Inductive behavior of electrolytes in AC conductance measurements

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Abstract

The alternating current conductance of various electrolytes contained inside a capillary is measured as a function of frequency from 1 kHz to 10 MHz. The response is found to be characteristic of the concentration and composition of the electrolyte. A simple model is able to reproduce well the dispersive shape of the frequency-dependent conductance.

Despite the importance of electrolytes in different applications, their response to an alternating current (AC) at variable frequency has not yet been systematically studied. Already in the 1950s, models of electrode-less arrangements were reported [1] based on a condenser-type cell approach. The models did not consider inductance and did not reflect the nature of the electrolyte. More recent theoretical modeling and numerical simulations reveal a rather complex dispersive character of such liquids, particularly at high concentrations [2–4]. A realistic model of the frequency dependence of the ionic conductivity of an electrolyte solution must consider the contributions to the conductivity both from ion atmosphere relaxation and from electrophoretic effects. The frequency-dependent conductivity is intimately related to the frequency-dependent electrolyte friction [2]. Approximations must be made in theoretical models, especially regarding the molecular details of the ion–solvent and solvent–solvent correlations. For that reason, these theories are limited to solutions having a concentration 0.1 M or less [2]. In this Letter, we report on AC measurements and interpretation of the dispersive character of electrolytes. It is shown that dispersion curves are characteristic of electrolyte composition and concentration. We are able to model the dispersive behavior by incorporating the effect of the frequency-dependent impedance of the electrolyte on the output signal.

We have built a simple experimental system for measuring the conductivity inside a fused silica capillary with inner diameter 75 μm using two external 5 mm wide Cu foil electrodes capacitively coupled to the electrolyte. This arrangement avoids direct contact with the electrolyte. Similar systems with non-invasive electrodes capacitively coupled to the electrolyte have already been tested by other workers [5,6] for conductivity measurements. The AC output signal from the measured liquid in such circuits depends sensitively on the actual construction and geometry of the electrodes as well as on the amplifying and measuring electronic circuits. Our objective was to optimize our measurement circuit to achieve a strong effect of the electrolyte on the measured output signal. The circuit was designed to obtain the highest possible frequency stability of both the input and the output AC signals, in order to use the experimental circuit to investigate the frequency dependence of the impedance of several electrolytes.

Fig. 1 presents a schematic drawing of the AC circuit. The Cu electrodes were tightly wound around the capillary to insure good coupling to the electrolyte. The spacing between the electrodes was chosen to be 1 cm (which
is considerably larger than in previous work [5,6]) to achieve the largest possible effect of the electrolyte on the output signal at a negligible risk of coupling capacity between the electrodes, while still having a large enough output signal. The capacitance $C$ of each Cu electrode was estimated to less than 0.5 pF by considering each electrode as a coaxial capacitor, where the electrolyte is the inner conductor and the capillary wall (coated by polyamide) together with a possible air gap between the capillary and the Cu foil form the dielectric, taking into account the different relative permittivities of the materials comprising the dielectric. The voltage source used guaranteed stable input voltage at all frequencies over which the output voltage signal was measured across a 55.2 kΩ metal film resistor, the value of which is stable in the frequency range considered here. Finally, the signal was measured by an oscilloscope with an input impedance of 1 MΩ.

Assuming a pure resistive behavior of the electrolyte, the imaginary part of the impedance in the circuit is given only by capacitors (identical at both sides) formed between the electrodes and the electrolyte. In this case, the frequency curves should reach saturation values dependent on the conductivity of the electrolyte. Our experimental results revealed, however, a much more complex dispersive character of the ionic liquids.

Fig. 2 compares typical results of the frequency variation of the output AC voltage for solutions of ammonium acetate, urea, ammonia, NaCl, and pure water. Examination of Fig. 2 shows large variations in circuit output for different electrolytes, both in signal strength and dispersion shape. Clearly, NaCl is a better conductor (a strong electrolyte) as opposed to for example a 7 M urea–water solution. The fact that water has an almost flat profile and air has basically no signal shows that the dispersive character reflects the electrolyte impedance and does not result from the circuit itself.

The effect of concentration on the electrolyte impedance is obvious in Fig. 3, where the output signals increase with increasing concentrations of urea (Fig. 3a) and NaCl (Fig. 3b). An interesting effect of the electrolyte composition is shown in Fig. 4, featuring the time evolution of a 7 M urea–water solution. Concentrated aqueous solutions of urea are sensitive to higher temperatures, which makes such solutions decompose (hydrolyze) to yield free ammonia (the rate of decomposition increases with concentration) even at room temperature. In Fig. 4, a 7 M urea solution maintained at room

Fig. 1. (a) Schematic diagram of the measurement circuit. $Z_{\text{liq}}$ represents the impedance of the liquid. The capacitance $C$ of each Cu electrode was estimated to less than 0.5 pF. $V_0 = 15$ V (peak-to-peak), $R = 55.2$ kΩ. (b) Cross-section of conductivity detector viewed from above.

Fig. 2. Output voltage signal of the experimental system as a function of generator input frequency for several electrolytes. The dispersion varies greatly.
temperature was measured over the course of several days. The results show how the change in ion composition of the solution shifts the dispersion peak to the right (toward the dispersion peak of ammonia) and also increases the output signal (caused by a stronger ionic strength of the hydrolyzed solution).

Fig. 3. Output voltage signal of the experimental system as a function of generator input frequency for: (a) two different concentrations of urea in water; (b) two different concentrations of NaCl in water. The output signal increases with concentration.

Fig. 4. Output voltage signal of the experimental system as a function of generator input frequency for a series of urea solutions in consecutive stages of decomposition. As the decomposition progresses with time, the ion composition of the electrolyte and its characteristic dispersion profile changes.
To explain the experimental results, we have considered the possible contribution of an inductive component $L_{\text{liq}}$ to the impedance of the electrolyte. Assuming a complex impedance $Z_{\text{liq}}(\omega)$ of the electrolyte

$$Z_{\text{liq}}(\omega) = R_{\text{liq}} + j\omega L_{\text{liq}},$$  \hspace{1cm} (1)$$
where $R_{\text{liq}}$ is the resistance of the electrolyte, the output voltage signal $v(\omega)$ measured in our AC circuit can be expressed as

$$v(\omega) = Ri(\omega) = RV_0/Z(\omega),$$  \hspace{1cm} (2a)$$

with

$$Z(\omega) = 2Z_C + Z_{\text{liq}}(\omega) + Z_R$$  \hspace{1cm} (2b)$$

and

$$|v(\omega)| = R|i(\omega)|$$

$$= RV_0\omega C/\left[2 - \omega^2 CL_{\text{liq}} + \left(\omega C(R_{\text{liq}} + R)\right)^2\right]^{1/2},$$  \hspace{1cm} (2d)$$

where $V_0$ is the constant input AC voltage signal ($V_0 = 15$ V peak-to-peak in most experiments) with variable frequency up to 50 MHz.

Fig. 5 compares the calculated and experimental curves for urine, an ammonium acetate buffer solution (5 mM, pH 4.3) and a 7 M urea–water solution. The resistance $R_{\text{liq}}$ of an electrolyte was estimated to be around 75 M$\Omega$ from center of one electrode to the center of the other electrode using current readings in high voltage capillary electrophoresis (CEC) separations with ammonium acetate (5 mM, pH 4.3) as a running buffer. This value was adjusted for individual electrolytes to fit the experimental dispersion curves (31.5 M$\Omega$ for urine, 93 M$\Omega$ for ammonium acetate and 275 M$\Omega$ for urea).

In our theoretical dispersion model, increasing the resistance $R_{\text{liq}}$ decreases the output voltage but does not affect the overall shape of the dispersion. Increasing the inductance $L_{\text{liq}}$, however, changes the shape of the curve and shifts the peak frequency to lower values. Comparing these characteristics to what is shown in Figs. 2–4, we conclude that increasing the concentration of an electrolyte can be associated mainly with a decrease of $R_{\text{liq}}$ and a slight decrease of $L_{\text{liq}}$. A change of electrolyte ion composition leads to both a change in $R_{\text{liq}}$ and a change in $L_{\text{liq}}$. For the decomposing urea–water solution in Fig. 4, the hydrolysis is reflected by a decrease of $R_{\text{liq}}$ as well as by a decrease of $L_{\text{liq}}$.

For pure water, the theoretical dispersion model predicts an inductance of less than 1 H; for a dispersion curve like the one of NaCl, the value of $L_{\text{liq}}$ must be below 10 H. The higher the inductance, the narrower the dispersion peak; values of $L_{\text{liq}}$ above 1 kH yield increasingly spike-shaped dispersion curves not seen in the liquids tested experimentally. We have also examined the possibility of an even more complex impedance of the electrolyte by considering it to have a small parallel capacitance. We concluded, however, that the effect of the parallel capacitance was negligible.

Excellent fits of the experimental dispersion profiles with the theoretical response of our AC circuit confirm that the AC impedance of electrolytes can be approximated by a resistive component $R_{\text{liq}}$ and an inductive component $L_{\text{liq}}$, as expressed in Eq. (2). The resistance $R_{\text{liq}}$ can be considered in first approximation to be independent of frequency. It obviously depends on the ionic strength, that is, the extent of ionization (strong vs. weak electrolytes), as well as on the concentration and the type of ions.

The interpretation of the inductance $L_{\text{liq}}$ in electrolytes is more complex. As inductance is generally defined in terms of an electromagnetic force generated to oppose
a given change in current, we believe that in electrolytes such a force can be generated by frictions resulting from the ion atmosphere relaxation effect and the electrophoretic effect [7]. We believe that the fact that the value of $L_{\text{liq}}$ decreases slightly with increasing concentration is associated with the ion atmosphere relaxation effect. Increasing concentration may lead to a form of shielding of the effect from the relaxation friction, arising from an ion atmosphere of a closer range, which in turn means a smaller deformation and hence a lower friction.

The inductance of electrolytes is a new approach to the AC characterization of the conductivity. Test experiments with different electrolytes and a sensitive response of the circuit to changes in electrolyte, for example from hydrolysis, together with a perfect agreement of the experimental dispersion profiles with the theoretical fit confirm that the inductance value might serve as an important parameter, for example, in comparison of age and quality of electrolytes.

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References