\mu_1$, and dashed line to $\mu = 0.5\mu_1$.

$$I_{\text{lim}} = KC_{\text{eq}}, \quad (11)$$

typical of an ideal capacitor. From Eq. (9), taking into account Eq. (11), it follows that

$$n_0 q d = \int_0^\infty \frac{I - I_{\text{lim}}}{\gamma A} dt. \quad (12)$$

Using the numerical value reported above, the charging current is of the order of 0.24 nA, rather small with respect to the current of ionic origin. It is small enough not to perturb the ionic concentration.

The analysis presented above can be useful to obtain information on the density of ions and on the mobility of the ions in a liquid by means of measurements of electrical current. This equation can be useful to determine the bulk density of ions in thermodynamical equilibrium, by means of a simple measurement of electrical current.

Furthermore, from the experimental analysis of the location of the maximum of the current, one can also obtain the value of the mobility of the ions. The maximum of I , according to Eq. (9), is defined by $d^2\sigma/dt^2 = 0$. By indicating with $(^*)$ the quantities relevant to the maximum of I , we have

$$\mu = \frac{kd^2}{\gamma V_c} \frac{1}{(1 + u^* - 2s^*)(u^* - s^*)}. \quad (13)$$

From the experimental data, t^* is easily determined and so u^* and s^* . Consequently, Eq. (13) allows the determination of the mobility, which is an important characteristics for the display applications of liquid crystals. In Fig. 4 are shown a few $I=I(t)$ curves for different values of the mobility. As is evident, increasing μ , t^* decreases. In Fig. 5, we report the dependence of t^* on μ . A curve of this kind can be used for the experimental determination of the mobility.

Previous analysis holds only in the case in which the chemical equilibrium relevant to the ionic dissociation is not perturbed by the presence of the external electric field. This means, actually, that it is valid for applied fields much

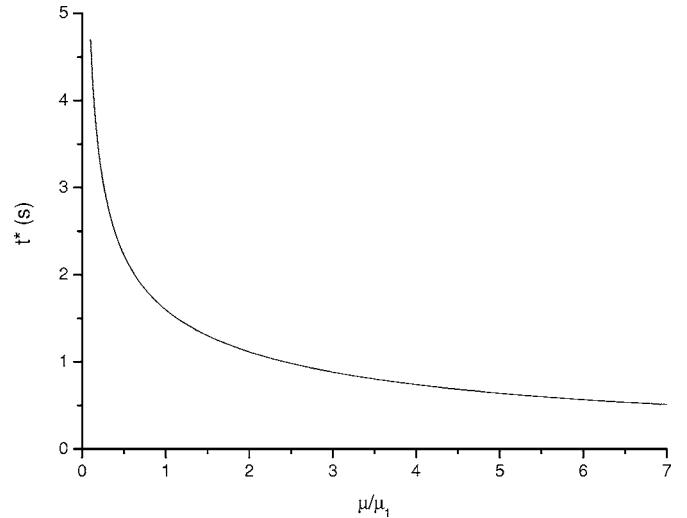


FIG. 5. t^* is the instant corresponding to the maximum in the current. μ_1 is the reference mobility given in Fig. 4.

smaller than $1 \text{ V}/\mu\text{m}$. However, when this kind of measurement is performed on a ferroelectric liquid crystal, the applied field is of the order of several volts per micrometer. In this case, previous assumption is not valid and the analysis presented above has to be generalized to take into account the influence of the electric field on the electrolytic dissociation, as discussed in [3]. According to the model proposed by Onsager, the density of ions depends on the actual electric field as

$$n(E) = n_0 + p|E|, \quad (14)$$

where p takes into account the effect of the external electric field on the electrolytic dissociation. In this framework, the differential equation describing the time evolution of the surface density of ions is, instead of Eq. (4),

$$\frac{d\sigma}{dt} = \mu \left(n_0 + p|E_B| - \frac{\sigma}{d} \right) E_B, \quad (15)$$

where E_B is given by Eq. (3) and we have taken into account that the actual field in the sample is E_B . In Fig. 6, we show the numerical integration of Eq. (15) relevant to the case $K = 100 \text{ V/s}$, and $p = 10^{14} (\text{V m}^2)^{-1}$, whereas the other physical parameters are the same as above. In the same figure, we compare the behavior of σ when Onsager's effect is considered with the one in which it is neglected. From this figure, it follows that for small t the two trends are coincident, as expected. On the contrary, for large t the Onsager effect is responsible for a linear increase of $\sigma(t)$. In Fig. 7, the electrical current in the circuit for the same situations is reported. We note that the behaviors are the same, but Onsager's effect is responsible for a constant value of the electrical current observed for large t , coming from the second term of Eq. (9). It is possible to obtain analytically information on the current in the circuit for large t , by operating as follows. From Fig. 6, we derive that in the limit of large t , $d\sigma/dt$ tends to a constant value. This means that, in this limit, $\sigma(t) = Ht + M$. By substituting this expression for σ and $V_0 = Kt$ into Eq. (15), we get

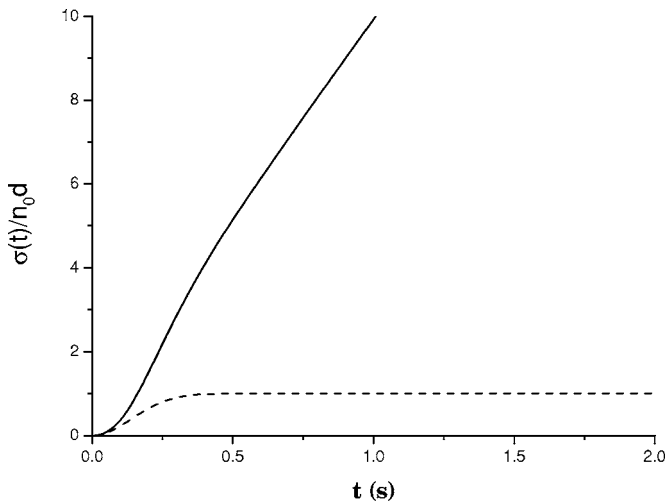


FIG. 6. Surface charge density obtained from Eq. (15) vs t . Solid line refers to the case $p \neq 0$ (Onsager effect) and dashed line $p=0$.

$$H = At^2 + Bt + C, \quad (16)$$

where A , B , and C are defined in terms of H and M . From Eq. (16), it follows that $A=0$, $B=0$, and $H=C$. By solving these equations, we obtain

$$M = \frac{\epsilon_S dn_0}{\epsilon_S + 2\gamma pqL} \quad \text{and} \quad H = \frac{\epsilon_S \gamma K p}{\epsilon_S + 2\gamma pqL}. \quad (17)$$

The other solution giving $H = \epsilon_S K / 2qL$ and $M=0$ is not important in this context, since we are looking for a solution for which σ increases with the time because $p \neq 0$. By taking into account (17) we get that, in the limit of large t , the current tends to

$$I_{\text{lim}}(p) = I_{\text{lim}}(p=0) \left[1 + \gamma \left(\frac{\epsilon_S}{\epsilon_B} \right) \frac{qpd}{\epsilon_S + 2\gamma pqL} \right]. \quad (18)$$

From Eq. (18) it follows that the increasing of the current in the limit of large t depends on p . Consequently, a measurement of this quantity can give useful information on this parameter.

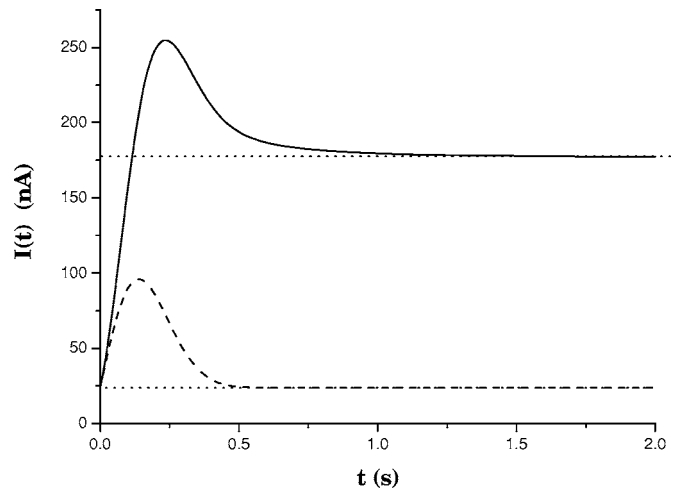


FIG. 7. Electrical current obtained with Eqs. (9) and (15) vs t . Solid line refers to the case $p \neq 0$ (Onsager effect) and dashed line $p=0$. The dotted line indicates the limiting value given by Eq. (18), $I_{\text{lim}}(p=0) \approx 24$ nA, and $I_{\text{lim}}(p \neq 0) \approx 176$ nA. The curves were depicted for $K=100$ V/s.

We have analyzed the contributions of the ions to the electrical current in a cell of isotropic liquid when the electrodes can be considered as perfectly blocking when the external voltage is a linearly increasing function of the time. The analysis has been performed in the limit of low and large electric field. In the first case, the chemical equilibrium relevant to the dissociation of impurities in ions is field-independent. In this framework, we have shown that from the experimental data $I=I(t)$ it is possible to determine the mobility of the ions and the density of ions in the sample, by analyzing the maximum of the current versus the time and the limiting value of the current for large t . In the case in which the applied field is so large such that the chemical equilibrium depends on it, the analysis has been performed by taking into account the effect predicted by Onsager, relevant to the ion formation due to the presence of the field. In this case, we have shown that in the limit of large t , the limiting value of the current depends on the Onsager coefficient. Hence, an investigation of the kind discussed here can allow its determination.

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