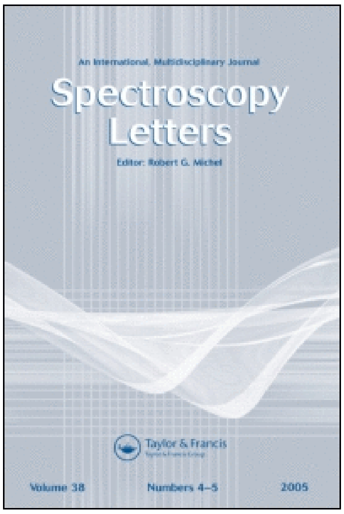

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K. Carney[a]; K. Ghowsi[a]; R. J. Gale[a]
[a] Chemistry Department, Louisiana State University, Baton Rouge, LA

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INTERACTIONS OF ELECTROMAGNETIC RADIATION WITH ELECTROLYTES AT HIGH TO ULTRA-HIGH FREQUENCIES

K. Carney, K. Ghowsi, and R. J. Gale
Chemistry Department,
Louisiana State University,
Baton Rouge, LA 70803

ABSTRACT

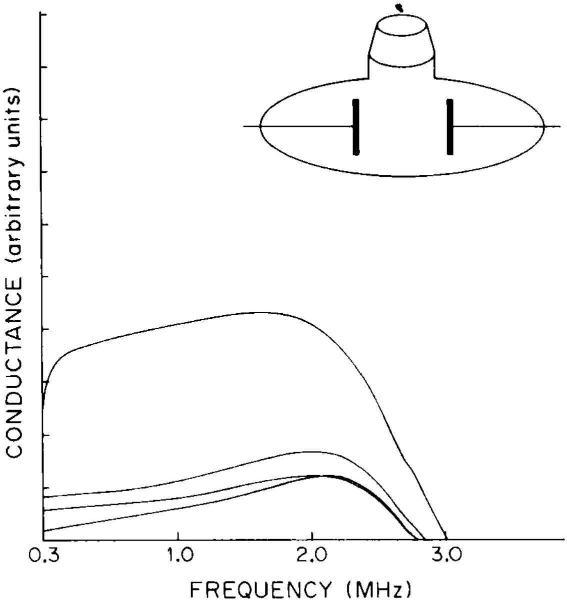
At frequencies above one megahertz, the behaviour of electrolytic solutions changes from an ionic conductor to a lossy dielectric. High frequency conductance measurements of aqueous electrolytes (Na_2SO_4 and KCl) have been made by continuous wave and pulse admittance methods, in cells with immersed, shiny Pt electrodes to study this transition. Peak conductance frequencies as a function of concentration did not conform to the classical circuit representation of a resistance and capacitance. Measured phase angles indicate that relatively concentrated electrolytes (0.001 - 1 M) exhibit inductance due to electromagnetic and perhaps mass (inertial) effects. Modelling was possible with a constant value of the inductance, L, and capacitance, C, using a simple RLC equivalent circuit. Ion and solvent perturbations in high frequency electrical fields first are discussed in terms of a damped harmonic oscillator model, whose macroscopic response is self-consistent and equivalent mathematically to RLC network. However, it is improbable that mass effects are sufficiently large to explain the majority of the inductance, which arises primarily from the transmission of energy through the solution. Obviously, the skin effects found in electrolytes will be distinct from those for metallic conductors.

INTRODUCTION

In condensed phases, the dissipation of electromagnetic radiation generally is complicated by a variety of concurrent processes, perhaps involving translational, rotational, vibrational and electronic transitions, e.g., consider the (uphill) emission of visible radiation from a bulb filament due to the passage of a direct electric current. Spectroelectrochemistry, in its broadest sense, can be defined to include those electrochemical methods in which the responses are analyzed on the basis of wavelength or frequency (1). We believe, accordingly, that the study of the electrical properties of electrolyte solutions at high frequencies may further our understanding of the conduction energetics of complicated systems, hopefully to ultimately enable the resolution and quantification of all of the discrete molecular contributions. Present day dielectric spectroscopies of ions or molecules in solution have ignored magnetic interactions, although it is well known that for frequencies in the range 1-100 MHz cell design becomes critical and inductive effects begin to manifest themselves, e.g., (2-4).

Physical theories of ionic mobility have been subdivided into continuum models and molecular approaches, e.g. (5). Most theoretical efforts, however, pertain to the difficult problem of ion transport through a solvent under dc or relatively low frequency conditions. In the so-called high frequency electrochemical methods ($f < 3$ MHz), the current response to a sinusoidal imposed voltage is attributed classically to the net rate of migration of the ions and the displacement of charge throughout the system (6). Admittance (Y) is interpreted in terms of the conductance (G) and the susceptance (B), which latter terms are in-phase and 90°-out-of-phase with the voltage, respectively. The former contribution, ascribed predominately to ion migration, converts electrical energy into heat. The frictional losses may be considered to involve both solvent (molecule)-ion and solvent-solvent collisions by which energy is dissipated as heat into rotational and vibrational energy levels. The susceptance is believed to arise mainly from the polarization of molecular electronic densities (induced polarization) and from the alignment of dipoles (orientation polarization). For electrochemical cells studied at these frequencies, there is generally no account taken of electrical inductance by which energy is stored as in the magnetic field of a coil.

Above a few MHz, however, effects due to self inductance of the electrochemical cell and its leads may arise (2). Certainly, a better understanding of ion dynamics at high frequencies (3-30 MHz)), very high frequency (30-300 MHz), and ultra-vhf (300 MHz - 3 GHz) electric fields is desirable. It is noted that classical electrolyte theories of frequency effects, such as that due to Debye and Falkenhagen (7,8), do not consider an inductance contribution (7,8), to the overall circuit response. This omission may explain, in part, the lack of definitive proof and understanding of high frequency effects in electrolyte studies (9). Unquestionably, there are many examples of experimental results in the literature that support the need for a more comprehensive analysis of loss mechanisms in high frequency electrolyte conductance measurements. Studies by Hasted and Roderick (10) and earlier work by Little and Smith (11) have reported increases in ionic conductivities at high frequencies, which they consider to be larger than those predicted by the Debye-Falkenhagen theory. Gorpinchenko (12) has studied the dielectric properties of KCl solutions in the 150-600 MHz frequency range and, again, it is concluded that the increase in conductivity found with frequency was much larger than that predicted by D-F theory. Similar results have occurred in the data of Scherbakov et al. (13,14), who recommend the use of measuring cells of the "electrodeless" condenser type for dielectric constant measurements. Finally, Ghowsi and Gale (9) have measured experimental deviations from the theoretical peak positions in conductance-concentration curves as the frequency is increased above 5 MHz. It should be noted that at frequencies below 25 MHz, the effects that arise on the dc solution resistance and capacitance (net dielectric constant) from DF theory predictions are only second order ones (7,9). In this paper, we discuss the classical under-

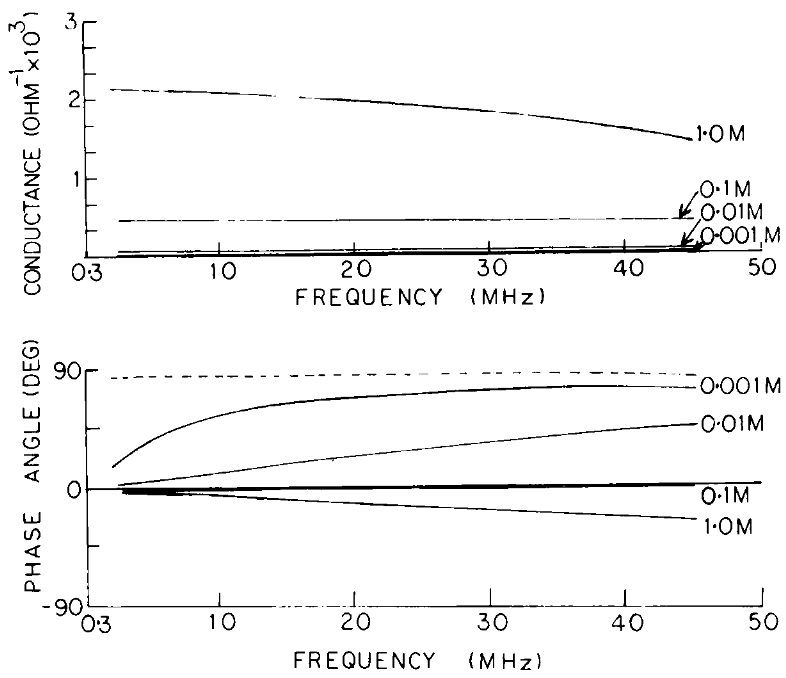


1. Conductances of aqueous KCl as a function of frequency and concentration in a traditional cell (lower to upper curves, 0.0011 M, 0.005 M, 0.01 M and 0.05 M).

standing of the responses of ionic solutions to imposed electromagnetic excitation and attempt to quantify the macroscopic magnetic behaviour of a simple aqueous electrolyte using network theory.

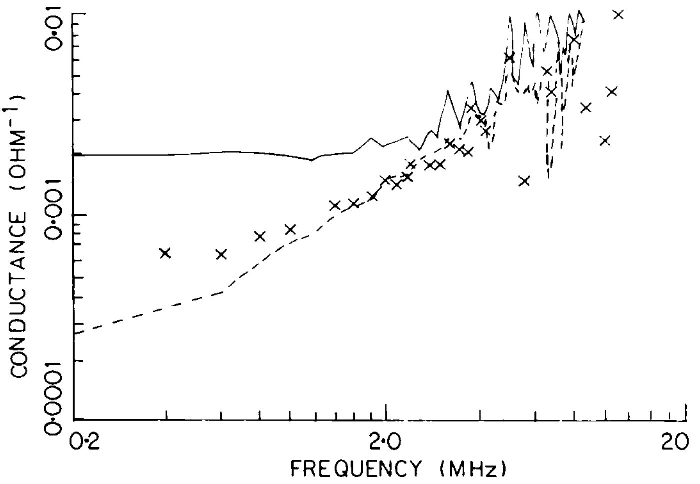
RESULTS

Figure 1 shows the conductance as a function of frequency and concentration for some aqueous KCl electrolytes, measured with a Hewlett Packard, model HP8753A Network Analyzer. This instrument has a facility to correct for lead impedance with a scaled passive circuit element correction. Its wide dynamic range (100 dB) permits use of very small amplitude sinusoidal



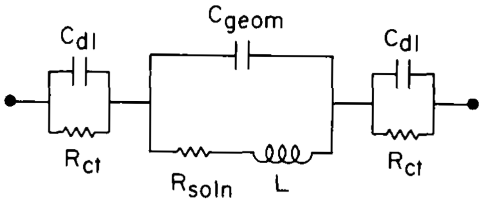
2. (a) Cell conductances of aqueous Na_2SO_4 electrolytes (25°C) measured by network analyzer, (b) phase angles of aqueous Na_2SO_4 electrolytes (dotted line - conductivity water); cell constant 0.026, approx. 0.42 cm I.D., shiny Pt electrodes.

excitation. With KCl and some other electrolytes tested, e.g., Na_2SO_4 and tetrabutylammonium iodide, a peak occurs at circa 2 MHz, whose shape and location depends on the geometry of the electrolytic cell. Because the traditional cell (shown in inset) has an ill-defined geometry, quantitative measurements described below were made using a columnar cell based on an nmr tube. The cell tested was chosen to minimize the Parker effect (4.6 cm long x 0.5 cm O.D.), and the cell geometric capacitance is estimated to be 0.2 pF. Figures 2(a) and (b) contain conductance and phase measurements of aqueous



3. Cell conductances of aqueous KCl electrolytes (25°C) calculated from a Fourier transform admittance (1 x 10^{-3} M solid line; 1 x 10^{-4} M crosses; conductivity water broken line); cell constant 10 conventional design, approx. 1.3 cm diam. shiny Pt electrodes.

Na_2SO_4 electrolytes prepared from purified (recrystallized) chemical and high purity conductivity water. The conductivity water behaved as expected in the limited frequency range of approx. 0.3-50 MHz, showing large resistance and almost pure capacitance (ϕ ~ 90°) throughout. Depending somewhat on cell design, solutions of KCl and Na_2SO_4 electrolytes of concentrations, 5 x 10^{-5} M - 1.0 M, all gave a broad conductance increase to peak in the region 1 - 10 MHz. We have confirmed this effect using complementary Fourier transform pulse measurements, figure 3 (upper frequency value was limited by the digitization (Nyquist) limit and the increase in error is due to fall off in amplitudes of the sinc function with frequency). This behaviour is not consistent with the response expected classically from a simple RC element (6), for which ϕ = 45° at the peak. Particularly, at 10 MHz for example, the



4. Equivalent electrical circuit for high frequency electrochemical cell (inductance and other elements due to the leads are not shown).

phase angle approaches zero with increase of concentration and becomes negative for 0.1 M electrolyte.

If, however, the circuit shown in figure 4 is considered, it becomes possible to model the experimental conductances and phase responses. An approximation is made to neglect the large double layer capacitance and faradaic reaction impedances at these high frequencies. Then, the circuit can be described in terms of passive elements by writing the impedance,

$$Z = \frac{1}{j\omega C + \frac{1}{R + j\omega L}} = \frac{R + j\omega L}{j\omega RC - \omega^2 LC + 1} \quad [1]$$

The admittance, Y, after rearrangement is given by

$$Y = \frac{(1 - \omega^2 LC + j\omega RC)(R - j\omega L)}{R^2 + \omega^2 L^2} \quad [2]$$

and the conductance, G, the real part of the admittance, by

$$G = \frac{R(1 - \omega^2 LC) + \omega^2 LRC}{R^2 + \omega^2 L^2} \quad [3]$$

If we denote, for simplication, the solution conductance R = 1/K,

$$G = \frac{K(1 - \omega^2 LC) + \omega^2 LKC}{1 + \omega^2 L^2 K^2} \qquad [4]$$

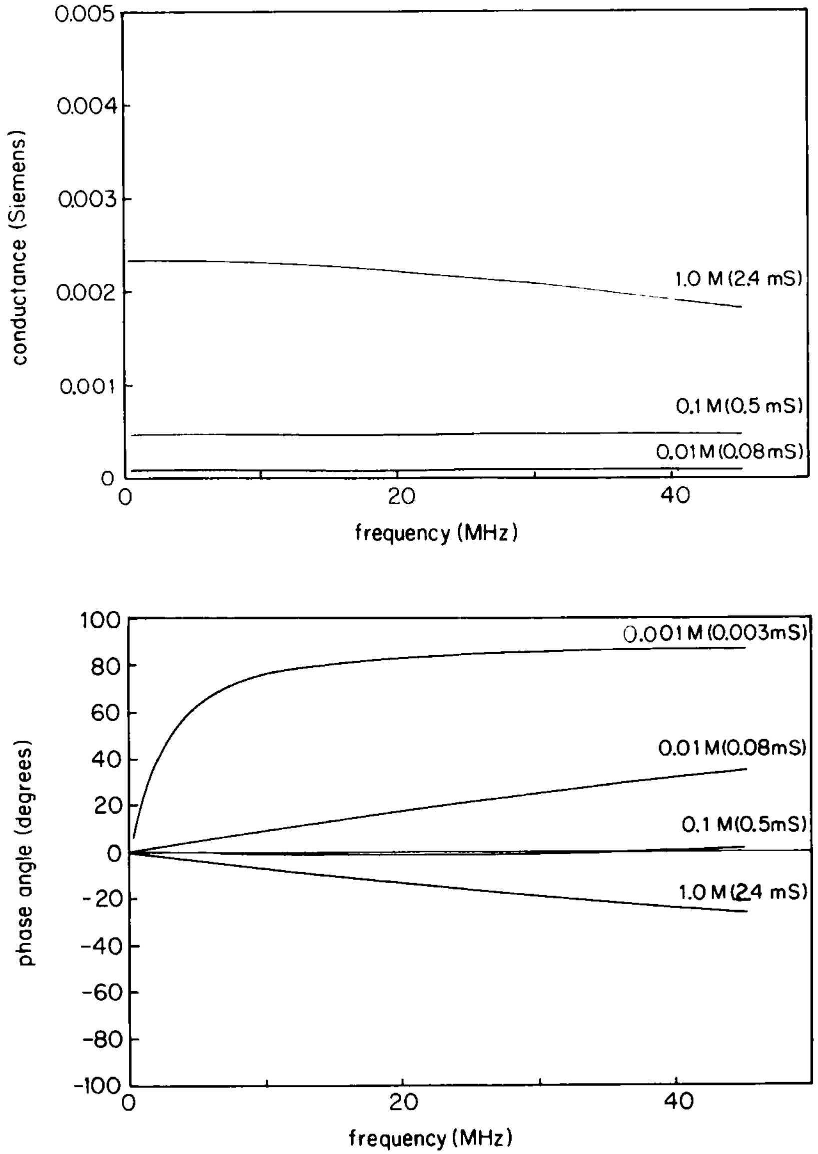
$$\phi = \tan^{-1} \frac{\omega C}{K(1 - \omega^2 LC)} - \tan^{-1} \omega LK \qquad [5]$$

where G represents the overall cell conductance and ϕ the phase angle, both measurable parameters. Note, that in terms of passive elements, there are three variables (R, L and C) that may be functions of frequency. If we further assume that the capacitance is a weak function of frequency and can be modelled by the dielectric constant of water (independent of salt concentration), then we can calculate the overall cell response by simulating the circuit response of figure 4. The results, shown in figures 5(a) and (b), closely model the experimental data of figures 2(a) and (b). Conductances used in the simulation were the experimental values obtained at 300 kHz, where $\phi \sim 0°$. The electrolyte inductance appears to be approximately constant for the concentration range investigated and its value is large (~ 1.7 μH/cm) compared to that for typical metallic conductors (~ 8 nH/cm).

DISCUSSION

The ability to unravel the various contributions to conductance depends upon satisfactory network models for the experimental cell. This task is not an easy one because the analytic responses may be nonlinear in comparison to aperiodic components. Nonetheless, in principle it is possible to substitute nonlinear values, of R and L for example, into circuit models and compute the overall response, cf. (9). The conductance may be modelled by using the Debye-Onsager relations, however, the validity of this extrapolation to high frequencies is not known.

If one considers the responses of ions to a very high frequency sinusoidal electric field, for example, the amplitudes of displacement are



5. (a) Simulated conductance of aqueous Na_2SO_4 electrolytes (25°C) based on C = 0.2 pF, L = 0.8 μH and G as shown, (b) simulated phase response using parameters given in 5(a).

extremely small and the mechanical analogy of a damped harmonic oscillator in forced motion may be appropriate,

$$(\ell + m)\,\ddot{x} + f\,\dot{x} + k\,x = F\,e^{i\omega t} \qquad [6]$$

where the real part of the driving force is given by the real part of $Fe^{i\omega t}$ (the imposed signal, $\ell\ddot{x}$ is the electromagnetic induction), $-\,f\dot{x}$ is the frictional force which may be a function of the amplitude as well as secondary molecular effects, and kx is the elastic restoring force(s). Using mechanical terms, the vibrating particle gives rise to a real part of the impedance, known similarly in electrical terms as resistance, and to imaginary (orthogonal) components known as reactance. Here the analogy to the classical treatment of electrochemical cells differs because this latter term comprises three contributions; the elastic reactance (e.g. ion-ion and ion-solvent interactions), the electromagnetic inductance, and inertial reactance (mass effect). We assign circuit elements as follows. Frictional forces due to the ion's oscillations and the solvent restructuring this produces represent the resistive element. Elastic (capacitive) contributions that might be present include solvent (molecule) rotation and polarization (Parker effect), solvated ion reorientation, as well as ionic interactions; ion-solvent collisional attractions/repulsions, solvent-solvent forces caused by the ion vibration, and long range ion atmosphere forces (D-F). Finally, electromagnetic inductive and mass inductive effects will be present, the latter due to ion and/or ion-solvent shell inertial components induced by the imposed field. Intuitively, it seems reasonable that the elastic and inductive contributions might increase relative to frictional losses as the frequency is increased, i.e., smaller net amplitudes cause less secondary solvent-solvent losses due to the ion dynamics.

A priori in eq (6), the parameters ℓ,f and k may be functions of frequency and even the equivalent mass, m of an ion is not easily estimated as a constant, as it may have single ion, solvated ion, or ion atmosphere mass properties. In his classical assessment of mass effects in electrolytes, Debye (15) noted that the dynamical masses due to ions are neglected because the frictional forces are so much larger (however, this argument was based on a "low frequency" value for f, the frictional coefficient for water, whose magnitude may be quite different from that for small amplitude oscillations. A detailed discussion has been presented by Zana and Yeager for the theoretical development of ion vibration potentials at high frequencies and it has been found experimentally that extremely small potential perturbations result (16). For the concentration range of aqueous Na_2SO_4 studied (0.01 M - 1.0 M), we are able to fit the data with a constant value of L but it is desirable to measure L precisely over a wider range of concentrations. Thus, we are at present unable to discriminate mass inertial effects (likely small) from the overall induction.

Qualitatively, however, the electromagnetic induction is physically distinct from that due to a metallic conductor of the same dimensions carrying the same current. Further studies of the transmission of electromagnetic radiation through electrolytes is highly desirable. Novel practical devices such as electrodeless conductivity detectors for liquid chromatography could be developed. Additionally, studies of the dispersion in permeability of condensed phases may be useful for the development of new spectroscopic methodologies.

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REFERENCES

1. Gale, R. J., in "Spectroelectrochemistry: Theory and Practice", Gale, R. J. (Ed.), Chapt. 1, Plenum Press, NY and London (1988)

2. Grant, E. H.; Sheppard, R. J.; South, G. P., "Dielectric Behaviour of Biological Molecules in Solution", Oxford University Press, 1978.
3. Pethig, R., "Dielectric and Electronic Properties of Biological Materials", John Wiley, Chichester (1979).
4. Kell, D. B., in "Biosensors: Fundamentals and Applications", Turner, A.P.F., Karube, I., and Wilson, G. S. (Eds.), Oxford University Press (1987), pp. 427-68.
5. Wolynes, P. G., Ann. Rev. Phys. Chem. 1980, 31, 345-376.
6. Reilley, C. N., in "New Instrumental Methods in Electrochemistry", Delahay, P. (Ed.), Interscience Publishers, Inc., 1954; Chapt. 15, pp. 319-345.
7. Harned, H. S.; Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Publ. Corp., 1943.
8. Falkenhagen, H., "Electrolytes", Oxford Publication, 1934.
9. Ghowsi, K.; Gale, R. J., J. Electrochem. Soc., 1989, 136, 2806-2811.
10. Hasted, J. B.; Roderick, G. W., J. Chem. Phys. 1958, 29(1), 17-26.
11. Little, V. I.; Smith, V., Proc. Phys. Soc. (London) 1955, B68,65; V. I. Little, ibid 357.
12. Gorpinchenko, I. M. Vestn. Mosk. Univ., Khun. 1969, 24(5), 110-111.
13. Ermakov, V. I.; Shchermakov, V. V.; Khubetsov, S. B., Elektrokhimiya 1976, 12(1), 133-136.
14. Shchermakov, V. V.; Ermakov, V. I., ibid 1977, 13(7), 1091-1092.
15. Debye, P., J. Chem. Phys. 1933, 1, 13-16.
16. Zana, R.; Yeager, E. B., "Modern Aspects of Electrochemistry No. 14", Bockris, J. O' M.; Conway, B. E.; White, R. E. (eds.); Plenum Press, N.Y. 1982; pp. 1-60.

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