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Theory of small-signal ac response of a dielectric liquid containing two groups of ions

G. Barbero,¹ F. Batalioto,^{2,a)} and A. M. Figueiredo Neto²

¹*Dipartimento di Fisica and CNISM, Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129 Torino, Italy*

²*Instituto de Física, Universidade de São Paulo P.O. Box 66318, São Paulo 05315-970, Brazil*

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The analysis of Macdonald for electrolytes is generalized to the case in which two groups of ions are present. We assume that the electrolyte can be considered as a dispersion of ions in a dielectric liquid, and that the ionic recombination can be neglected. We present the differential equations governing the ionic redistribution when the liquid is subjected to an external electric field, describing the simultaneous diffusion of the two groups of ions in the presence of their own space charge fields. We investigate the influence of the ions on the impedance spectroscopy of an electrolytic cell. In the analysis, we assume that each group of ions have equal mobility, the electrodes perfectly block and that the adsorption phenomena can be neglected. In this framework, it is shown that the real part of the electrical impedance of the cell has a frequency dependence presenting two plateaux, related to a type of ambipolar and free diffusion coefficients. The importance of the considered problem on the ionic characterization performed by means of the impedance spectroscopy technique was discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908044]

The fundamental equations describing the redistribution of the ions dissolved in a dielectric liquid subjected to an external electric field have been discussed long ago by Macdonald.¹ These equations determine the time evolution of the local bulk density of ions generated by decomposition of impurities present in the liquid, taking into account the recombination phenomenon, when the sample is subjected to an external field. The actual electric field in the liquid is deduced by solving the equation of Poisson, relating the divergence of the electric field to the net electrical charge of ionic origin. The equations of Macdonald have been written for the general case, where the mobility of the positive ions is different from that of the negative ions. However, all the ions of a given sign are considered identical. The equations of Macdonald have been used to analyze several situations of practical interest, with different boundary conditions on the electrodes.^{2–6} In particular, these equations have been used to investigate the impedance spectroscopy of an electrolytic cell,⁷ where the exact solution for the small-signal ac response, in the continuum approximation, of an electrolytic cell with blocking electrodes has been presented. The analysis presented in Ref. 7 is valid for arbitrary mobilities, arbitrary valence numbers, and any degree of charge dissociation. More recently, simple versions of the equations of Macdonald, relevant to the case in which the impurities dissolved in the liquid are completely dissociated, have been discussed for several cases.^{6–14} Our goal now is to generalize the analysis of Macdonald to the case in which the dielectric liquid contains two groups of ions. Very detailed treatments of two carrier systems exist in the liquid and solid electrochemistry.^{15–17} However, we are convinced that the reanalysis of the problem, focused on the similarities and differences between the impedance of a liquid containing one or two groups of ions, can be of some importance since the

impedance spectroscopy is used to determine the ionic density in liquid crystal.^{18–20} In this case, the number of groups of ions dissolved in the liquid crystal, as well as their mobility, are unknown. Consequently, to extract information from the impedance spectra is not a trivial task, as we will see in the following. For a general review on the impedance spectroscopy technique, see Ref. 21. We assume that the ions of both groups are monovalent of charge q , are dimensionless, that they are not adsorbed by the electrodes, and that the recombination-dissociation phenomenon can be neglected. Furthermore, we assume that in each group, the positive and the negative ions have the same mobility and that the electrodes perfectly block. Blocking electrodes means that there is no charge injection into the liquid and, therefore, the charge in the sample is constant in time. Before the application of the external voltage, the ions are randomly distributed in the sample with densities N_1 and N_2 , where 1 and 2 are used to distinguish each group. In this situation of thermodynamical equilibrium, the liquid is locally and globally neutral. However, as an external voltage is applied, the ions are redistributed in the sample and the liquid remains globally neutral but becomes locally charged. We consider a sample in the shape of a slab of thickness d and surface area S . The Cartesian reference frame used in the description has the z axis perpendicular to the bounding surfaces, coinciding with the electrodes, at $z = \pm d/2$. Let $n_{p1}(z, t)$, $n_{p2}(z, t)$, $n_{m1}(z, t)$, and $n_{m2}(z, t)$ be the densities of positive (p) and negative (m) ions of groups 1 and 2. We indicate by $\lambda = \sqrt{\epsilon k_B T / [2(N_1 + N_2)q^2]}$ the Debye length of the liquid containing ions. The fundamental equations of the problem under investigation are the equations of continuity

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

where $J_{lk}(z, t)$ are the densities of current of ions of charge l and group k , and the Poisson equation

^{a)}Electronic mail: fbata@if.usp.br.

$$\frac{\partial^2 V(z,t)}{\partial z^2} = -\frac{q}{\epsilon} [n_{p1}(z,t) + n_{p2}(z,t) - n_{m1}(z,t) - n_{m2}(z,t)], \quad (2)$$

as discussed in Ref. 22 In Eq. (1) $J_{lk}(z,t)$ are given by⁹

$$J_{lk}(z,t) = -D_k \left[\frac{\partial n_{lk}(z,t)}{\partial z} \pm \frac{qN_k}{kT} \frac{\partial V(z,t)}{\partial z} \right], \quad (3)$$

where the first term in the bracket is the diffusion current and the second is the drift current. The plus sign of the drift current term holds for $l=p$ whereas the minus sign refers to $l=m$.⁹ This regime is valid for small applied potential $V(z,t)$, in which $n_{lk} \sim N_k$ (Refs. 23 and 24). Equations (1) and (2) have to be solved with the boundary conditions

$$J_{lk}(\pm d/2,t) = -D_k \left(\frac{\partial n_{lk}}{\partial z} \pm \frac{qN_k}{K_B T} \frac{\partial V}{\partial z} \right) = 0$$

$$V(\pm d/2,t) = \pm \frac{V_0}{2} e^{i\omega t}, \quad (4)$$

related to the hypothesis of blocking electrodes and to the presence of the external power supply, respectively. The solution of Eqs. (1) and (2) with the boundary conditions (4) can be easily obtained. The electrical impedance of the sample is defined as $Z=V/I$, where $I=d\Sigma(t)/dt$ is the electrical current and $\Sigma(t)$ is the surface electric charge on one electrode, given by $\Sigma(t)=-\epsilon E(d/2,t)$. The impedance Z can be analytically obtained although its expression is very long. From this, we obtain its real and imaginary part. Let us consider the limit of $\omega \rightarrow 0$ in the special case in which $N_1=N_2=N$. We get $R=\lambda^2 d/(2D_{II}\epsilon)$ and $\chi=-\sqrt{2}\lambda(S\epsilon\omega)$, where $D_{II}=2D_1D_2/(D_1+D_2)$. These relations are valid in the limit $\lambda \ll d$, as assumed. From this result, we conclude that the diffusion of two groups of ions, with $N_1=N_2$, in the presence of an external field is similar to the ambipolar diffusion. As discussed in Ref. 22, the ambipolar diffusion, when there is just one group of ions, is the simultaneous diffusion of positive and negative ions in the presence of their own charge fields. In that case, by indicating as D_p and D_m the diffusion coefficients of the positive and negative ions, in the low frequency range the effective diffusion coefficient, responsible for the electrical resistance of the cell, is $D_a=2D_pD_m/(D_p+D_m)$. The analysis reported above shows that in the case in which two types of ions are present, with $N_1=N_2$, the effective diffusion coefficient is D_{II} . The physical mechanism responsible for D_{II} is the same for D_a . If $D_1=D_2=D$, we again obtain the results reported in Ref. 9. To perform numerical simulations, let us consider a water solution of two groups of ions of concentration $N_1=N_2=6.02 \times 10^{23} \text{ m}^{-3}$, which means $10^{-3}M$. We assume $S=2 \times 10^{-4} \text{ m}^2$ and $d=1 \text{ mm}$, with $\epsilon=78.5\epsilon_0$, where ϵ_0 is the dielectric permittivity of free space. In Fig. 1, we show the real part $R(\omega)$ of $Z(\omega)$ as a function of the angular frequency ω of the applied voltage for various values of D_1/D_2 , in which we have used $D_2=1 \times 10^{-9} \text{ m}^2/\text{s}$, typical diffusion constant of ions in water.²² As we can see, the curves present the usual behavior in which $R(\omega) \rightarrow 0$ in the limit of $\omega \rightarrow \infty$, and a plateau in the lower frequency range that we designate by I. However, in the limit of $\omega \rightarrow 0$, we have an additional plateau, that we call region II in the figure. The gap between the magnitudes of these two frequency range depends on the

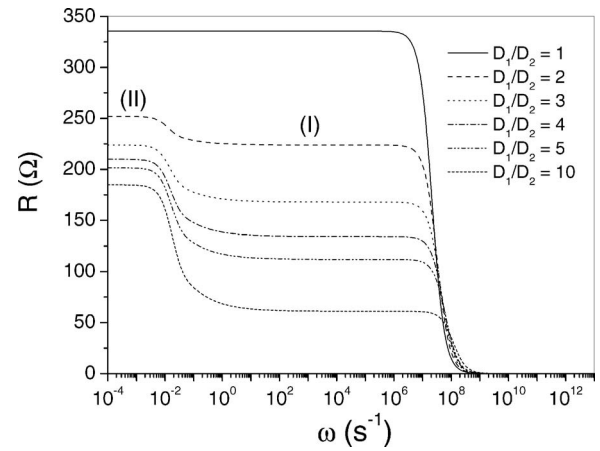


FIG. 1. $R=R(\omega)$ for various values of D_1/D_2 and $N_1=N_2$.

difference of D_1 and D_2 . In the particular case where $D_1/D_2=1$, $R(\omega)$ is the same in both frequency range. This result is similar to the one reported in Ref. 9 for the case of a system of only one group of ions. In the Fig. 2, we present the imaginary part $\chi(\omega)$ of the impedance Z as a function of the angular frequency ω for the same values of the ratio D_1/D_2 , as those in Fig. 1. All the curves tend to $-\infty$ for $\omega \rightarrow 0$. In this limit, the divergence of $\chi(\omega)$ is independent of the values of the diffusion coefficients. In the opposite limit of $\omega \rightarrow \infty$, $\chi(\omega) \rightarrow 0$ from the negative side, independent again of the values of the diffusion coefficients. Between these two limits, there exist a local minimum which depends on the ratio D_1/D_2 . The presence of two plateaus in the real part of the impedance have already been predicted in Ref. 12. In that work, however, this trend in $R(\omega)$ is due to the difference of the ionic mobilities of the positive and negative ions. In our case, this behavior is due to the difference of the ionic mobilities of the groups 1 and 2. Actually, as a result of this difference, the system behaves, in the case where $N_1=N_2$, as all the ions have an effective diffusion constant $D_I=(1/2)(D_1+D_2)$ in region I and $D_{II}=2D_1D_2/(D_1+D_2)$ in the region II.²⁵ In Fig. 3 we show the real part R of the impedance Z as a function of the angular frequency ω for $D_1/D_2=5$ (solid line) and for the effective diffusion constants $D_I=(1/2)(D_1+D_2)$ (dashed line) and $D_{II}=2D_1D_2/(D_1+D_2)$ (dotted line). As we can see, in the limit of $\omega \rightarrow 0$, $R(\omega) \rightarrow R_{II}(\omega)$ while in the higher frequency region $R(\omega) \rightarrow R_I(\omega)$. In Figs. 1 and 2, we presented

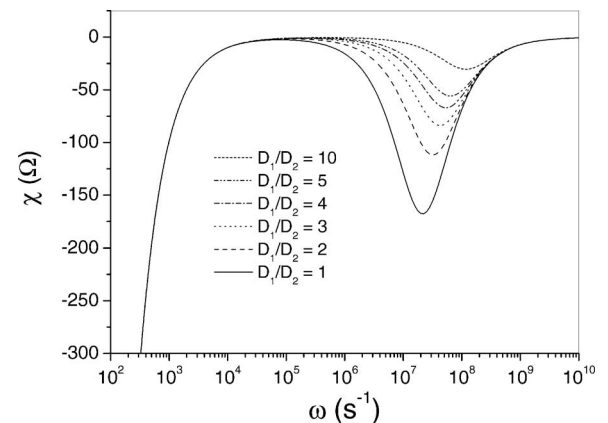


FIG. 2. $\chi=\chi(\omega)$ for various values of D_1/D_2 and $N_1=N_2$.

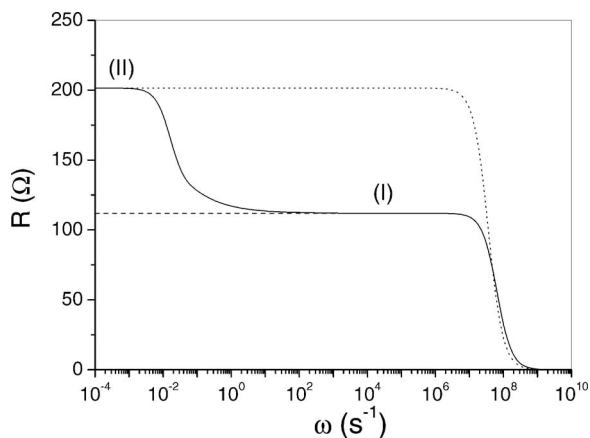


FIG. 3. $R=R(\omega)$ for $D_1/D_2=5$ and $N_2=N_1$ compared to R calculated with the effective diffusion constants $D_I=1/2(D_1+D_2)$ (dashed line) and $D_{II}=2D_1D_2/(D_1+D_2)$ (dotted line).

the results relevant to $R(\omega)$ and $\chi(\omega)$ when $N_1=N_2=N$, for several D_1/D_2 . In the case in which $N_1 \neq N_2$, the effective diffusion coefficients D_{II} and D_I are given by the general equations

$$\frac{1}{D_{II}} = \frac{N_1}{N_1 + N_2} \frac{1}{D_1} + \frac{N_2}{N_1 + N_2} \frac{1}{D_2}, \quad (5)$$

i.e., it is the weighted harmonic average of D_1 and D_2 . In the other plateau, it corresponds to the free diffusion of the two groups of ions,¹³ the effective diffusion coefficient responsible for the ionic conduction is

$$D_I = \frac{N_1}{N_1 + N_2} D_1 + \frac{N_2}{N_1 + N_2} D_2, \quad (6)$$

i.e., it is the weighted arithmetical average of D_1 and D_2 . From the definition of D_I and D_{II} , it follows that $D_I > D_{II}$. From our analysis, it follows that the impedance spectra of a system that are composed only by one group of ions of density $2N$ and diffusion constants D_p and D_m are identical to the impedance spectra of a system composed by two groups of ions, 1 and 2 of densities $N_1=N$ and $N_2=N$ and diffusion constants $D_1=D_m$ (or $=D_p$) and $D_2=D_p$ (or $=D_m$). A numerical calculation shows that a large difference in the densities N_1 and N_2 could result in a very small change in the magnitude of the impedance spectra, depending on the difference of the diffusion constants. For example, if we maintain $N_1+N_2 \equiv cte$, in a system in which $D_1/D_2=10$, a variation of about 10% in N_1 and in N_2 causes a maximum variation of about 13% in the magnitude of the real and imaginary parts of the impedance. However, for a system in which the diffusion constants D_1 and D_2 are much closer, say $D_1/D_2=1.1$, a variation of 50% in N_1 and N_2 causes a maximum variation of about only 2% in the magnitude of the real and imaginary parts of the impedance. The value of D_2 used in this calculation was the same used in the simulations shown in the various figures in this work. This result is of some importance because the values of the ratio D_1/D_2 are in the range presented by actual systems.²²

In summary, we have generalized the analysis of Macdonald for electrolytes for the case in which two groups of ions are present. We assumed that (1) the electrolyte can be considered as a dispersion of ions in a dielectric liquid, (2) the ionic recombination can be neglected, (3) each group of ions have equal mobility, (4) the electrodes are perfectly blocking, and (5) the adsorption phenomena can be neglected. From the investigation reported above, it follows that the real part of the electrical impedance of the cell has a frequency dependence presenting two plateaux, related to a type of ambipolar and free diffusion coefficients. According to our analysis, the impedance spectroscopy technique can give useful information on the dielectric properties of an insulating liquid containing ions only if one group of positive and negative ions is present in it.¹³ In the opposite case, where several groups of positive and negative ions are dissolved in liquid, the impedance spectroscopy alone does not allow a complete characterization of the ions,^{18–20} because the sensitivity of this technique decreases very much as the diffusion constants of the two groups of ions involved are numerically close.

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