I. INTRODUCTION

The impedance spectroscopy technique is widely used to investigate the dielectric properties of solid or liquid materials. The theoretical model to evaluate the electrical impedance of an insulating liquid containing ions was developed by Ross Macdonald in 1953. This model is valid for perfectly blocking electrodes, and takes into account the dissociation of neutral particles in ionic products and the recombination of ions to give rise to neutral particles. The model was generalized by Ross Macdonald and Franceschetti. Since then, Ross Macdonald and colleagues have investigated several aspects of the physics related to the impedance spectroscopy in several situations, and discussed how they can be used in the fitting and analyzing of experimental data. A large part of the work on the impedance spectroscopy was done by Ross Macdonald and reported in his papers. The recent papers published on the dielectric characterization of materials indicate that the subject is mainly for scientists working in the domain. They are hardly accessible for scientists working in other areas. The problems related to the choice of the model for the fit, as discussed in Ref. 2, very often are not explained, and the reader is lost in a long list of acronyms. Of course, as other branches of physics, also the theory of the impedance spectroscopy has been improved, but according to us, it seems that the fit of the experimental data is the most important goal of the theory. Sometimes, the proposed theory looks as a fitting theories and their applicability is questionable.

For this reason we want to follow the line drawn initially by Ross Macdonald and base our analysis on simple equations having a clear physical meaning. As discussed recently, an application of equations without a clear understanding of the phenomenon under investigation can be the source of mistakes. In this paper we want to investigate, in some detail, an aspect of the theory of Ross Macdonald reported in Ref. 4. Our interest is the analysis of the importance of the dissociation-association phenomenon on the electrical impedance of an insulating medium containing ions. The problem is well defined and we will face it by assuming first that the diffusion coefficients of the positive and negative ions are identical. The case in which the diffusion coefficients of the positive and neutral particles are zero will also be considered. Our paper is organized as follows. In Sec. II we present the fundamental equations of the problem relevant to the drift-diffusion problem for the ions in an insulating gel, in the presence of the generation-recombination phenomenon, described as a first order chemical reaction. The case where the diffusion coefficients of the positive and negative ions are equal is considered in Sec. III. The particular case where the positive and neutral particles are stuck on the polymer chains forming the gel is discussed in Sec. IV, where it is shown that the generation-recombination phenomenon is responsible for a new low frequency plateau. Although the work of Ross Macdonald includes both that herein and more general situations as well, he presented in...
Ref. 5 only complex plane plots at the complex capacitance level to illustrate these theoretical results. It is therefore of interest to shed more light on the situation by showing here direct frequency response results for the impedance and dielectric constant response levels and, instead of directly using Ross Macdonald’s response equations simplified for the present situations, to present alternate derivations as a check on their correctness. Section V is devoted to the conclusions.

II. POSITION OF THE PROBLEM

Let us consider a cell in the shape of a slab of thickness \( d \). The cell is limited by two identical plane-parallel electrodes that we suppose perfectly blocking. The medium is assumed to be an insulating gel, of dielectric constant \( \varepsilon \), containing impurities. The impurities can decompose according to the chemical reaction \( A^+B^++C^- \), where \( A \) indicates the neutral specie, and \( B^+ \) and \( C^- \) are the positive and negative ions created in the decomposition of \( A \). The dissociation constant is indicated by \( k_d \) and the association constant by \( k_a \). The ions are supposed monovalent, with electrical charge \( q=1.6 \times 10^{-19} \text{ A s} \).

The Cartesian reference frame used in the description has the \( z \)-axis perpendicular to the electrodes, located at \( z = \pm d/2 \). We indicate by \( n_p \), \( n_n \), and \( n_m \) the bulk density of neutral, positive, and negative particles, respectively. In the presence of an electric field, of electrical potential \( V \), due to the presence of an external power supply or to a charge separation, the bulk densities of current of the particles are

\[
j_n = -D_n n_{nz},
\]

\[
j_p = -D_p (n_{pz} + (q n_p/k_B T) V_{z}),
\]

\[
j_m = -D_m (n_{mz} - (q n_m/k_B T) V_{z}),
\]

for the neutral, positive, and negative species, whose diffusion coefficients are \( D_n \), \( D_p \) and \( D_m \), respectively. In Eq. (1) the notation comma for the derivatives is used, according to which \( X_{,z} = \partial X/\partial z \). The equations of continuity, stating the conservation of the particles, are

\[
n_{nz} = j_n - k_d n_n + k_d n_p n_m,
\]

\[
n_{pz} = j_p - k_d n_n - k_d n_p n_m,
\]

\[
n_{mz} = j_m + k_d n_n - k_d n_p n_m.
\]

The final equation of the model is the equation of Poisson, relating the effective electric field to the net charge density,

\[
V_{z} = -(q/\varepsilon)(n_p - n_m).
\]

The terms \( (k_d n_n - k_d n_p n_m) \) appearing in Eqs. (4)–(6) take into account the generation and recombination of the ions from the neutral species. Equations (4)–(7) have to be solved with the boundary conditions

\[
j_n (\pm d/2, t) = 0,
\]

\[
j_p (\pm d/2, t) = 0
\]

related to the assumption that the electrodes are blocking, and to the presence of the external power supply of emf \( V_0(t) \).

In an infinite sample \( (d \to \infty) \) and in the absence of an external power supply, we are in the conditions of thermodynamical equilibrium, where the bulk density of neutral, positive, and negative ions is position independent. If we indicate by \( N_o \) the bulk density of dissociable particle, and by \( N_n \) and \( N \) the bulk densities of neutral and charged particles in thermodynamical equilibriam, we have

\[
N + N_n = N_0 \quad \text{and} \quad k_d N_n = k_a N^2.
\]

It follows that the bulk density of ions, in thermodynamical equilibrium, is \( N = \rho N_0 \), where the ratio of dissociation \( \rho \) is given by

\[
\rho = \frac{\kappa}{2} + \sqrt{\left(\frac{\kappa}{2}\right)^2 + \kappa}.
\]

In Eq. (13) we have introduced the dimensionless parameter \( \kappa \) related to the generation and recombination coefficients by \( \kappa = k_d/(k_a N_0) \). From Eq. (13) it follows that for \( \kappa = 0 \), \( \rho = 0 \), i.e., there are not dissociated particles (ions). In the limit of \( \kappa \to 0 \) we get

\[
\rho = \sqrt{\kappa}.
\]

In the opposite case where \( \kappa \to \infty \), from Eq. (13) we obtain, at the first order in \( 1/\kappa \),

\[
\rho = 1 + \frac{1}{\kappa}.
\]

From Eq. (15) it follows that the case of complete dissociation corresponds to the situation \( \kappa \to \infty \), where \( N = N_0 \), and hence \( N_n = 0 \). Note that for \( \kappa \to 0 \), \( dp/d\kappa = 1/(2/\kappa) \), and for \( \kappa \to \infty \), \( dp/d\kappa = 1/\kappa^2 \). Consequently the degree of dissociation \( \rho \) is very sensible to small variations of \( \kappa \), for small \( \kappa \). On the contrary, in the limit of large \( \kappa \), \( \rho = \rho(\kappa) \) tends to 1, as it follows from Eq. (15), and it is rather insensitive to the variations of \( \kappa \).

In the presence of an external electric field, and for finite \( d \), the actual bulk density of particles differs from that in thermodynamical equilibrium, and depends on \( z \) and \( t \). If the cell has a thickness \( d \), the conservation of the number of particles requires that

\[
\int_{-d/2}^{d/2} \left( n_n + n_p + n_m \right) dz = N_0 d.
\]

Since the medium remains globally neutral we have also that

\[
\int_{-d/2}^{d/2} n_p dz = \int_{-d/2}^{d/2} n_m dz,
\]

and condition (16) can be rewritten as
can be rewritten as
\[
\int_{-d/2}^{d/2} (n_a + n_p)dz = N_0d. \tag{18}
\]

We limit our analysis to the case where the variations in the bulk density of ions due to the presence of the external power supply are very small with respect to the values in thermodynamical equilibrium. By setting \(n_a = N_a + \delta n_a, \quad n_p = N + \delta n_p, \quad n_m = N + \delta n_m\), this assumption implies that the difference of potential applied to the cell is such that \(N_p \approx \delta n_p, \quad N \approx \delta n_m\), and \(N_p \approx \delta n_p\). In this case the equations of the problem, Eqs. (4)–(7), can be linearized and written as
\[
\begin{align*}
\delta n_{a,j} &= D_a \delta n_{a,z} - k_d \delta n_a + k_w N (\delta n_p + \delta n_m), \\
\delta n_{p,j} &= D_p \delta n_{p,z} + (qN/k_B T)V_z, \\
\delta n_{m,j} &= D_m \delta n_{m,z} - (qN/k_B T)V_z, \\
V_{zz} &= (q/e)(\delta n_p - \delta n_m),
\end{align*}
\]
which are the fundamental equations for the theory of small-signal ac response of a medium with recombining mobile charges.\(^5\) The boundary conditions for Eqs. (19)–(22) at the first order in the variations with respect to the equilibrium state are
\[
\begin{align*}
D_n \delta n_{n,z} &= 0, \\
D_p[\delta n_{p,z} + (qN/k_B T)V_z] &= 0, \\
D_m[\delta n_{m,z} - (qN/k_B T)V_z] &= 0,
\end{align*}
\]
at \(z = \pm d/2\). In this approximation Eq. (18) is
\[
\int_{-d/2}^{d/2} (\delta n_a + \delta n_p)dz = 0. \tag{27}
\]

We are interested in the particular case \(V_0(\pm d/2, t) = \pm (V_0/2)\exp(i\omega t)\), where \(V_0\) is the amplitude and \(\omega\) is the circular frequency of the applied voltage. Since in the limit of small applied voltage the equations governing the redistribution of ions in the presence of the external voltage are linear with constant coefficients, we have that \(\delta n_{a,z}(z, t), \quad \delta n_{p,z}(z, t), \quad \delta n_{m,z}(z, t), \quad \text{and } V(z, t)\) depend on \(t\) as \(\exp(i\omega t)\). It is then possible to look for a solution of the problem of the type
\[
[\delta n_a, \delta n_p, \delta n_m, V](z, t) = [\eta_a, \eta_p, \eta_m, \phi](z) \exp(i\omega t). \tag{28}
\]

Using ansatz (28) the fundamental equations of the problem can be rewritten as
\[
\begin{align*}
i\omega \eta_a &= D_a \eta_a'' - k_d \eta_a + k_w N (\eta_p + \eta_m), \\
i\omega \eta_p &= D_p[\eta_p' + (qN/k_B T)\phi''] + k_d \eta_p - k_w N (\eta_p + \eta_m), \\
i\omega \eta_m &= D_m[\eta_m'' - (qN/k_B T)\phi''] + k_d \eta_m - k_w N (\eta_p + \eta_m),
\end{align*}
\]
using \(\phi'' = -(q/e)(\eta_p - \eta_m)\). \tag{31}

III. \(D_p = D_m = D\) AND \(D_n \neq D\)

We assume that in this case all diffusion coefficients are different from zero. In this case the equations of the problem are
\[
\begin{align*}
i\omega \eta_a &= D_a \eta_a'' - k_d \eta_a + k_w N (\eta_p + \eta_m), \\
i\omega \eta_p &= D_p[\eta_p' + (qN/k_B T)\phi''] + k_d \eta_p - k_w N (\eta_p + \eta_m), \\
i\omega \eta_m &= D_m[\eta_m'' - (qN/k_B T)\phi''] + k_d \eta_m - k_w N (\eta_p + \eta_m),
\end{align*}
\]
with the boundary conditions, at \(z = \pm d/2\),
\[
\begin{align*}
\eta_a &= 0, \tag{42}
\eta_p + (qN/k_B T)\phi' &= 0, \tag{43}
\eta_m' - (qN/k_B T)\phi' &= 0, \tag{44}
\phi(\pm d/2) &= \pm V_0/2. \tag{45}
\end{align*}
\]
\[ \psi' - (2Nq^2 e k_B T) \psi = i(\omega/D) \psi \]  
(46)

subjected to the boundary condition, at \( z = \pm d/2 \),

\[ \psi' + (2qN/k_BT) \phi' = 0, \]
(47)

where \( \psi = \eta_p - \eta_m \). By solving Eq. (46) and the equation of Poisson for the potential, with the imposed boundary conditions we obtain that

\[ \phi(z) = 2A \sinh(\beta z), \]
(48)

\[ \phi(z) = - \frac{2q}{e \beta^2} A \sinh(\beta z) + Cz, \]
(49)

where

\[ A = - \frac{(qN\nu_B)/(2k_BT)}{\sinh(\beta d/2)/((\lambda^2 \beta) + i\omega \cosh(\beta d/2)/(2D))}, \]
(50)

\[ C = \frac{[i(\omega \nu_B)/(2D)] \cosh(\beta d/2)}{\sinh(\beta d/2)/((\lambda^2 \beta) + i\omega \cosh(\beta d/2)/(2D))}. \]
(51)

In Eqs. (48)–(51),

\[ \beta = \frac{1}{\sqrt{1 + i\omega \lambda^2/D}}, \]
(52)

and \( \lambda = \sqrt{e k_B T/(2Nq^2)} \) is the length of Debye evaluated for the bulk density of ions \( N \), resulting from the generation-recombination phenomenon. Note that this result coincides with that found in Ref. 27 in the absence of the dissociation-recombination terms. This result implies that the impedance for this particular case coincides with the one obtained in Ref. 27, whose expression is

\[ Z = -i \frac{2}{\omega e \beta^2 S} \left\{ \frac{1}{\lambda^2 \beta} \tanh \left( \frac{\beta d}{2} \right) + \frac{i\omega d}{2D} \right\}, \]
(53)

where \( S \) is the surface area of the electrodes. Expression (53) was first reported in Ref. 3 using different parameters than those used here. From Eq. (53) it follows that in the series representation, the resistance of the cell presents a plateau, ending at the frequency of Debye \( \omega_D \), and for \( \omega = \omega_D \) presents a minimum. The characteristics of the spectra for the real and imaginary parts of the impedance are described in Ref. 27.

Due to the particular symmetry of the problem, \( \eta_p \) and \( \eta_m \) are expected to be odd functions of \( z \). Furthermore, the positive ions will be confined close to the negative electrode and the negative ions close to the positive electrode. Since \( D_p = D_n = D \) the dynamics will be the same for the two types of ions and \( \eta_p + \eta_m = 0 \). Consequently Eq. (38) can be written has

\[ i\omega \eta_n = D \eta_n' - k_d \eta_n, \]
(54)

that, by taking into account the boundary condition of Eq. (42), gives \( \eta_n = 0 \). This means that at the first order in the variations, the bulk density of the neutral particles does not change in the presence of the external electric field.

IV. \( D_p = D_n = 0 \) AND \( D_m = D \neq 0 \)

Let us address our attention to the case \( D_p = D_n = 0 \) with \( D_m = D \neq 0 \). For this case, the set of equations Eqs. (29)–(32) reads

\[ i\omega \eta_n = -k_d \eta_n + k_o N(\eta_p + \eta_m), \]
(55)

\[ i\omega \eta_p = k_d \eta_n - k_o N(\eta_p + \eta_m), \]
(56)

\[ i\omega \eta_m = D[\eta_m' - (qN/k_BT) \phi' + k_d \eta_n - k_o N(\eta_p + \eta_m)], \]
(57)

\[ \phi' = -(q/\epsilon)(\eta_p - \eta_m). \]
(58)

The boundary conditions on \( \eta_p \) and \( \eta_m \) are identically satisfied because \( D_p = D_n = 0 \) imply that the bulk densities of currents for the two types of particles vanish. The remaining boundary conditions are

\[ \eta_m' - (qN/k_BT) \phi' = 0 \quad \text{and} \quad \phi(\pm d/2) = \pm V/2. \]
(59)

From Eqs. (55) and (56) it follows that \( \eta_p + \eta_m = 0 \) and

\[ \eta_p = - \frac{Nk_m}{k_d + Nk_m + i\omega \eta_m}, \]
(60)

for the spatial parts of the variations of the bulk densities of the neutral and positive particles. The remaining equations, by taking into account Eq. (60), are

\[ \eta_m' - \xi^2 \eta_m = 0 \quad \text{and} \quad \phi' = \frac{q}{\epsilon \xi} \eta_m, \]
(61)

where

\[ \xi^2 = i \frac{\omega Y}{D} + \frac{Y}{\lambda^2} + \frac{i\omega k_o N}{(i\omega + k_d + k_o N)D}, \]
(62)

and

\[ Y = \frac{i\omega + k_d + 2k_o N}{i\omega + k_d + k_o N}. \]
(63)

Equations (61) have to be solved with the boundary conditions Eqs. (59). We get

\[ \eta_m(z) = \bar{A}e^{\xi z} + \bar{B}e^{-\xi z}, \]
(64)

and

\[ \phi(z) = \frac{q}{e \xi} \bar{Y} \eta_m(z) + \bar{C}z, \]
(65)

where

\[ \bar{A} = \frac{V_0 q \xi \bar{N}/(4k_BT)}{(Y/(\xi^2)) \sinh(\xi d/2) + (d\xi/2) \cosh(\xi d/2)}. \]
(66)
\[ \bar{\mathcal{C}} = \frac{V_0 e \cosh(\xi d/2)}{(Y/(\xi \lambda^2)) \sinh(\xi d/2) + (d e/2) \cosh(\xi d/2)}, \]  

(67)

and \( \bar{\mathcal{B}} = \bar{\mathcal{A}} \), with \( \xi = \bar{\xi} - Y / \bar{\lambda}^2 \) and \( \bar{\lambda}^2 = 2\bar{\lambda}^2 \). By using these results we deduce that the impedance of the system governed by the set of Eqs. (55)–(58) is given by

\[ \bar{Z} = -\frac{2i}{\omega \epsilon \bar{S}} \frac{\xi}{\xi \lambda^2} \sinh \left( \frac{\xi d}{2} \right) + \frac{d \xi}{2}. \]  

(68)

Equation (68) generalizes the expression for the electrical impedance of an electrolytic cell to the case where the generation recombination of ions is present. It is valid in the case where \( D_e = D_p = 0 \) and \( D_m = D \). Equation (68) is a simplification of the more general one reported in Ref. 2.

From Eq. (68) by expanding at the first order on \( \omega \) the bracket we get

\[ \bar{Z} = \frac{1}{\omega \epsilon \bar{S}} (\bar{Z}^{(0)} + \bar{Z}^{(1)} \omega), \]  

(69)

where

\[ \bar{Z}_0 = 2\bar{\lambda} \sqrt{\frac{k_d + k_a N}{k_d + 2k_a N}}. \]  

(70)

and

\[ \bar{Z}_1 = \bar{\lambda} \left\{ \frac{d \bar{\lambda} + \sqrt{\frac{k_d + k_a N}{k_d + 2k_a N}}} {\frac{D k_a N}{(k_d + k_a N)(k_d + 2k_a N) - 3\bar{\lambda}^2}} \right\}. \]  

(71)

The expressions reported above for \( \bar{Z}^{(0)} \) and for \( \bar{Z}^{(1)} \) are valid in the limit of

\[ \frac{d}{2 \bar{\lambda}} \sqrt{\frac{k_d + 2k_a N}{k_d + k_a N}} \gg 1. \]  

(72)

In this case, in the limit of \( \omega \rightarrow 0 \), we get that the effective resistance of the cell, in the series representation, is given by

\[ R = \frac{\bar{\lambda}}{\varepsilon \sigma D} \left\{ \frac{d \bar{\lambda} + \sqrt{\frac{k_d + k_a N}{k_d + 2k_a N}}} {\frac{D k_a N}{(k_d + k_a N)(k_d + 2k_a N) - 3\bar{\lambda}^2}} \right\}, \]  

(73)

which defines the plateau of the real part of the impedance in the low frequency limit. In the same limit the reactance, in the series representation, is

\[ X = \frac{1}{\omega} \frac{\bar{\lambda}}{\varepsilon \sigma D} \sqrt{\frac{k_d + k_a N}{k_d + 2k_a N}}. \]  

(74)

Let us consider now the particular situation where the impurities are completely dissociated. In this case, as discussed in Sec. II, \( k_p = 0 \), that implies \( N_0 = 0 \), and the equations governing the bulk evolutions of the ionic charges are, as it follows from Eqs. (55)–(58), \( \eta_p = 0 \), \( \eta_a = 0 \), \( \phi' = (q/\epsilon) \eta_m \), and

\[ i \omega \eta_m = D (\eta_m'' - (q\bar{N}k_BT) \phi''). \]  

(75)

By substituting the expression for \( \phi'' \) into Eq. (75) we obtain

\[ i \omega \eta_m = D \left( \eta_m'' - \frac{1}{\lambda^2} \eta_m \right). \]  

(76)

where \( \bar{\lambda}^2 = 2\bar{\lambda}^2 = \varepsilon k_BT / (N\bar{q}^2) \) has been introduced above and plays the role of the effective length of Debye for the present problem. Using Eq. (76) and the relevant boundary conditions, we get that the electrical impedance of the cell in this framework is still given by Eq. (53), with \( \lambda \) substituted by \( \bar{\lambda} \). Consequently, the resistance of the cell, in the series representation, presents just one plateau ending at the frequency of Debye \( \omega_0 = D / \bar{\lambda}^2 \). In the same representation, the reactance of the cell diverges as 1/\( \omega \) in the limit of \( \omega \rightarrow 0 \), and the effective capacitance of the cell, in this limit, tends to \( \varepsilon S / (2\bar{\lambda}) \), as discussed in Ref. 27.

V. DISCUSSION

The frequency dependencies of the resistance \( R \) and reactance \( X \) of the layer, in the series representation, can be investigated by means of the formulas reported above for

![FIG. 1. Real part of the electrical impedance of the cell, \( R \), vs the frequency of the applied voltage, \( f \), for different values of \( k_p \) and \( k_a \). Black line: \( k_p = 0 \) (fully dissociated impurities); red dashed-dotted line: \( k_p = 1 \times 10^{-3} \) m/s with \( k_a = 10^{-10} \) m/s; green (olive) dashed line: \( k_p = 1 \times 10^{-20} \) m/s; green dotted line: \( k_p = 1 \times 10^{-21} \) m/s. The horizontal blue dashed-dotted lines correspond to Eq. (73). In the inset we show the limit for the low frequency part of the spectrum for the green (olive) dashed line \( k_p = 1 \times 10^{-3} \) m/s and the green dotted line \( k_p = 1 \times 10^{-21} \) m/s, to underline that they tend to different limiting values, not visible in the main figure. Note that the values of the plateaus depend on \( k_p \) since the actual bulk density of ions depends on this parameter. The case where only the negative ions are mobile is considered.](http://jcp.aip.org/abs/10.1063/1.3476478)
different values of the phenomenological constants $k_a$ and $k_d$. We limit our analysis to the case where only the negative ions are mobile. This case is of some importance in the study of the dielectric response of insulating gels or polymers to an external electric field. In fact, in these cases, the positive ions can be stuck on the polymer chains and do not contribute directly to the net electrical current in the sample. For the numerical calculation we assume that the dielectric constant of the insulating solid is $\varepsilon = 6.7 \times \varepsilon_0$, the bulk density of impurities in thermodynamic equilibrium is $N_0 = 10^{22}$ m$^{-3}$, and the diffusion coefficients are $D_p = D_n = 0$, $D_m = 8.2 \times 10^{-11}$ m$^2$s$^{-1}$. The ions are monovalent with $q = 1.6 \times 10^{-19}$ A and the temperature such that $k_B T / q = 0.025$ V. The geometrical parameters of the cell are supposed to be $d = 25$ $\mu$m and $S = 2 \times 10^{-4}$ m$^2$.

In Fig. 1 we show the real part of impedance, $R$, as a function of frequency $f = \omega / (2 \pi)$ for four sets of $k_d$ and $k_a$. The black line corresponds to the case where the impurities are fully dissociated, $k_a = 0$ m$^{-1}$s$^{-1}$ (that means $\kappa = \infty$, $\rho = 1$). In this case, the resistance presents just one plateau, as discussed at the end of the preceding section. The red dashed-dotted line corresponds to $k_d = 1$ s$^{-1}$ with $k_a = 10^{-19}$ m$^3$s$^{-1}$ (for which $\kappa = 10^{-3}$ and the dissociation ratio is $\rho = 0.031$), the green (olive) dashed line to $k_d = 1$ s$^{-1}$ with $k_a$ = $10^{-20}$ m$^3$s$^{-1}$ (corresponding to $\kappa = 10^{-2}$ and $\rho = 0.095$), and the green dotted line to $k_d = 1$ s$^{-1}$ with $k_a = 10^{-21}$ m$^3$s$^{-1}$ (corresponding to $\kappa = 10^{-1}$ and $\rho = 0.270$). Note that decreasing $k_a$ increases $N$, and hence the plateau corresponding to the resistance of the cell, in the series representation, ending at the frequency of Debye decreases too.

In Fig. 2 the imaginary part of impedance, $X$, versus $f$, is shown for the four sets of $k_d$ and $k_a$ and for the same diffusion coefficients considered in Fig. 1. From this figure it follows that the presence of the association-dissociation phenomenon does not change the shape of the spectrum. It only modifies the numerical values of the reactance in the low frequency region.

The result obtained for $k_a = 0$ on the real part of the impedance means that the plateau of $R$ in the low frequency region dependence is not visible if $D_p = 0$. However, from Sec. III we notice that the second plateau disappears in the absence of dissociation and also when $D_m = D_n$, which can be stated due to comparison of the present results with the earlier work.$^{25}$ On the other hand, this plateau appears, for example, when $D_m / D_p = 10$ as it was shown also in the absence of dissociation.$^{28}$ This indicates that the existence of the second plateau depends on the ratio $D_m / D_p$ in rather complex way.

In Fig. 3 we show the ratio between the resistance of two cells of thicknesses $d_1 = 50$ $\mu$m and $d_2 = 25$ $\mu$m, for the four sets of $k_d$ and $k_a$ considered in Fig. 1. From this figure it follows that in the absence of the association-dissociation phenomenon the values of $R$ on the plateaus are proportional to the thickness of the cell in all frequency range. On the
In our analysis the temperature has been assumed fixed, of the order of 300 °K. This quantity enters directly in the definition of the length of Debye. The influence of the temperature on the considered problem could be important because the phenomenological parameters $k_p$ and $k_d$ are expected to depend strongly on it as discussed in Ref. 2.

The set of Eqs. (4)–(7) with the boundary conditions (8)–(11) was solved numerically. The results confirmed the existence of two plateaus in the presence of dissociation and recombination processes. The low frequency plateau appeared in the case of immobile positive ions; however it did not occur if all the ions had the same diffusion constants. No low frequency plateau was found in the absence of dissociation and association phenomena.

By means of the free LEVM complex nonlinear least squares fitting program,29 circuit H includes the full Ross Macdonald–Franceschetti fitting model and can be used to either generate results at any or all immittance levels or to fit relevant data. It could be used to generate and check all the plot results reported in our paper.30

VI. CONCLUSIONS

We have investigated the role of the generation-recombination phenomenon on the frequency dependence of the electrical impedance of a cell of an insulating solid containing ions, in the shape of a slab. The ionic generation from neutral impurities and their recombination is modeled as a chemical reaction of the first kind. According to our results, the generation-recombination phenomenon can be respon-

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**FIG. 4.** Parametric plot of $X$ vs $R$ for different values of $k_d$ and $k_o$. Black line: $k_o=0$ (fully dissociated impurities); red dashed-dotted line: $k_d=1$ s$^{-1}$ with $k_o=10^{-19}$ m$^3$ s$^{-1}$; green (olive) dashed line: $k_d=1$ s$^{-1}$ with $k_o=10^{-20}$ m$^3$ s$^{-1}$; green dotted line: $k_d=1$ s$^{-1}$ with $k_o=10^{-21}$ m$^3$ s$^{-1}$. In the inset we show the limit for the low frequency part of the spectrum for the green (olive) dashed line $k_d=1$ s$^{-1}$ with $k_o=10^{-20}$ m$^3$ s$^{-1}$ and the green dotted line $k_d=1$ s$^{-1}$ with $k_o=10^{-21}$ m$^3$ s$^{-1}$, to underline that they tend to different limiting values, not visible in the main figure. The case where only the negative ions are mobile is considered.

**FIG. 5.** $\varepsilon'/\varepsilon_0$ vs $f$ for different values of $k_d$ and $k_o$. Black line: $k_o=0$ (fully dissociated impurities); red dashed-dotted line: $k_d=1$ s$^{-1}$ with $k_o=10^{-19}$ m$^3$ s$^{-1}$; green (olive) dashed line: $k_d=1$ s$^{-1}$ with $k_o=10^{-20}$ m$^3$ s$^{-1}$; green dotted line: $k_d=1$ s$^{-1}$ with $k_o=10^{-21}$ m$^3$ s$^{-1}$. In the limit of $f\rightarrow 0$, $\varepsilon'\rightarrow \varepsilon_0(2\varepsilon)/(\varepsilon_0+2k_oN)/(k_d+k_oN)$, where the effective length of the Debye depends on the generation and dissociation coefficients via $N$. The case where only the negative ions are mobile is considered.
positive ions and the neutral impurities generating the ions for decomposition are stuck on the polymeric chains. This is considered possible of a new plateau for the real part of the electrical impedance of the cell in the dc limit. Our results can be of some importance in the analysis of the electrical properties of gels, where the positive ions and the neutral impurities generating the ions for decomposition are stuck on the polymeric chains.

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23 All the works of J. Ross Macdonald are accessible, in pdf format, at http://jrossmacdonald.com.
40 J. Ross Macdonald, private communication (2010).