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Influence of the rheological properties on the electrical impedance of hydrogels

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We show that the anomalous frequency dependence of the real part of the electrical impedance of hydrogels can be interpreted by taking into account their non-Newtonian character, according to which the effective viscosity, η, depends on the frequency of the imposed deformation. Our experimental results are in good agreement with the Poisson–Nernst–Planck model if the ionic viscosity is taken proportional to the macroscopic one, measured by means of a viscositymeter, and the diffusion coefficient is assumed frequency dependent according to the formula of Stokes $D = K_B T/(\kappa \eta)$, where κ is a shape coefficient. From this result it follows that the non-Newtonian character of complex liquid can be investigated by means of the impedance spectroscopy technique. © 2012 American Institute of Physics. [doi:10.1063/1.3675522]

I. INTRODUCTION

The model of Poisson–Nernst–Planck (PNP) has been proposed to take into account the contribution of the ions dissolved in an insulating medium on its electrical response to an external excitation.[1] The mathematical formulation of this model is based on the equations of continuity for the groups of ions present in the host medium, and on the equation of Poisson relating the actual electrical potential to the ionic charge density.

The model is based on the continuum description of the medium under consideration. This means that the ions, assumed point like, are dispersed in a dielectric medium. The parameters entering in the model are the bulk density of ions in thermodynamical equilibrium, N_0, the charge of the ions, q, the dielectric constant of the medium in which the ions are dispersed, ε, and the diffusion coefficient of the ions in the host medium, D. The model, proposed initially for fully dissociated impurities, has been generalized to take into account the generation-recombination effect in different manners.[2–6] The previous mentioned equations, valid in the bulk, have to be solved with the boundary conditions, related to the properties of the electrodes.[7,8]

The model allows the evaluation of the electrical impedance of the cell, usually assumed in the shape of a slab of thickness d and surface are S, when the sample is submitted to an external sinusoidal voltage of angular frequency ω. However, in this case, some problem arises. In fact, if the external excitation, applied to the sample, depends on ω is it correct to assume that the parameters of the model are frequency independent? For what concerns ε this assumption is usually reasonable when the medium under investigation is a hydrosolution and the frequency of the applied voltage is

smaller than few MHz. In fact the dielectric dispersion is expected in the range of GHz. A similar question concerns D. According to elementary physics, D is related to the mobility, μ, by the relation of Einstein $\mu/D = q/(K_B T)$, where $K_B T$ is the thermal energy. The mobility, μ, is related to the drift of the ions connected with the presence of an external electric field. In this sense it is related to an average motion along the field. It is not, as well known, a microscopic quantity, but a statistical property of the solution host medium-ions. In elementary physics, this quantity is introduced by means of the model of Drude, where the concept of effective viscosity acting on the ions, η, is used. By equating the force due to the electric field to the viscous force, one gets $\mu = q/(\kappa \eta)$, where κ is a coefficient related to the shape of the ions.[9] Using the relation of Einstein we obtain $D = K_B T/(\kappa \eta)$. However, the use of these relations in the framework of the PNP model is not straightforward. In fact what is the relation of the η introduced above with the one we measure with a viscositymeter is unclear. In particular, since for non-Newtonian liquid η depends on the frequency of the applied shear, is it correct to assume in the PNP model the diffusion coefficient frequency independent? This point is rather delicate because the dispersion of the viscosity takes place in the low frequency region (of the order of a few tens of Hz) and hence a possible frequency dependence of the diffusion coefficient could be responsible for unexpected frequency dependencies in the low part of the spectrum, usually attributed to surface effects, and modeled as constant phase elements.[10,11]

In a recent paper[12] we have investigated the curves of voltammetry of a sample of hydrosolution. In Ref. 12 we measured the macroscopic viscosity, by means of a Brookfield apparatus, and we have shown that it is possible to have a good fit of the experimental data by means of the PNP model assuming that the effective viscosity of the ions is proportional to the macroscopic one. In order to test the validity of the

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procedure used in Ref. 12, in the present paper we measure the macroscopic viscosity and elastic, G', and viscous, G'', modulus versus the frequency, and the crossing frequency f_c, where $G'(f_c) = G''(f_c)$ for two types of hydrogels doped with different concentration of NaCl. We measure also the frequency dependence of the real and imaginary parts of the electrical impedance of different samples, in the range 5 Hz, 13 MHz. Our experimental data can be interpreted by means of the PNP model, by assuming the validity of the relation of Stokes, where the effective ionic viscosity is proportional to the macroscopic one. This result confirms the analysis presented in Ref. 12 and allows to identify the characteristic frequency entering in the dispersion of the viscosity as the crossing frequency f_c. It follows that the impedance spectroscopy technique can give useful information on the non-Newtonian character of complex liquids.

II. RHEOLOGICAL MEASUREMENTS

In this work we report on the rheological and dielectric properties of conducting hydrogels containing hydroxyethyl-cellulose (HEC) and NaCl in different concentration, in depurated water. The first group has 2% of HEC, and the concentrations of NaCl are 1, 3, 5, and 7%. The second group has 4% of HEC, and the concentrations of NaCl are 1, 3, 5%. The effective viscosity has been measured by means of a stress controlled rheometer (modular advanced rheometer system, RS150 from Haake) using a thermostated cone-and- plate cell. The cone has a diameter of 35 mm, an angle of 0.5° and a truncation of 25 μm. The experiments were done at room temperature and sample evaporation was restricted via a cover piece. Two kinds of experiments were performed: under flow rheology and oscillatory flow experiments. The under flow rheological measurements are done imposing the stress in the range [1 Pa – 1200 Pa] and corresponding measured steady-state values of shear-rate are reported. The experimental data relating to these shear flow experiments are shown in Fig. 1. As it is evident from this figure, the effective viscosity of the hydrogels depend on the HEC concentration, but it is independent of the concentration of NaCl. The data for η are in good agreement with a power law of the type[13]

$$\eta(\omega) = \eta_{\infty}[1 + A(\omega\tau)^{-\nu}], \qquad (1)$$

where $A = (\eta_0 - \eta_{\infty})/\eta_{\infty}$, η_{∞} and η_0 are the effective viscosity in the high frequency limit and in the static case, respectively, τ is a typical relaxation time, and ν a constant related to the non-Newtonian character of the hydrogel.

From the experimental results, ν is the same for all gels, and it is of the order of 0.8. The characteristic time τ is of the order of 0.5 s for the hydrogels with 2% of HEC, and of the order of 5 s for those with 4% of HEC.

For the same gels oscillatory flow experiments are performed. The first step consists of applying constant strain to find the linear viscoelastic regime for a frequency value fixed at 1 Hz. Then for a given value of the shear-stress inside the linear regime, we investigate the evolution of both storage G' and loss modulus G'' as a function of frequency 10^{-2} Hz, $\leq f \leq 10$ Hz. The results are reported in Fig. 2 for the
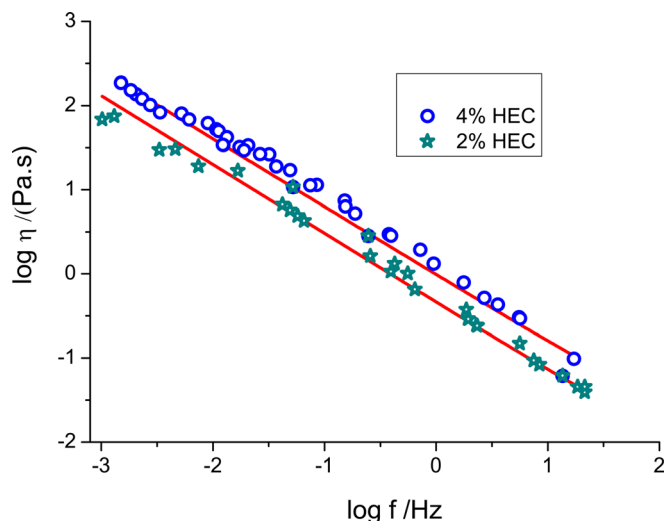

FIG. 1. (Color online) Effective viscosity η vs the shear rate $\propto \omega$. Note the independence of the NaCl concentration, the dependence on the HEC concentration, and the parallelism between the two curves in the high shear rate regime. The best fit parameters for the gels with 4% of HEC are $\eta_{\infty} = 8.4 \times 10^{-3}$ Pas, $A = 1838$, $\tau = 4.82$ s, and $\nu = 0.8$, whereas for the gels with 2% of HEC are $\eta_{\infty} = 4.0 \times 10^{-3}$ Pas, $A = 288$, $\tau = 0.49$ s, and $\nu = 0.8$.

hydrogel with 2% of HEC, and in Fig. 3 for that with 4% of HEC. The experimental results have been obtained with different imposed shear stress. From Figs. 2 and 3 it follows that the hydrogels are viscoelastic. The intersection between G' and G'' gives the cut frequency f_c, that is of the order of 2 Hz for 2% of HEC, and 0.2 for 4% of HEC. It is interesting to observe that $\tau \sim 1/f_c$.

III. DIELECTRIC MEASUREMENTS

For the same set of hydrogel we measured the spectra for the real and imaginary parts of the electrical impedance of cells with different thicknesses. The experimental setup is the same described in Ref. 11. We performed measurements on sample of thickness d ranging from 0.5 to 2 mm. In the
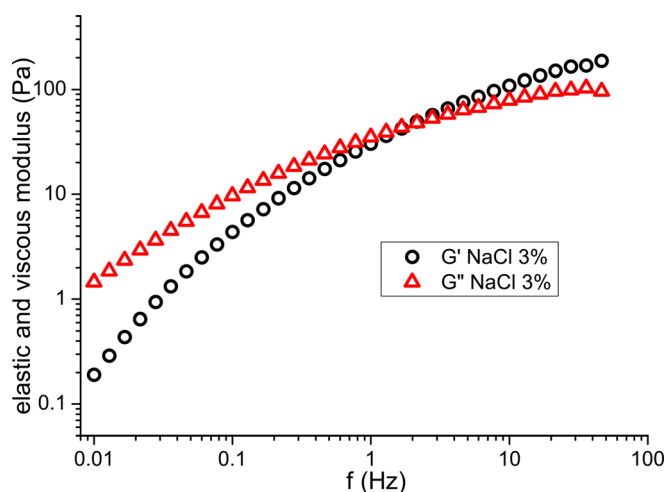

FIG. 2. (Color online) G' and G'' vs f for the hydrogel with 2% of HEC and 3% of NaCl. Imposed shear stress $\sigma = 5$ Pa. Similar results are obtained when the concentration of NaCl is changed. The cut frequency $f_c \sim 5$ Hz.
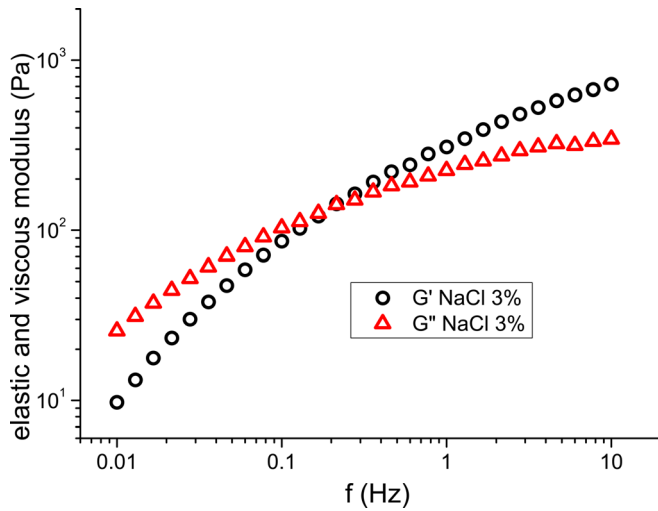
FIG. 3. (Color online) G' and G'' vs f for the hydrogel with 4% of HEC and 3% of NaCl. Imposed shear stress $\sigma = 50$ Pa. Similar results are obtained when the concentration of NaCl is changed. The cut frequency $f_c \sim 0.5$ Hz.

following we discuss only the data relevant to the situation where $d \sim 0.5$ mm, where the electrode border effects are negligible. However, similar results have been obtained with the other values of d. In Fig. 4 we show the real, R, and imaginary, X, parts of the electrical impedance of the hydrogel 2% HEC, 3% NaCl. In Fig. 5 the experimental data correspond to the hydrogel with 4% HEC and 3% NaCl. The resistance, R, and the reactance, X, of the cell in the series representation, decrease monotonically with the frequency. The plateaux of R for the two considered hydrogel, proportional to the thickness of the sample, are very small, of the order of a few Ohms.

IV. INTERPRETATION

To investigate the validity of the assumption that the ionic viscosity in the hydrogel is proportional to the macroscopic one, measured by the viscositymeter, we analyze the spectra of the real and imaginary parts of the impedance of the cell with the PNP model. We assume that the diffusion coefficient entering in the PNP model is proportional to $1/\eta$, where η is proportional to the measured viscosity, shown in Fig. 1, according to the formula $D(\omega) = D_0/(1 + A(\omega\tau)^{-\nu}$, as it follows from Eq. (1). We assume that the negative ions dispersed in the hydrogel are stuck on the polymer chains, and that only the positive ions can move under the effect of the electric field. In this case the effective length of Debye of the medium is $\Lambda = \sqrt{\varepsilon K_B T/(N_0 q^2)}$, where ε is the dielectric constant of the hydrogel, free of ions, $K_B T$ the thermal energy, N_0 the bulk density of ions, in thermodynamical equilibrium, and q the modulus of the electrical charge. The electrodes are considered not blocking, and we assume that the ionic current density on the electrodes is given by $j(\pm d/2, t) = sE(\pm d/2, t)$, where s is the parameter taking into account the transparency of the electrodes.[14] In this framework, the electrical impedance of a cell in the shape of a slab of thickness d and surface area S, subjected to an external voltage $V(t) = V_0 \exp(i\omega t)$, is
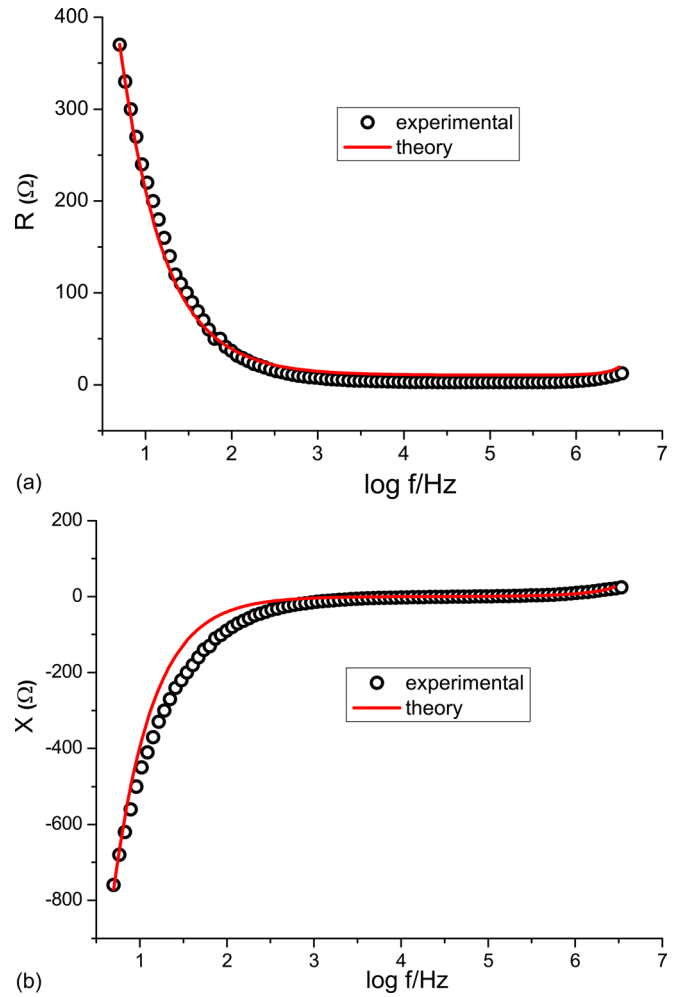

FIG. 4. (Color online) Real, R, and imaginary, X, parts of the electrical impedance of the hydrogel 2% HEC, 3% NaCl. The data refer to a sample with $d = 0.54$ mm and $S = 5 \times 10^{-5}$ m^2. The best fit parameters are $D_0 = 0.22 \times 10^{-10}$ m^2/s, $N_0 = 3.6 \times 10^{26}$ m^{-3}, $s = 9 \times 10^{10}$ 1/(m V s).

$$Z = \frac{d\beta[\Lambda^2 qs + D\varepsilon(-1 + \Lambda^2\beta^2)] + 2(\varepsilon D - qs\Lambda^2)\tanh(\beta d/2)}{i\varepsilon D\Lambda^2 S(-iqs + \varepsilon\omega)\beta^3},$$

(2)

where $D = D(\omega)$ is the diffusion coefficient of the positive ions in the hydrogel, and $\beta = (1/\Lambda)\sqrt{1 + i\omega(\Lambda^2/D)}$.[14]

By a best fit procedure of the data reported in Figs. 4 and 5, we evaluate the bulk density of ions in thermodynamical equilibrium, N_0, D_0, and s, using for $A = (\eta_0 - \eta_\infty)/\eta_\infty$ the values obtained by the best fit of the data shown in Fig. 1. The value of N_0 has been found proportional to the concentration of NaCl, and of the same order of magnitude estimated by assuming complete dissociation. This result confirm the assumption of full dissociated salt, with negligible recombination.

The experimental data relevant to the impedance spectroscopy are in good agreement with the model of PNP assuming that the effective ionic viscosity is proportional to the macroscopic one. The small increasing of the real part of the electrical impedance, in the high frequency region, and
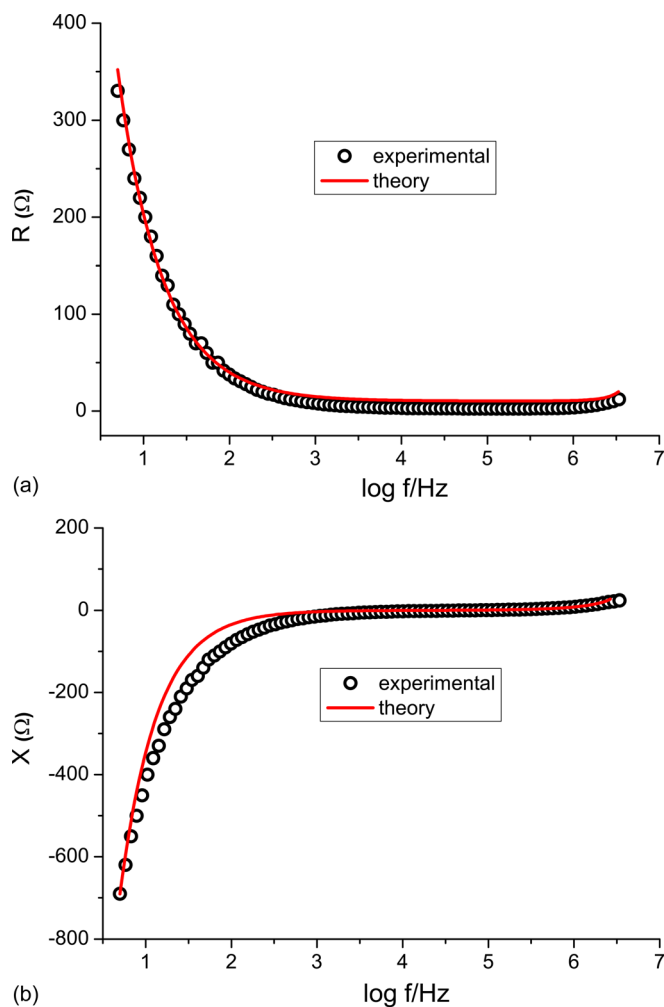
FIG. 5. (Color online) Real, R, and imaginary, X, parts of the electrical impedance of the hydrogel 4% HEC, 3% NaCl. The data refer to a sample with $d = 0.57$ mm and $S = 5 \times 10^{-5}$ m^2. The best fit parameters are $D_0 = 0.25 \times 10^{-10}$ m^2/s, $N_0 = 3.4 \times 10^{26}$ m^{-3}, $s = 9 \times 10^{10}$ 1/(m V s).

the tendency for the reactance to pass from capacitive to inductive behavior, can be interpreted by means of a modification of the PNP model, by incorporating a finite speed of response propagation, as proposed in Ref. 15.

The frequency at which the viscosity passes from the value in the low frequency range to the value in the high frequency range coincides with the crossing frequency f_c.

V. CONCLUSION

We have investigated the rheological and dielectric properties of conducting hydrogel containing hydroxyethylcellulose (HEC) and NaCl in different concentrations, in depurated water. According to our experimental data, the spectra of the real and imaginary parts of the electrical impedance of the cell can be well interpreted by means of the Poisson–Nernst–Planck model by assuming that the diffusion coefficient of the ions, D, entering in the model, depends on the frequency of the applied external voltage. This dispersion of the diffusion coefficients can be understood by assuming that D is related to the effective viscosity of the gel, η, measured by means of a viscositymeter, by the usual formula of Stokes $D = K_B T/(\kappa \eta)$, and taking into account the non-Newtonian character of the gel. The data have been fitted by assuming $\eta(\omega) = \eta_\infty [1 + A(\omega \tau)^{-\nu}]$, that is in good agreement with our rheological measurements. The relaxation time, τ, has been found coincident with the $1/f_c$, where f_c is the frequency at which the elastic and viscous modulus coincide. According to our results, the frequency variation of the electrical impedance of a complex liquid depends on its rheological properties. Consequently, the impedance spectroscopy technique can give useful information on the non-Newtonian character of liquids.

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