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Free ions in kerosene-based ferrofluid detected by impedance spectroscopy

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The influence of the free ions on the electric response of cells filled with kerosene-based ferrofluids in the low-frequency region is explored. The experimental investigations have been performed on cells limited by different types of electrodes, with the same kind of ferrofluid, by means of the impedance spectroscopy technique. The electrodes considered in our study are made of titanium, platinum, gold, brass and surgical steel. The analysis of the spectra of the real and imaginary parts of the electric impedance of the cell data has been done by means of a simplified version of the Poisson–Nernst–Planck model, in which only the carriers of a given sign are mobile. The agreement between the theoretical predictions and the experimental data is rather good on the whole frequency range. From the analysis of the data in the low-frequency range, dominated by the properties of the electrodes, we discovered that only gold electrodes behave in a manner different from the other electrodes. From the best fit of the experimental data the free-ions density is determined as well as their diffusion coefficient in kerosene. The estimated dielectric constant of the kerosene is in good agreement with the values reported in the literature. In the framework of our model, the surface conductivity of the electrodes has been also determined.

1 Introduction

Ferrofluids (FF) are colloidal suspensions of magnetic nanoparticles (NP) dispersed in a liquid carrier. These materials behave, from the rheological point of view, as an isotropic liquid, but exhibit magnetic properties. Because of this unique characteristic, they have many technological applications in different fields.[1–5]

Generally, a FF suspension belongs to one of two main classes: the water-based and the oil-based ferrofluid. In water-based FF, the NP surface is usually electrically charged, and the colloidal stability is achieved through electrostatic repulsion. The charge arises from the amphoteric behavior of surface sites, which can be protonated or deprotonated by pH changing to provide positive or negative charge, respectively.[6,7] The charge can be also engineered by functionalization of bare NP using polyfunctional carboxylic acids,[8–10] amino acids,[11] silanes[12,13] and ionic surfactants.[14] Additionally, water-based FF can be stabilized by coating the NP surface with hydrophilic polymers, such as alginate,[15] chitosan,[16] dextran,[17] PVA[18] and PEG[19] In this case, the colloidal stability is achieved by steric repulsion and hydrogen bonding formation between the polymer chains leading to a hydrogel structure, which embeds the NP.[18] In oil-based FF, the NP surface is coated with a monolayer of organic ligands, such as oleic acid[20] and lauric acid,[21] where the stability is governed by steric repulsion provided by the alkyl chains of the surfactants. Thus, this type of FF is usually dispersed in non-polar solvents as kerosene, hexane, and cyclohexane. Apart from this general classification, FF dispersions can be also obtained in more complex media as ionic liquids[22] and deep eutectic solvents,[23] where the stability is ensured by steric repulsion between particles due to a complex interplay of elastic and osmotic effects.[24]

In this work, we study a kerosene-based FF stabilized by grafting oleic acid molecules at the NP surfaces. From the electrical point of view, this type of FF is characterized by a very low electric conductivity. Furthermore, it is not expected the presence of free charges in suspensions made of non-polar liquids as kerosene. However, although in very small quantities, they can be detected by the impedance technique. This type of FF is used in cooling high-power transformers, mainly due to the leakage magnetic flux in the insulating liquid where the transformer is immersed.[25,26] In this context, the determination of the concentration of free ions in this type of fluid is of some interest and may have impacts on the technological applications of oil-based FF.

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We investigate not only the presence of free ions in our samples, but their interaction with various types of electrodes made of different metals. The theoretical analysis of the experimental data is done by means of the Poisson–Nernst–Planck (PNP) model that allows the determination of the FF diffusion constant in kerosene and the ionic concentration. The PNP model consists of a set of equations involving the equations of continuity for the positive and negative ions and Poisson's equation for the actual electric potential inside the sample. The resulting differential equations must be solved with appropriate boundary conditions imposed on the two electrodes limiting the cell. Several models for boundary conditions have been proposed.[27–31] In the presented version of the PNP-model we assume that the boundary conditions are of Ohmic type, where the surface-ionic density current is proportional to the surface electric field. Furthermore, since the size of the nanoparticles is very large (typically of the order of 10 nm) with respect to the dimension of the free ions, we consider the particular case in which only the counterions can move under the influence of the external electric field. This version of the PNP model has been called the One Mobile Ion approximation, which has been discussed in ref. 32 for the simple case of blocking electrodes.

2 Experimental part

The material used in this study is a ferrofluid composed of mono-crystalline magnetic nanoparticles (NP), based on manganese–zinc ferrite ($Mn_{0.5}Zn_{0.5}Fe_2O_4$), suspended in kerosene. The NP were synthesized by a thermal decomposition route, which allows the controlling of size distribution and shape of the particles.[33–35] Briefly, metal–oleate complexes were first prepared in a mixture of solvents. The waxy solid product obtained after solvent evaporation is then mixed with oleic acid, sodium oleate and 1-octadecene. The system was heated to a reflux temperature ($\sim$300 °C), leading to a black product that was cooled to room temperature and washed with ethanol to precipitate the NP. Finally, the NP were separated by centrifugation and then dispersed in kerosene. The obtained NP are of cube-like shape, with side a $\sim 10 \pm 1$ nm[36] and coated with a single layer of oleic acid molecules, which ensures FF stability due to steric hindrance. The original ferrofluid suspension of volumetric concentration of 1.1% (1.1×10^{22} NP m^{-3}) was diluted 10 times with plain kerosene, resulting in a 0.11% (1.1×10^{21} NP m^{-3}) sample employed in the measurements. As the main goal of this work is to investigate the free charge origin and the electrode effect on the impedance measurements, only one sample concentration is required. The commercial kerosene used in the dilution was filtered by a membrane of 0.22 μm pore size and has $\varepsilon = 2.0$. This value is indistinguishable from the dielectric constant of the oleic acid and, therefore, it is used in the whole paper. It well compares with the one reported by Fannin *et al.*[37] The diluted sample was stable for many weeks.

The impedance measurements were performed by means of a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1296 Dielectric Interface. The samples of FF were subjected to an ac voltage of frequency ranging from 3 mHz to 25 kHz of small amplitude V_0(RMS) = 30 mV. In each measurement we used two parallel-plate electrodes made of the same material, in shape of disk, of area S = 3.14 cm^2, separated by a distance d = 25 mm, controlled by a spacer made of kapton. All the spectra were performed at room temperature. The spacer was in the shape of a ring of internal radius of 0.85 cm, such that the useful area of the electrode in contact with FF is S = 2.3 cm^2. The samples were placed between electrodes made of five different metals: Ti, Pt, Au, brass and surgical steel, all identical in shape and size.

3 The fundamental equations

As anticipated in the introduction, the electric response of an insulating liquid containing ions, in the low frequency region (below the MHz) is well described by a model based on the equations of continuity for the positive and negative ions, and on the Poisson's equation, which connects the electric potential with the bulk ionic charge. In this section we recall the main equations of the model for a cell in the shape of a slab, limited by Ohmic electrodes. Then, these equations are solved and the expression for the electric impedance of the cell deduced.

We indicate by n_{p0} and n_{m0} the bulk densities of ions in thermodynamical equilibrium, in the absence of external electric field, and with n_p and n_m their values in the presence of the external field. The electric charge of the positive and negative ions are indicated by q_p and q_m, respectively, and the dielectric constant of the insulating liquid in which the ions are dispersed by ε. The cell is assumed a slab, of thickness s and surface area S, in such a manner that the problem can be considered one-dimensional. The cartesian reference frame used for the description has the z-axis perpendicular to the limiting surfaces, coinciding with the electrodes by means of which the external difference of potential is applied to the cell. The electrodes are assumed identical. In this framework, the fundamental equations of the model are

$$\frac{\partial n_\alpha}{\partial t} = -\frac{\partial j_\alpha}{\partial z}, \tag{1}$$

where $\alpha = p, m$, and

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

The ionic current densities are

$$j_\alpha = -D_\alpha\left(\frac{\partial n_\alpha}{\partial z} \pm \frac{q_\alpha n_\alpha}{K_B T}\frac{\partial V}{\partial z}\right), \tag{3}$$

where + for $\alpha = p$, and – for $\alpha = m$, and D_p and D_m are the diffusion coefficients of the positive and negative ions. Eqn (1)–(3) are valid in the Einstein approximation for ionic mobility. In the absence of the external field the sample is assumed locally neutral, hence $q_p n_{p0} = q_m n_{m0}$. The general solution of the equations of the model has been recently discussed.[38] In the following we are interested in the particular case in which the ions of a given sign do not contribute to the electric response of the cell. This simplifying assumption is valid when the ions of a given sign move in a gel, over which are stuck the ions of the other sign. It is also a good approximation to describe the case in which the ions of one sign are very large concerning the ions of the other sign. This corresponds to our case where the ions of one sign are stuck on the magnetic particles, and the ions of the other sign move individually. In this case we can put $D_m = 0$ and assume that $n_m = n_{m0}$ even in the presence of the external electric field. In this framework, the electric response of the cell is due just to the positive ions. We introduce the dimensionless quantities u_p, u_v and the intrinsic length Λ defined by

$$u_p = \frac{n_p - n_{p0}}{n_{p0}}, \quad u_v = \frac{q_p}{K_\mathrm{B}T}V, \quad \Lambda = \sqrt{\frac{\varepsilon K_\mathrm{B}T}{n_{p0}{q_p}^2}}. \tag{4}$$

Λ coincides with the length of Debye for the present problem. In terms of these quantities the equations of the problem, in the linear limit in which $u_p \ll 1$, can be rewritten as

$$\frac{\partial u_p}{\partial t} = D_p\left(\frac{\partial^2 u_p}{\partial z^2} + \frac{\partial u_v}{\partial z^2}\right), \tag{5}$$

$$\frac{\partial^2 u_v}{\partial z^2} = -\frac{1}{\Lambda^2}u_p. \tag{6}$$

Substituting (6) into (5) we get

$$\frac{\partial^2 u_p}{\partial z^2} - \frac{1}{D_p}\frac{\partial u_p}{\partial t} - \frac{1}{\Lambda^2}u_p = 0. \tag{7}$$

In the case of harmonic excitation, where the external difference of potential applied to the cell is a harmonic function of time $V(t) = V_0\mathrm{e}^{i\omega t}$, of amplitude V_0 and circular frequency ω, the $u_p(z,t)$ and $u_v(z,t)$ can be separated as $u_p(z,t) = \eta_p(z)\exp(i\omega t)$, and $u_v(z,t) = \phi(z)\exp(i\omega t)$. The functions $\eta_p(z)$ and $\phi(z)$ are solutions of the ordinary differential equations

$$\eta_p''(z) = \beta^2\eta_p(z), \tag{8}$$

$$\phi''(z) = -\frac{1}{\Lambda^2}\eta_p(z) \tag{9}$$

where $\beta = (1/\Lambda)\sqrt{1 + i(\omega/\omega_\mathrm{D})}$, and $\omega_D = D_p/\Lambda^2$. Taking into account the symmetry of the problem we get

$$\eta_p(z) = C_p\sinh(\beta z). \tag{10}$$

It follows that

$$\phi(z) = -\frac{1}{\beta^2\Lambda^2}C_p\sinh(\beta z) + C_v z. \tag{11}$$

The integration constants C_p and C_v are determined by the boundary conditions on the current density and the electric potential on the electrodes. The total electric current density defined by $J = q_p j_p + \varepsilon\partial E/\partial t$, using the results reported above for $\eta(z)$ and $\phi(z)$ is found to be

$$J = -n_{p0}q_pD_p\Lambda^2\beta^2C_v\mathrm{e}^{i\omega t}. \tag{12}$$

As expected, it is position independent. The impedance of the cell, given by $Z = V_0\mathrm{e}^{i\omega t}/I$, where $I = JS$, is the total current across the cell of surface area S, is

$$Z = \frac{v_0}{\varepsilon D_p\beta^2C_vS}, \tag{13}$$

in which $v_0 = q_pV_0/(K_\mathrm{B}T)$.

To determine the integration constants C_p and C_v we must impose the boundary conditions on j_p and V at $z = s/2$. The presence of the external power supply implies that

$$V(\pm s/2,t) = \pm(V_0/2)\exp(i\omega t). \tag{14}$$

The charge exchange on the electrodes is supposed to be of Ohmic type, where the current density from the sample to the external circuit is approximated by

$$j_p(\pm s/2,t) = \kappa_pE(\pm s/2,t), \tag{15}$$

where $E = -\partial V/\partial z$ is the electric field. The Ohmic model has been proposed a few years ago.[29] It has been generalized recently to take into account that $j_p(t)$ is delayed with respect to $E(t)$.[39] To extend (15) to the dynamical case, in the linear limit, it is necessary to invoke a distribution of relaxation times, related to different types of mechanisms for the charge exchange, or to a random energy barriers distribution of the potential wells where the transfer of charge takes place. Details of the model are reported in.[39] According to the analysis presented in[39] the parameter κ_p is given by

$$\kappa_p = \kappa_0\frac{i\omega\tau}{\log(1 + i\omega\tau)}, \tag{16}$$

where τ is the maximum relaxation time. Expression (16) has been obtained assuming that all relaxation time are equivalent. It can be identified with a reaction time related to the chemical reaction by means of which the electric charge is passing from the ion to the electrode. Frequency dependence of κ is similar to the frequency dependence of the ac hopping electric conductivity in disordered solids.[40] Expression (16) has been successfully used to describe the surface conductivity in ionic liquids,[39] and the impedance spectroscopy data relevant to electrolytic solution of KCl in water.[41] We observe that in the limit of $\tau \to 0$, $\kappa_p \to \kappa_0$, *i.e.* we recover the case in which the surface conductivity is not dispersive.

Substituting (10,11) into (14,15) we get for the integration constants the expressions

$$\begin{aligned} C_p &= -\frac{\beta^2\Lambda^2B}{2B + \beta s(-B + \beta^2\Lambda^2)\coth(\beta s/2)}\frac{v_0}{\sinh(\beta s/2)}, \\ C_v &= \beta\frac{-B + \beta^2\Lambda^2}{\beta s(-B + \beta^2\Lambda^2) + 2B\tanh(\beta s/2)}v_0, \end{aligned} \tag{17}$$

where we have defined an intrinsic surface conductivity $\kappa_c = D_pN_0q_p(K_\mathrm{B}T)$, a dimensionless surface conductivity by $k = \kappa_p/\kappa_c$, and introduced the dimensionless quantity $B = 1 - k$. For $k = 0$ we recover the case of blocking electrodes. Taking into account eqn (17), the impedance of the system under consideration given by (13) can be rewritten in the final compact form

$$Z = \frac{\beta s(-B + \beta^2 \Lambda^2) + 2B \tanh(\beta s/2)}{\beta^3 \varepsilon S(-B + \beta^2 \Lambda^2) D_p}. \tag{18}$$

Expression (18) will be used to fit the experimental data.

4 Results and discussions

In Fig. 1 it is shown the real, R, and imaginary, χ, parts of the electric impedance, Z, as a function of the frequency, $f = \omega/(2\pi)$, of the applied voltage. The FF was placed between the electrodes of each metal. The curves are typical spectra of a dielectric liquid containing ions.[42] The $R(f)$ has a large plateau until $f_D \sim \omega_D/2\pi$, while $-\chi(f)$ presents a local maximum. As $f \to \infty$, $R \propto f^{-2}$ and $\chi \propto f^{-1}$, just as in common electrolytic solutions. This behavior is not present in the spectra of pure kerosene (see supporting material). In the low frequency range, however, all $R(f)$ spectra have an additional plateau and the imaginary part $\chi(f)$ has an extra relaxation. This kind of relaxation, in the ultra-low frequency range, has already been reported in the literature and is due to the ionic conductivity of the interface electrode-solution.[38] The standard deviation in this frequency range is about 0.1 while in higher frequency region, say $f \gtrsim 1$ Hz it is 0.05.

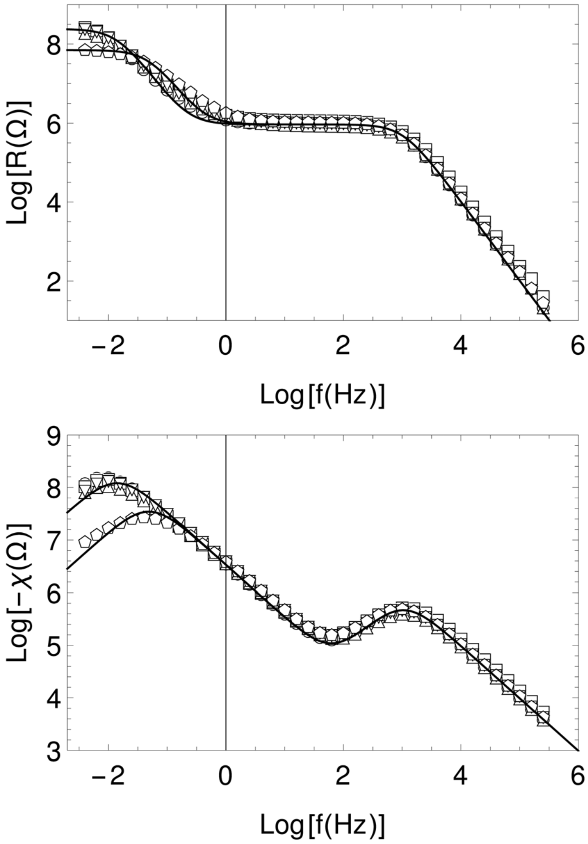

Fig. 1 The R and χ spectra of the FF 0.11 vol% measured between electrodes made of different materials: ☐ platinum; Δ surgical steel; ∇ titanium; ○ brass and gold. The solid lines are fits made with the one sign mobile ion model.

In our investigation, the experimental results are analyzed by means of the one sign mobile ion model presented in the previous section. In this framework, the presence of free charges in the FF detected by the impedance spectroscopy technique can be explained considering some important features of the NP production and surface coating. The modification of the surface of iron-based NP by oleic acid/oleate to produce ferrofluids may lead to different forms of interactions between the metal surface ion and the carboxylic/carboxylate groups.[43] Carboxylic acids can interact with the surface through hydrogen bonds (physisorption) while carboxylates can covalently bind to surface ions (chemisorption). Both experimental and theoretical studies demonstrate that the latter type of interaction can occur through different types of coordinative linkages, where bridging bidentate and chelating bidentate are predominant.[44–46] Moreover, depending on the synthesis conditions, a small amount of non-bonded oleic acid/oleate species can be also present.[43,47] In the case of our sample, the results of impedance spectroscopy are consistent with the presence of residual free oleic acid and sodium oleate from the synthesis medium. These non-bonded species may interact with the surface coated oleic acid/oleate through hydrophobic interactions between their long carbon chains, remaining stuck on the NP. The small sodium ions, in turn, may play as the mobile charge, being the main responsible for the signal in the impedance spectroscopy experiments.

It is interesting to note that, except the spectra using gold, all other spectra relevant to the sample limited by other type of electrodes, are practically coincident. The small differences between them are inside the experimental error. The results relevant to the sample limited by electrodes in gold differ in a significant manner, in the low frequency region, from the other set of data. The observed relaxation in this region is at $\sim$0.04 Hz for gold electrodes and $\sim$0.01 Hz for all others.

Since only the sample with gold electrodes behaves differently from the other samples, we fitted separately the two set of spectra. From the fit of the spectra relevant to the samples with electrodes in titanium, platinum, brass and surgical steel electrodes we obtained $D_p = 1.23 \times 10^{-11}$ m^2 s^{-1}, $n_{p0} = 1.48 \times 10^{21}$ m^{-3} and $\kappa_p = 9.8 \times 10^6$ (m s V)$^{-1}$. Of course, the diffusion constant and the ionic concentration are bulk parameters that depend only on the system used in the measurements and not on the kind of electrodes. Therefore, these two values are also valid for the spectra obtained with gold electrodes and were used in the fit to find κ_p for gold. The result is $\kappa_p = 3.39 \times 10^7$(m s V)$^{-1}$. The parameter τ, entering into eqn (16), does not play any role in the fitting procedure. This means that the charge exchange process is a rather fast phenomenon, and hence $\kappa_p \sim \kappa_0$.

Although the simplicity of the model, the fits are rather good. The small systematic deviation of the imaginary part from the theoretical predictions in the low frequency region is due to the non linearity related to the amplitude V_0 of the measuring applied voltage. As discussed elsewhere, the linearized PNP model is expected to work well for V_0 smaller that a critical voltage, V_c, which is frequency dependent.[48] In the dc limit, V_c is of the order of the thermal voltage $KBT/q \sim 25$ mV. In our experimental set up we were limited, by the precision of the impedance meter, to apply $V_0 = 30$ mV. Consequently, at very low frequency, a non linear contribution to the real and imaginary parts is expected.

According to the model, the ionic density is similar to the nanoparticle concentration N. This result indicates that there is, in average, one ion per nanoparticle. Furthermore, the mobility of the ions in kerosene is very low, about 100 times lower than a typical ion in water, for example.[49] Finally, it is interesting to note that the electric conduction at the interface electrode-solution is higher for gold than any other measured metal.

5 Conclusions

The impedance spectroscopy technique has been used to investigate the influence of the presence of free ions and the nature of the electrodes on the electric response of a kerosene-based ferrofluid cell. The measured spectra of the real and imaginary parts of the electric impedance of the cell have been analyzed with a simplified version of the Poisson–Nernst–Planck model, where only one of the charge carrier is mobile. The presence of the charges in the FF system is attributed to a residual concentration of sodium oleate from the synthesis procedure. In the framework of our model, the oleate ions are stuck on the particles while the sodium ions represent the mobile charge, which is supported by the high quality of the fitting of the experimental results. The charge exchange at the electrode is a fast phenomenon, and the surface conductivity is not dispersive. The bulk density of ions is of the order of the bulk density of magnetic particles. Moreover, both the ions's diffusivity and the concentration determined in our experiments are independent of the electrodes used. Finally, only the gold electrodes behave peculiarly.

Conflicts of interest

There are no conflicts to declare.

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