



Electric response of cells containing ferrofluid particles

A.M. Antonova^{a,b,c}, G. Barbero^{a,b,*}, F. Batalioto^d, A.M. Figueiredo Neto^d, K. Parekh^e

^a Dipartimento di Scienza Applicata Del Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129, Torino, Italy

^b National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, 115409, Moscow, Russian Federation

^c Scientific Research Institute of System Analysis of the Russian Academy of Sciences, Nakhimovsky Avenue 36, 1, Moscow, 117218, Russia

^d Instituto de Física, Universidade de São Paulo, P.O. Box 66318, São Paulo, 05389-970, SP, Brazil

^e Dr. K C Patel R & D Centre, Charotar University of Science & Technology, Changa, 388 421, Dist. Anand, Gujarat, India

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ABSTRACT

The Poisson-Nernst-Planck model for electrolytic solutions is generalized to take into account the difference in the diffusion coefficients and in the electric charge of the ions dissolved in an insulating liquid. The electric impedance of the cell is evaluated by considering the case in which the electric charge transfer from the cell to the external circuit is proportional to the surface electric field. An analytical expression for the electric impedance of the cell is derived. The model is used to interpret experimental data relevant to cell of kerosene doped with ferrofluid particles. We show that the impedance spectroscopy data can be well interpreted by the proposed model. An estimation of the electric conductivity of the system kerosene based ferrofluid is reported and compared with the value obtained by means of the analysis based on equivalent electric circuits. A few considerations on the applicability of Debye's model with a dc conductivity to our data are reported.

1. Introduction

The role of the ions on the electric response of an electrolytic cell to an external stimulus is usually described by means of the Poisson-Nernst-Planck model based on the continuity of the positive and negative ions, and on the equation of Poisson for the actual electric potential across the sample for the bulk [1,2]. The boundary conditions by means of which the bulk equations have to be solved depend on the properties of the electrodes of the cell. In the simple case where the electrodes are blocking, the current densities of the two type of ions vanish on the electrodes. Other boundary conditions have been proposed. In the Ohmic boundary conditions the transfer of electric charge from the cell to the external circuit is assumed to be proportional to the surface electric field [3]. These boundary conditions are equivalent to Chang-Jaffe boundary conditions [4] where the same quantity is assumed to be proportional to the surface variation of the bulk density of ions with respect to the value corresponding to the thermodynamical equilibrium [5]. Very often it is assumed that there is not an exchange of electric charge from the bulk to the external circuit, but that the ions are adsorbed at the electrodes [6]. In this case, the surface current density is considered responsible for the time variation of the surface density of adsorbed ions. Very often the bulk partial differential equations are solved, in the linear limit, assuming that the diffusion coefficients of the positive and negative ions are identical,

or that the electric charge of the two ions are equal [7,8]. Another simplifying assumption is that the phenomenological parameters describing the electrodes properties are the same for the two type of ions [9]. In our manuscript we remove these simplifying hypotheses, and derive analytical expressions for the electric impedance of the cell for Ohmic boundary conditions. We will use our model to analyse the impedance spectroscopy data relevant to cells of kerosene containing particles of ferrofluid [10], and show that the theoretical predictions are in good agreement with the experimental data. A value for the conductivity of the kerosene+ferrofluid is derived.

Our paper is organized as follows. The bulk equations are presented in Sect.II, and the one dimensional problem discussed in Sect.III. The linear approximation is considered in Sect.IV, and the case in which the applied voltage is harmonic analysed in Sect.V. The electric impedance of the sample is determined in Sect.VI. The boundary conditions used in the mathematical description of non-blocking electrode are presented in Sect.VII. The experimental set up and the experimental data are reported in Sect.VII, where the fit of the data is done by means of our model. In Sect.IX we discuss the model of Debye for a medium with a dc conductivity. In that section we show that a good fit of the experimental data could be obtained also with this model, but that the interpretation of the conductivity is far from being evident. The conclusions of the paper are reported in Sect.X.

* Corresponding author. Dipartimento di Scienza Applicata del Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy.

E-mail address: giovanni.barbero@polito.it (G. Barbero).

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2. Bulk equations

The influence of the ions on the electric response of a cell is investigated by means of the Poisson-Nernst-Planck model, based on the equations of continuity for the positive and negative ions and on the equation of Poisson for the actual potential across the cell [11]. We indicate by n_p , n_m , q_p , q_m , and D_p and D_m the bulk densities, electric charges and diffusion coefficients of the positive and negative ions, respectively. The dielectric constant of the medium in which the ions are dispersed is indicated by ε and assumed not dispersive in the region experimentally explored. The actual potential in the cell is V responsible for the electric field, in the range of frequency considered, $\mathbf{E} = -\nabla V$. The equations of continuity and the equation of Poisson are

$$\frac{\partial n_p}{\partial t} = -\nabla \cdot \mathbf{j}_p, \quad (1)$$

$$\frac{\partial n_m}{\partial t} = -\nabla \cdot \mathbf{j}_m, \quad (2)$$

and

$$\nabla \cdot \mathbf{E} = \frac{1}{\varepsilon} (n_p q_p - n_m q_m), \quad (3)$$

where the current densities are given by

$$\mathbf{j}_p = -D_p \left(\nabla n_p - \frac{q_p n_p}{K_B T} \mathbf{E} \right), \quad (4)$$

$$\mathbf{j}_m = -D_m \left(\nabla n_m + \frac{q_m n_m}{K_B T} \mathbf{E} \right), \quad (5)$$

valid in the Einstein-Smoluchowski approximation [12]. Generalizations of Eq.(1) and (2) to the case in which the diffusion is anomalous have been considered by several authors [13–20], and recently critically analysed by Evangelista and Lenzi [21]. However, in the following, we limit the analysis to the case of normal diffusion, since in our case this extension of the model seems not necessary.

3. One dimensional problem

We consider the case where the cell is in the shape of a slab, of thickness d , and problem 1-dimensional [22,23]. The cartesian reference frame used for the description has the z -axis normal to the electrodes, coinciding with the surfaces limiting the cell, located at $z = \pm d/2$. In this framework, Eqs. (1)–(3) are equivalent to

$$\frac{\partial n_p}{\partial t} = D_p \frac{\partial}{\partial z} \left(\frac{\partial n_p}{\partial z} + \frac{q_p n_p}{K_B T} \frac{\partial V}{\partial z} \right), \quad (6)$$

$$\frac{\partial n_m}{\partial t} = D_m \frac{\partial}{\partial z} \left(\frac{\partial n_m}{\partial z} - \frac{q_m n_m}{K_B T} \frac{\partial V}{\partial z} \right), \quad (7)$$

and

$$\frac{\partial^2 V}{\partial z^2} = -\frac{1}{\varepsilon} (q_p n_p - q_m n_m). \quad (8)$$

In this case, the current densities have only z -component and are given by

$$j_p = -D_p \left(\frac{\partial n_p}{\partial z} + \frac{q_p n_p}{K_B T} \frac{\partial V}{\partial z} \right), \quad (9)$$

$$j_m = -D_m \left(\frac{\partial n_m}{\partial z} - \frac{q_m n_m}{K_B T} \frac{\partial V}{\partial z} \right). \quad (10)$$

In the absence of external field the sample is supposed locally neutral,

with a bulk density of positive and negative ions equal to n_{p0} and n_{m0} . The presence of the external field is responsible for a bulk variation of the ionic density. The sample remains globally neutral, but the actual bulk densities n_p and n_m differ from n_{p0} and n_{m0} . We indicate by

$$n_p(z, t) = n_{p0} + \delta n_p(z, t), \quad n_m(z, t) = n_{m0} + \delta n_m(z, t), \quad (11)$$

where δn_p and δn_m are the density bulk variations induced by the external electric field. The ionic charges are written as $q_p = eZ_p$, $q_m = eZ_m$, where e is the electronic charge ($e = 1.6 \times 10^{-19}$ A.s), and $Z_{p,m}$ integer numbers. We define the dimensionless quantities

$$u_p(z, t) = \delta n_p(z, t)/n_{p0}, \quad u_m(z, t) = \delta n_m(z, t)/n_{m0}, \quad (12)$$

$$u_v(z, t) = eV(z, t)/K_B T,$$

to characterize the state perturbed by the external field. Since the system was initially assumed locally neutral we have the condition $q_p n_{p0} = q_m n_{m0}$, that implies $Z_p n_{p0} = Z_m n_{m0}$ [24]. The net charge appearing in Poisson's equation is $n_p q_p - n_m q_m = eZ_p n_{p0} (u_p - u_m)$.

4. Linear approximation

We limit our analysis to the linear case, corresponding to the situation in which $\delta n_p \ll n_{p0}$, $\delta n_m \ll n_{m0}$ [25]. In this frame work the bulk partial differential equation of the problem are

$$\frac{\partial u_p}{\partial t} = D_p \left(\frac{\partial^2 u_p}{\partial z^2} + Z_p \frac{\partial^2 u_v}{\partial z^2} \right), \quad (13)$$

$$\frac{\partial u_m}{\partial t} = D_m \left(\frac{\partial^2 u_m}{\partial z^2} - Z_m \frac{\partial^2 u_v}{\partial z^2} \right), \quad (14)$$

and

$$\frac{\partial u_v}{\partial z^2} = -\frac{1}{2\lambda^2} (u_p - u_m), \quad (15)$$

where $\lambda = \sqrt{\varepsilon K_B T / (2n_{p0} Z_p e^2)}$, is the length of Debye [25]. We put

$$D_p = \frac{D}{1 - \Delta}, \quad D_m = \frac{D}{1 + \Delta}, \quad (16)$$

from which it follows that

$$\Delta = \frac{D_p - D_m}{D_p + D_m}, \quad D = 2 \frac{D_p D_m}{D_p + D_m}. \quad (17)$$

The quantity Δ is related to the difference between the diffusion coefficients, whereas D coincides with the ambipolar diffusion coefficient [26]. We use dimensionless coordinates defined by

$$x = z/\lambda, \quad t_u = \lambda^2/D, \quad \tau = t/t_u \quad (18)$$

where $\omega_D = D/\lambda^2 = 1/t_u$ is related to Debye's frequency. In terms of these parameters and dimensionless coordinates bulk partial differential equations (13)–(15) are

$$(1 - \Delta) \frac{\partial u_p}{\partial \tau} = \frac{\partial^2 u_p}{\partial x^2} + Z_p \frac{\partial^2 u_v}{\partial x^2}, \quad (19)$$

$$(1 + \Delta) \frac{\partial u_m}{\partial \tau} = \frac{\partial^2 u_m}{\partial x^2} - Z_m \frac{\partial^2 u_v}{\partial x^2}, \quad (20)$$

and

$$\frac{\partial^2 u_v}{\partial x^2} = -\frac{1}{2} (u_p - u_m). \quad (21)$$

5. Harmonic excitation

Let us consider the case where the applied potential is an harmonic function of time, of amplitude V_0 and circular frequency ω

$$\Delta V(t) = V\left(\frac{d}{2}, t\right) - V\left(-\frac{d}{2}, t\right) = V_0 \exp(i\omega t) = V_0 \exp(i\Omega \tau), \quad (22)$$

where $\Omega = \omega/\omega_D$. This case is important for practical application because in the electrochemical impedance spectroscopy the electric response of the cell is investigated versus the frequency of the applied difference of potential [1,2]. In the linear case under consideration Eqs. (19)–(21) have constant coefficients. Consequently the solutions we are looking for are also harmonic function of time of the type

$$(u_p, u_m, u_v)(x, \tau) = (p, m, v)(x) \exp(i\Omega \tau). \quad (23)$$

Substituting ansatz (23) into Eqs. (19)–(21) we get

$$i(1 - \Delta)\Omega p = p'' + Z_p v'', \quad (24)$$

$$i(1 + \Delta)\Omega m = m'' - Z_m v'', \quad (25)$$

and

$$v'' = -\frac{1}{2}(p - m). \quad (26)$$

A simple calculation gives for p and m the system of ordinary differential equations

$$p'' - \left(i\Omega(1 - \Delta) + \frac{1}{2}Z_p\right)p + \frac{1}{2}Z_p m = 0, \quad (27)$$

$$m'' - \left(i\Omega(1 + \Delta) + \frac{1}{2}Z_m\right)m + \frac{1}{2}Z_m p = 0. \quad (28)$$

Since the electrodes are assumed identical, $p(x)$ and $m(x)$ are expected to be odd function of x , as well as $v(x)$. We look for a solution of the type

$$p(x) = C_p \sinh(\mu x), \quad m(x) = C_m \sinh(\mu x), \quad (29)$$

where C_p and C_m are integration constants to be determined by means of the boundary conditions. Substituting (29) into (27,28) we obtain

$$\left[\mu^2 - \left(\frac{1}{2}Z_p + i\Omega(1 - \Delta)\right)\right]C_p + \frac{1}{2}Z_p C_m = 0, \quad (30)$$

$$\frac{1}{2}Z_m C_p + \left[\mu^2 - \left(\frac{1}{2}Z_m + i\Omega(1 + \Delta)\right)\right]C_m = 0. \quad (31)$$

The homogeneous system formed by Eqs. (30) and (31) has a nontrivial solution only if

$$\begin{aligned} \mu^4 - \left[\frac{1}{2}(Z_p + Z_m) + i2\Omega\right]\mu^2 \\ + i\frac{\Omega}{2}(Z_p(1 + \Delta) + Z_m(1 - \Delta)) - \Omega^2(1 - \Delta^2) = 0, \end{aligned} \quad (32)$$

from which the possible wave vectors are found to be

$$\begin{aligned} \mu_{a,b}^2 = \frac{1}{2} \left\{ \left(\frac{Z_p + Z_m}{2} + 2i\Omega \right) \right. \\ \left. \pm \sqrt{\left(\frac{Z_p + Z_m}{2} \right)^2 - 2i\Omega(Z_p - Z_m)\Delta - (2\Delta\Omega)^2} \right\} \end{aligned} \quad (33)$$

As it follows from (30)

$$\frac{C_m}{C_p} = -\frac{2}{Z_p} \left(\mu^2 - \frac{i2\Omega(1 - \Delta) + Z_p}{2} \right). \quad (34)$$

Consequently, indicating by

$$k_{a,b} = -\frac{2}{Z_p} \left(\mu_{a,b}^2 - \frac{i2\Omega(1 - \Delta) + Z_p}{2} \right), \quad (35)$$

we get for the profiles of the bulk densities of ions the expressions

$$p(x) = C_{pa} \sinh(\mu_a x) + C_{pb} \sinh(\mu_b x), \quad (36)$$

$$m(x) = k_a C_{pa} \sinh(\mu_a x) + k_b C_{pb} \sinh(\mu_b x). \quad (37)$$

It follows that the potential profile is given by

$$v(x) = -\frac{1}{2} \left\{ \frac{1 - k_a}{\mu_a^2} C_{pa} \sinh(\mu_a x) + \frac{1 - k_b}{\mu_b^2} C_{pb} \sinh(\mu_b x) \right\} \quad (38)$$

where C_v is another integration constant to be determined by the boundary conditions.

6. Electric impedance of the cell

The total electric current across the cell is

$$j = q_p j_p - q_m j_m + \varepsilon \frac{\partial E}{\partial t}, \quad (39)$$

where the two first contributions are related to the conduction currents, and the last to the displacement current. Taking into account the expressions for j_p, j_m given by (9,10) we obtain

$$j = -j_0 \left\{ \frac{p'}{1 - \Delta} - \frac{m'}{1 + \Delta} + v' \frac{Z_p + Z_m + (Z_p - Z_m)\Delta + 2i\Omega(1 - \Delta^2)}{1 - \Delta^2} \right\} e^{i\Omega \tau}, \quad (40)$$

where $j_0 = eDZ_p n_{p0}/\lambda$, and using the analysis reported above we get, finally,

$$j = j_0 \frac{Z_p + Z_m + (Z_p - Z_m)\Delta + 2i\Omega(1 - \Delta^2)}{1 - \Delta^2} C_v e^{i\Omega \tau}. \quad (41)$$

Expression (41) indicates that the total electric current density depends only on C_v , and it is position independent, as expected [27,28]. The electric impedance of the cell defined by $Z = \Delta V(t)/(jS)$, where S is the surface area of the electrodes, is

$$Z = 2R_u \frac{v_0(1 - \Delta^2)}{[Z_p + Z_m + (Z_p - Z_m)\Delta + 2i\Omega(1 - \Delta^2)]C_v} \quad (42)$$

where $v_0 = qV_0/(K_B T)$ and $R_u = \lambda^3/(\varepsilon DS)$ an intrinsic resistance related to the surface layer where the ions are confined.

In the analysis reported above the integration constants present in the profiles of bulk densities of ions and electric potential, C_{pa} , C_{pb} and C_v have to be determined by the boundary conditions related to the presence of the external power supply and to the surface values of the current densities. According to Eq. (42) the impedance of the cell depends just on the integration constant C_v , related to the linear dependence of the potential on x . In the following we will consider two typical examples of boundary conditions for the surface density of currents, known as Ohmic and adsorbing.

7. Ohmic boundary conditions

In the Ohmic model the boundary conditions on the surface current densities are, at $z = d/2$,

$$j_p = \kappa_p E, \quad j_m = -\kappa_m E, \quad (43)$$

where κ_p and κ_m are phenomenological parameters by means of which we describe the electrode [3]. We define the dimensionless parameters

$$\delta = \frac{\kappa_p - \kappa_m}{\kappa_p + \kappa_m}, \quad \kappa = \frac{\kappa_p + \kappa_m}{2}, \quad (44)$$

connected with the anisotropy and the average of κ_p and κ_m , and

$$\kappa_c = \varepsilon \omega_D / (2e), \quad h = \kappa / \kappa_c. \quad (45)$$

The quantity κ_c is an intrinsic Ohmic parameter defined in terms of bulk quantities, and h is the Ohmic parameter expressed in terms of κ_c [28]. In terms of these phenomenological parameters the boundary conditions of the problem on the surface densities of current are,

$$p' + Z_p[1 - (1 - \Delta)(1 + \delta)h]v' = 0, \quad (46)$$

$$m' - Z_m[1 - (1 + \Delta)(1 - \delta)h]v' = 0, \quad (47)$$

beside the condition $v = v_0$ for $z = d/2$, related to the presence of the power supply.

Substituting expressions (36,37) and (38) into boundary conditions (46,47) and $v = v_0$ for $z = d/2$ a simple calculation allows the determination of C_{pa} , C_{pb} and C_v , and hence, by means of (42), of the electric impedance of the cell.

8. Experimental data

8.1. Chemical

All chemicals, including precursors: iron (III) chloride (FeCl₃ 6H₂O), Manganese (II) chloride (MnCl₂ 4H₂O), Zinc (II) chloride (ZnCl₂), sodium oleate (CH₃(CH₂)₇CH = CH(CH₂)₇COONa, ≥ 82%), oleic acid (C₁₈H₃₄O₂, 99%), 1-octadecene (CH₃(CH₂)₁₅CH = CH₂, 90%), ethanol, ethyl acetate, hexane and kerosene were purchased from Sigma-Aldrich. The chemicals were used as received without any further purification.

8.2. Synthesis of MZS fluid in kerosene

In the present work, the syntheses of MZS particles were carried out under oxygen-free conditions in four-neck round bottom reactor flask. In a typical synthesis, 10.8 g, (10 mM) of FeCl₃ 6H₂O, 1.9791 g of MnCl₂ 4H₂O, 1.3628 g of ZnCl₂ and 36.5 g, (40 mM) of sodium oleate were dissolved in solvent composed of 80 mL ethanol, 60 mL distilled water and 140 mL of hexane into a 500 mL four-neck flask. The reaction mixture was mechanically stirred at room temperature (RT) for at least 30 min before heating. The temperature continued to be increased to 70 °C and kept at that temperature for 4 h. On completion, the upper organic layer was removed and the iron-oleate complex was washed three times with 30 mL distilled water in a separating funnel. After washing, the remaining amount of hexane was evaporated off resulting in iron-oleate complex in a waxy solid form. This metal-oleate complex is then mixed with 6 mM of oleic acid and 200 g of 1-octadecene at room temperature. The reaction mixture was then heated to 120 °C with the heating rate of 3 °C/min, and was kept at this temperature for 30 min. Then, reaction solution was ramped with a heating rate of about 3 °C/min to a desired reflux temperature ca. 320 °C and maintained the reflux temperature for 30 min. When the reaction temperature reached to reflux, a severe reaction occurred and the initial transparent solution became turbid and brownish black. The resulting mixture after refluxing was cooled to room temperature in 50 min and purified with ethanol and ethyl acetate. The nanoparticles can be separated by process of centrifugation and then dispersed in hexane. The particles were further purified several times by precipitating using a mixture of ethanol and ethyl acetate. The nanoparticles were finally dispersed in kerosene. The final density of the fluid is 0.8487 g/cc.

8.3. Impedance spectroscopy measurements

The impedance spectroscopy measurements have been performed by means of a 1260A Impedance/Gain-Phase analyser with a 12962A sample holder. The electrodes consist of two parallel disks made of brass of radius $R = 18$ mm. The electrodes are classified as non-blocking. The measurements are performed in the frequency range from about 1 mHz to 10 MHz for various distance between the electrodes, $d = 24 \mu\text{m}$, $50 \mu\text{m}$, $137 \mu\text{m}$, and $209 \mu\text{m}$. On each sample a few measurements with different amplitude of the applied voltage have been performed on a dispersion of ferrofluid particles, with bulk density of particles $N_0 \sim 10^{22} \text{ m}^{-3}$, in kerosene. The ferrofluids particles, to avoid flocculation, are treated with a surfactant.

For the sample of thickness $24 \mu\text{m}$ we considered the case of $V_0 = 25 \text{ mV}$, 115 mV , 200 mV , 345 mV , 1 V , and 3 V .

8.4. Best fit procedure

The best fit of the set corresponding to $V_0 = 115 \text{ mV}$ is shown in Fig. 1, obtained with the Ohmic model. The parameters of the best fit are $\varepsilon = 1.41 \times \varepsilon_0$, $Z_p = Z_m = 1$, $n_{p0} = 6 \times 10^{21} \text{ m}^{-3}$, $D_p = 5 \times 10^{-12} \text{ m}^2/\text{s}$, $y = 10^{-3}$, $\kappa_p = 4 \times 10^6 \text{ 1/(mVs)}$, and $\kappa_m = \kappa_p$.

We have evaluated the frequency dependence of the relative residuals ΔR , and ΔX , defined by

$$\Delta R(\omega_i) = \frac{R(\omega_i) - R_i}{|Z(\omega_i)|}, \quad (48)$$

$$\Delta X(\omega_i) = \frac{|X(\omega_i)| - |X_i|}{|Z(\omega_i)|}, \quad (49)$$

where $R(\omega_i)$, $X(\omega_i)$ and R_i , X_i are the experimental and theoretical values of the resistance and reactance respectively, whereas $|Z(\omega_i)| = \sqrt{R(\omega_i)^2 + X(\omega_i)^2}$ the theoretical modulus of the electric impedance [29]. For each sample we have also determined the reduced χ^2_0 defined as

$$\chi^2_{R0} = \frac{1}{N} \sum_{i=1}^N \frac{[R(\omega_i) - R_i]^2}{R(\omega_i)}, \quad (50)$$

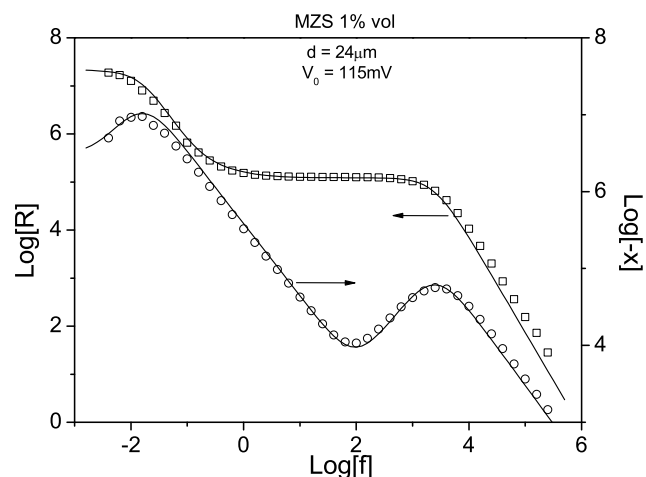


Fig. 1. Frequency dependence of $R = \text{Re}[Z]$, and $X = \text{Im}[Z]$, of a cell of kerosene containing ferrofluid particles of thicknesses $d = 24 \mu\text{m}$ subjected to an external voltage of amplitude $V_0 = 115 \text{ mV}$. The points are experimental data, the continuous lines are best fits obtained by means of the proposed generalization of PNP model with Ohmic boundary conditions.

$$\mathcal{X}_{X0}^2 = \frac{1}{N} \sum_{i=1}^N \frac{[X(\omega_i) - X_i]^2}{|X(\omega_i)|}, \quad (51)$$

where N is the number of experimental data (36). Since for all measurements \mathcal{X}_{R0}^2 and \mathcal{X}_{X0}^2 are small with respect to the critical limit at 5% level of the test (50,999), we can conclude that the proposed model is reasonable for describing the experimental data [30].

In the high frequency region the best fit weakly depend on y , κ_p and κ_m , indicating that in this region the electrodes properties do not play any role, and the effective diffusion coefficient is the free diffusion coefficient defined as $(D_p + D_m)/2$ [26]. In this region $R = \text{Re}[Z]$ presents a large plateau, and $-X = -\text{Im}[Z]$ a well defined maximum, and in log representation, a linear decreasing with slope 1, typical of an ideal condenser.

The result $\varepsilon = 1.41 \times \varepsilon_0$ is in agreement with the reported values of the dielectric constant of kerosene, and can be verified in the high frequency region. From the best fit value of n_{p0} we derive that the ionic density is of the order of 10^{22} m^{-3} , i.e. of the bulk density of ferrofluids particles. They can be considered as the responsible for the ionic contamination. The value of D_p is reasonable for diffusion coefficients of ions in kerosene. The small value of y indicates that the diffusion coefficient of ferrofluids particles is rather small. Our interpretation is then the following. The mixture of ferrofluid particles is globally neutral, but contains ions. The ions of one sign are adsorbed on the surfactant whereas the ions of the other sign remain in the mixture [31,32]. When the mixture is dissolved in kerosene, a macroscopically homogeneous solution is obtained, containing electrically charged ferrofluid particles and ions, dispersed in kerosene. Both of them contribute to the electric response of the cell to the external electric field. However, since the typical dimension of ferrofluid particles is rather large in comparison to that of the ions, their diffusion coefficients is very small with respect to that of the ions. With the same parameters we have fitted the other set of data, with different V_0 . The results indicate that the fit is good for $V_0 = 25 \text{ mV}$ and $V_0 = 200 \text{ mV}$. On the contrary, for higher values of the amplitude of the applied voltage the agreement, in the low frequency region, is gradually worse. This indicated that the hypothesis of linear response of the system is no longer valid, in this frequency range, as the amplitude increase. In the high frequency region the agreement remains good for all V_0 , as expected [24].

The set of data relevant to $d = 24 \mu\text{m}$ and $V_0 = 25 \text{ mV}$ can be fitted also with a simple electric circuit formed by a series of two simple elements made by a parallel of an ideal condenser and an ideal resistance. Indicating by R_s , C_s and R_b , C_b the corresponding elements related to the surface layer and to the bulk, we have for the corresponding electric impedances

$$Z_b = \frac{R_b}{1 + i\omega/\omega_b}, \quad Z_s = \frac{R_s}{1 + i\omega/\omega_s} \quad (52)$$

where $\omega_b = 1/(R_b C_b)$, and $\omega_s = 1/(R_s C_s)$. The total impedance of the cell is $Z = Z_s + Z_b$. The best fit of the data is obtained for $R_b = 1.5 \times 10^5 \Omega$, $R_s = 7 \times 10^7 \Omega$, $\omega_b = 2\pi 10^{3.5} \text{ rad/s}$ and $\omega_s = 2\pi 10^{-2} \text{ rad/s}$. With the same values of R_b , ω_b and R_s , ω_s the agreement with the experimental data is good, in the low frequency range, only for $V_0 \leq 200 \text{ mV}$. From the best fit parameters we get

$$\rho = \frac{R_b S}{d} \sim 6.4 \times 10^6 \Omega\text{m}, \quad \text{and} \quad \varepsilon \sim \frac{d}{\omega_b R_b S} \sim 1.42 \times \varepsilon_0. \quad (53)$$

The value of ρ well compare with that deduced by means of the best fit parameters for the model presented above. In fact the electric conductivity is of the order of $\sigma = (n_{p0} D_p + n_{m0} D_m) e^2 / (k_B T) \sim 5 \times 10^{-7} 1/(\Omega\text{m})$. Using the values of the best fit reported above we get $\rho \sim 1/\sigma \sim 5.5 \times 10^6 \Omega\text{m}$. We performed measurements for the other thickness and we verified that $R_b \propto d$, and ω_b is independent of it. From this result we infer that in the high frequency region the system behaves as a liner system and it is well described by the electric parameters ρ and ε reported above. On the contrary, in the low frequency region, the resistance and capacitance related to

the surface layer strongly depends on the amplitude of the applied voltage. Hence, the meaning of the equivalent circuit is not straightforward.

9. Debye's model with dc conductivity

The goal of this section is to show that our experimental data could be fitted also by means of a simple Debye's model with a dc conductivity, but the interpretation of the phenomenological parameters entering in the model is not straightforward. In the framework of Debye's model for dielectric material, in the approximation of one relaxation time, the frequency dependence of the dielectric constant is [1].

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D}, \quad (54)$$

where ε_∞ and ε_s are the high frequency and static dielectric constant, respectively. τ_D is the characteristics relaxation time of the system to the external stimulus. In the case where the medium under consideration has a dc conductivity σ_D , the effective dielectric constant is [33].

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D} - i \frac{\sigma_D}{\omega}. \quad (55)$$

Indicating by $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ the complex dielectric constant, by Eq. (53) we get for the real and imaginary parts of the effective dielectric constant the expressions [34].

$$\begin{aligned} \varepsilon'(\omega) &= \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau_D)^2}, \\ \varepsilon''(\omega) &= (\varepsilon_s - \varepsilon_\infty) \frac{\omega\tau_D}{1 + (\omega\tau_D)^2} + \frac{\sigma_D}{\omega}. \end{aligned} \quad (56)$$

Let us consider now our sample, and assume that it behaves as a dielectric medium with dc conductivity. In a first approximation the electric field across the sample is supposed to be homogeneous [34]. As in all Debye's models the medium is considered homogeneous, and surface effects not considered. In this framework, in the slab approximation, the complex capacitance is given by $\mathcal{C} = \varepsilon(\omega) (S/d)$, where S and d are the surface electrode and the thickness of the sample, respectively, and $\varepsilon(\omega)$ is given by Eq. (53). The electrical impedance of the sample, defined by $Z = 1/(i\omega\mathcal{C})$, has an equivalent resistance, R , and reactance, X , given by

$$R = \frac{1}{\omega} \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \frac{d}{S}, \quad \text{and} \quad X = -\frac{1}{\omega} \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \frac{d}{S}, \quad (57)$$

in such a manner that $Z = R + iX$. By taking into account the expressions for ε' and ε'' given by Eq. (IX) we get

$$\begin{aligned} R &= \frac{\sigma_D + (\varepsilon_s - \varepsilon_\infty + \sigma_D \tau_D) \tau_D \omega^2}{\sigma_D^2 + [-2\varepsilon_\infty \sigma_D \tau_D + (\varepsilon_s + \sigma_D \tau_D)^2] \omega^2 + \varepsilon_\infty^2 \tau_D^2 \omega^4} \frac{d}{S}, \\ X &= -\frac{\omega[\varepsilon_s + \varepsilon_\infty (\omega\tau_D)^2]}{\sigma_D^2 + [-2\varepsilon_\infty \sigma_D \tau_D + (\varepsilon_s + \sigma_D \tau_D)^2] \omega^2 + \varepsilon_\infty^2 \tau_D^2 \omega^4} \frac{d}{S}. \end{aligned}$$

The best fit of our experimental data, relevant to the cell of $24 \mu\text{m}$ and $V_0 = 25 \text{ mV}$, using these equations gives:

$$\begin{aligned} \varepsilon_\infty &= 1.41 \times \varepsilon_0, \quad \varepsilon_s = 1200 \times \varepsilon_\infty, \\ \tau_D &= 5 \times 10^{-2} \text{ s}, \quad \sigma_D = 10^{-9} 1/(\Omega \cdot \text{m}). \end{aligned} \quad (58)$$

The quality of the fit is comparable with the one shown in Fig. 1. The value of ε_∞ well compare with the one reported above. To connect the other best fit parameters with those derived by means of the physical description based on the PNP model presented in Sect.VIII, using these numerical values we get $\lambda \sim 1.3 \times 10^{-8} \text{ m}$, $\sigma \sim 2 \times 10^{-7} 1/(\Omega\text{m})$. The dielectric relaxation time, defined as $\tau_0 = \varepsilon/\sigma$ is then $\tau_0 \sim 6.4 \times 10^{-5} \text{ s}$. According to Klein et al. [35] in the presence of electrode polarization $\varepsilon_s = M\varepsilon_\infty$ and $\tau_D = M\tau_0$, where $M = d/(2\lambda)$. Using the best fit parameters of Sect.VIII we get $\varepsilon_s \sim 1300 \times \varepsilon_0$ and $\tau \sim 6 \times 10^{-2} \text{ s}$, in good agreement

with the numerical values reported in (IX). But at the present we are unable to connect σ_D with a physical phenomenon. Probably its value has to be connected to the electrode conductivity, but a phenomenological model relating the dc conductivity entering into Debye's model to the electrode properties is still absent. The only conclusion we can derive from our best fit parameters is that $\sigma_D \sim \sigma/M$.

10. Conclusion

We have analysed the electric response of a cell containing a dispersion of ferrofluids particles in kerosene in order to characterize, from the electrical point of view, the resulting medium. The impedance spectroscopy data, obtained on a samples in the shape of a slab with several thicknesses. We have proposed a model where the ions can differ in the electric charge, diffusion coefficients, and ohmic parameters describing the charge exchange on the electrode. The experimental data are in good agreement with the theoretical predictions only in the low frequency region, where the system behaves in a linear manner. A fit of the experimental data by means of a simple circuit, formed by resistance and capacitance related to the surface and bulk properties, has also been considered. From the best fit the bulk resistivity and dielectric constant have been derived with the two approaches, and found in reasonable agreement. We have also shown that our experimental data can be well fitted by means of a Debye's model containing a dc conductivity. In this case, the dc dielectric constant and the relaxation time, re-normalized for the electrode polarization, are in agreement with those derived by means of the extended PNP model. However, with this model, it is not obvious how the dc conductivity is related to the mobility and bulk density of ions in the medium.

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