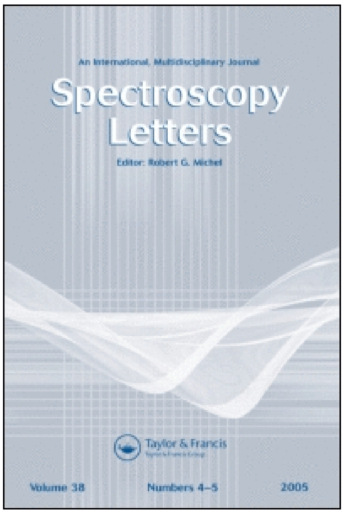

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Electric/Magnetic Cross-Field Investigations of Aqueous Electrolytes in the Dielectric Region 0.3 MHz-3GHz

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Preliminary Note

ELECTRIC/MAGNETIC CROSS-FIELD INVESTIGATIONS OF AQUEOUS ELECTROLYTES IN THE DIELECTRIC REGION 0.3 MHz-3GHz

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ABSTRACT

We are not aware of any techniques that have been developed to utilize the rotational magnetic properties of either ions or molecular dipoles in solution for analytical applications. Nor have any recent fundamental studies attempted to detect specific permeability dispersion of solutions in the upper-UHF region. The electromagnetic spectral regions which extend from high frequencies (MHz) to microwaves (THz) are presently used for liquid/solid nmr studies, esr studies, microwave spectroscopy of gases, and dielectric spectroscopy of electrolytes and solids. However, the effects of a magnetic field on the rotational behaviour of certain molecules, functional groups, and ions in solution also could be investigated using methodologies based on inductive coupled measurements from cross-field excitation. Some preliminary data are presented which indicate that a 1T magnetic field can cause what appears to be inductive peaks in concentrated aqueous lithium nitrate at approximately 0.84 and 2.14 GHz. Further studies are necessary to ascertain the origin of such phenomena, which are perhaps atomic nuclei relaxation and/or molecular effects.

INTRODUCTION

Electrolytes, as a class of conductors, can behave analogously to dielectrics (or insulators) and conductors, depending on the frequency. Of course, the transport of charge in electrolytes is due to ionic rather than electronic (metallic) conduction. The foundations and theories for the behaviour of dielectric media with electromagnetic radiation are outlined in such classical texts as Van Vleck (1), Frohlich (2), and Von Hippel (3). Traditionally, the dielectric properties of matter are described macroscopically, or on a microscopic (molecular) basis, in terms of polarization, magnetization, and conduction with a complex permitivity ε^* and permeability μ^*. Except in NMR and ESR spectroscopies, or unless Zeeman or associated effects are to be observed in microwave vapor measurements with a static magnetic field,the permeability is taken to be one and the magnetic properties of matter are neglected. This is especially true in all solution dielectric spectroscopy analyses (4-6). Classical texts such as Frohlich do not mention magnetic energy losses in dielectric dispersion phenomena. Van Vleck's earlier book, on the other hand, does discuss the effect of a magnetic field on the dielectric constant. It is concluded that a magnetic field strength of about 1T would change the electrical susceptibility by about one part in 10^7 at ordinary temperatures, an effect too small to be detected with the instrumentation available at that time.

Let us now consider why molecular and ionic magnetic effects may be utilizable for the development of novel spectroscopies for investigating solvents and analyzing solutions of dipolar ions and molecules. Relaxation polarization in liquids is reviewed in texts (1,2) and need only be briefly summarized here. The solution of Maxwell's field equations for the propagation of an electromagnetic wave through matter as a function of direction x and time t provide a plane wave described by:

$$E = E_0 e^{j\omega t - \gamma x} \tag{1}$$

$$H = H_0 e^{j\omega t - \gamma x} \tag{2}$$

in which γ is a complex propagation factor,

$$\gamma = j\omega\,(e^{*}\,\mu^{*})^{1/2} \tag{3}$$

that comprises the angular frequency w, the complex permittivity ε^{*}, and a complex permeability μ^{*}. At optical frequencies, the propagation factor γ used by the communications engineer is replaced by the complex index of refraction (3). Debye's theory assumed that the resistance to the orientation of molecules to incident fields arises primarily from a viscous force which is taken to be proportional to the angular velocity rather than angular acceleration. In consequence, an incident field would not have an appreciable orientating influence on molecules in a liquid unless the incident wavelength were so long as to be in the short radio rather than the far infrared. Thus we might expect appreciable dissipation in the UHF excitation range and less at higher frequencies closer to optical wavelengths. The ratio of the coupled electric and magnetic field vectors defines the intrinsic impedance of the dielectric and both ε^{*} and μ^{*} are complex in any medium that causes losses (ε^{*} and μ^{*} are interdependent),

$$E/H = \gamma/j\omega\varepsilon^{*} = Z \tag{4}$$

In general, the two complex parameters require four independent measurements; however, usually the approximation is possible to neglect the weak magnetic polarization in nonmagnetic materials. As outlined below, this results in a loss of valuable information.

A dielectric material can react to an electric field because it contains charge carriers that can be displaced. Additionally, atoms and molecules carry permanent magnetic moments that assume quantized orientations in an external magnetic field. Von Hippel has characterized polarization by an electronic polarizability, σ_a, an atomic polarizability, σ_a, and an orientation (dipole) polarizability, σ_d. When charge carriers such as solvated ions are impeded in their motion, a space charge polarization, σ_s, also can be present. The total polarizability is given by the general Clausius-Mossotti-Lorentz-Lorenz equation (3), however for the case of liquids because of local interactions only a scaled rather than an exact solution results, cf., Kell (6). In other words a pure polar liquid cannot be modelled quantitatively in microscopic theory with the standard Langevin-Debye formulism. Magnetic fields arise from charges in motion and those due to the presence of nuclear magnetic moments and unpaired electrons are well known. Magnetic relaxation must additionally be associated with the other forms of electronic polarization listed above, especially the rotation of molecular dipoles. It is the detection and characterization of such effects that was the objective of these preliminary experiments.

In the past, the electrical circuit equivalent for a liquid as an LRC shunted by a capacitor has been replaced by an RC shunted by a capacitor because it is generally assumed that the acceleration (inductance) term may be neglected. It has been demonstrated experimentally, however, that liquid electrolytes should be modelled as an LRC at frequencies above 1 MHz (7). The presence of a large inductive field means that it is relatively facile to use inductive coupling, as in nmr, to investigate the energy dissipation as a function of frequency.

An estimate of the distance an ion travels in a high frequency field is possible using a constant velocity model. Even the most mobile ion in aqueous solution, hydrogen ion, would oscillate with an amplitude of only 0.02Å at 1 MHz in an electric field 0.1 V/cm, based on its mobility in infinitely dilute solution (3.625 x 10^{-3} $cm^2/s.V$), if it is assumed that it travels at this constant limiting velocity.

RESULTS

Figure 1 illustrates the arrangement for the simple cross field experiment. The magnet was a laboratory susceptibility magnet with poor field uniformity but capable of fields from 0 to 1.0 T (these were approximately calibrated with a commercial Hall Effect device). The cell was a 10 cm length of nmr tube fitted with planar bright platinum electrodes at each end and inserted in 50 Ω coaxial cable. The HP analyzer provided a frequency sweep output (R) applied to one of the cell electrodes. B measures the absolute power amplitude at input B, R measures the absolute power amplitude at output R which is the source phase locking port, and B/R - M represents difference measurements for the magnetic field on/off (M is a memory stored sweep). The response signal B was detected with a 40 or 5 turn copper wire solenoid connected to 50 Ω cable.

Figure 2 is an example of a dielectric spectum recorded with the cell filled with saturated lithium nitrate solution. Two broad peaks appeared with only 128 averages due to the

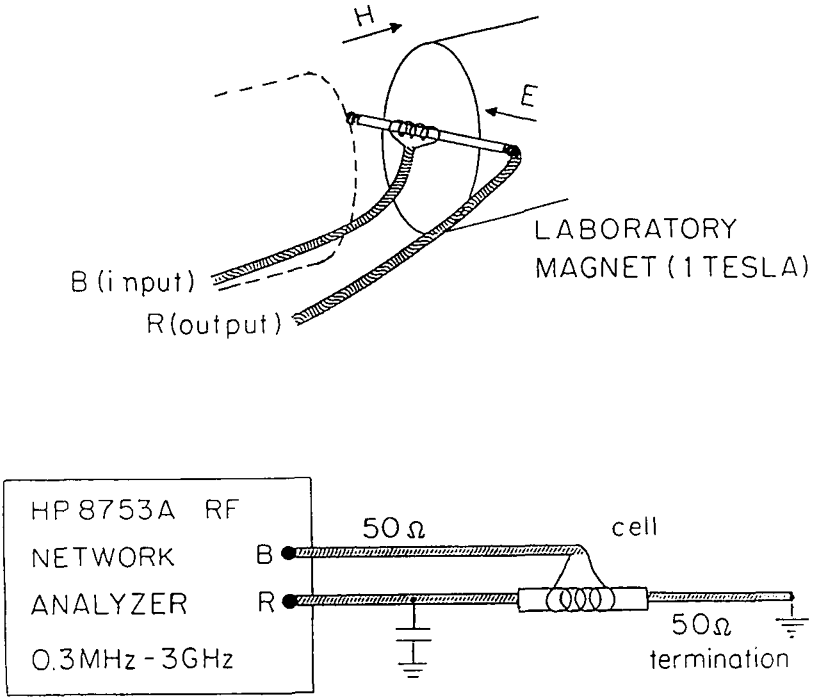

Figure 1. Experimental arrangement for electric/magnetic cross field measurements.

field at 0.84 GHz and 2.14 GHz, which have the expected profile for an LC resonance (at plus or minus 10% from resonant frequency, current is substantially unaffected). A 335 pF variable capacitor was placed in parallel with the cell, but would resonate with this coil at ~2 MHz, so is not close to the observed peaks. The field used was about 1T and the signals were not especially sensitive to the power of the electromagnetic source wave, but they were larger if the cell was not terminated to ground and they were proportional to the magnetic field strength. Interestingly, the ratio of NMR resonance frequencies, $\nu_{Li^6}/\nu_{Li^7} = 0.38$ (44.162 and 116.626 MHz at 7.05T), which compares with 0.39 for the observed induction peaks. The overall profile has the appearance of fine structure, which seems evenly spaced. If this is the case, the nuclear spins of 1 and 3/2 for Li^6 and Li^7 may have split by a factor of 2 to 6 and 8 peaks on a broad background, respectively. A reproducible, narrower peak was observed at ~770MHz in

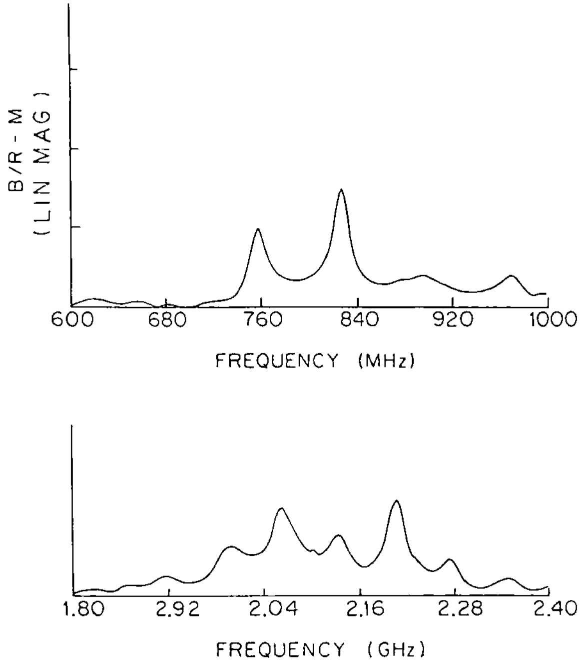

Figure 2. Dielectric spectra for the frequency ranges 600-1000 MHz and 1.80-2.40 GHz of saturated $LiNO_3$. B/R-M represents a difference spectrum between the magnetic field on (B/R) and off (M, stored sweep).

0.1M $LiNO_3$, without the external capacitor. Similar tests were made with the cell containing conductivity distilled water (Gilmont High Purity still) and peaks, which we cannot assign at this time, occurred at 157, 613, 1348, and 1939 MHz with water but not at the frequencies observed in lithium nitrate solutions. Since the frequencies of precession of nuclei in the Larmor relation are directly proportional to the magnetic field, H_0, the nuclear frequencies associated with Li^6 and Li^7 in a 1T field should be 6.26 and 16.5 MHz, respectively. Clearly, the frequencies observed in these experiments occur at much higher energies (x132) and may be caused by a natural, bulk circuit resonance, or other effects. A quantitative understanding of which circuit elements contribute to the observed effects may be possible with additional study of the experimental parameters of chemical composition and cell design.

CONCLUSIONS

One of the questions to be addressed by these investigations and our previous work [7] is the microscopic (molecular) nature of the bulk inductance found with electrolytes. Following the nomenclature of Schumacher [8], angular momenta may be labeled s for single electron spins, **L** for electron orbits, **I** for nuclei, and **F** = **I**+**L**+**s** for atoms. For rotating molecules or functional groups, there are also identifiable momentum vectors which we can label **M**. One explanation for the observed experimental resonances might be that the magnetic field causes preferential alignments of both rotating water (collective atomic) dipoles and lithium nuclei. An energy exchange system between these in the form of nuclear spin absorption representing a circuit inductance, ΔL, and a change in the dielectric property of the medium caused by rotating molecular alignment (ΔC) might account for the resonances. Nuclear spin relaxation to the lattice may be due to dipolar relaxation, chemical shift anisotropy, and spin rotation relaxation with the latter most likely to contribute to major bulk circuit property changes. However, further experimental work is needed to substantiate these effects and determine which fundamental system interactions are responsible for the electrical phenomena.

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