PROTON NMR RELAXATION IN HYDROUS MELTS*  
J. Braunstein, A. L. Bacarella, B. M. Benjamin,  
L. L. Brown, and C. Girard**  
Chemistry Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830  

ABSTRACT  
Pulse and continuous wave NMR measurements are reported  
for protons in hydrous melts of calcium nitrate at tempera­  
tures between -4° and 120°C. Although measured in different  
temperature ranges, spin-lattice (T1) and spin-spin (T2) re­  
laxation times appear to be nearly equal to each other and  
proportional to the self-diffusion coefficients of solute  
metal cations such as Cd2+. At temperatures near 50°C mean  
Arrhenius coefficients, ΔH (kcal/mol), are 7.9, 7.3, and  
4.8, respectively, for melts containing 2.8, 4.0 and 8.0  
moles of water per mole of calcium nitrate, compared to 4.6  
kcal/mol for pure water. Temperature dependence of T1 and  
T2 in Ca(NO3)2·2.8 H2O between -4 and 120°C are non-Arrhenius  
and can be represented by a Fulcher-type equation with a  
"zero mobility temperature" (T0) of 225 K, close to the value  
of T0 for solute diffusion, electrical conductance and vis­  
cosity. Resolution of the relaxation rates into correlation  
times for intramolecular (rotational) and intermolecular  
(translational) diffusional motion is discussed in terms of  
the Bloembergen-Purcell-Pound and more recent models for  
dipolar relaxation.  

INTRODUCTION  
Hydrous melts are highly concentrated aqueous electrolytes which  
may be characterized as molten salts containing water in amounts insuf­  
ficient to form hydration shells about the ions and an intervening  
hydrogen bonded solvent structure. They include the hydrate melts,  
which are fused stoichiometric hydrates such as Ca(NO3)2·1H2O and  
CaCl2·6H2O, as well as melts of nonstoichiometric composition of both  

*Research sponsored by the Energy Research and Development Adminis­  
tration under contract with Union Carbide Corporation.  

By acceptance of this article, the publisher or recipient acknowl­  
edges the U. S. Government's right to retain a non-exclusive, royalty­  
free license in and to any copyright covering the article.  

**Visiting scientist, Centre College, Danville, Kentucky.
higher and lower water content. Thermodynamic, transport and theoretical investigations of hydrous melts have demonstrated the usefulness of molten salt models in understanding the behavior of concentrated electrolytes in the region where the structure is predominantly an ionic distribution perturbed by water molecules, rather than a hydrogen bonded structure perturbed by ionic charges (1). A basic understanding of such electrolytes, is important not only for theoretical reasons but also because the properties of these melts lend themselves to application in a number of developing technologies, including: geothermal systems, some geothermal brines being very concentrated electrolytes; thermal energy storage with Glauber’s salt or sodium thiosulfate; high temperature fuel cells (water is an anode product and a proposed cathode gas additive in molten carbonate fuel cells); interactions of water with magmas; improved water electrolyzers for hydrogen production; and thermochemical cycles for hydrogen production, in which steam-molten salt reactions may be invoked (2).

Transport studies of hydrous melts have been concerned largely with bulk properties such as the shear viscosity or electrical conductance (3). Diffusivities have been reported for dilute solute cations dissolved in hydrous melt solvents, (4,5) but little attention has been given to diffusivities or mobilities of water in hydrous melts. Proton chemical shifts have been reported for some hydrous melts (5) but these provide no information on transport properties. Nuclear spin relaxation measurements have been carried out on less concentrated aqueous electrolytes approaching the hydrous melt range (6) as well as on protons of nitric acid dissolved in molten nitrates (7) and of alkali metal ions in molten nitrates (8), but the application of this method to transport studies of hydrous melts has not been reported.

In this paper we report new measurements concerned with water transport properties in hydrous melts. We have determined spin-lattice and spin-spin relaxation times of protons, using pulsed and continuous wave NMR measurements, as a function of water content and temperature. The temperature dependence and the dependence of water concentration are compared with those for other transport and thermodynamic properties of hydrous melts. We present preliminary results on the resolution of the observed relaxation rates in terms of correlation times for intramolecular (rotational) and intermolecular (translational) motion.

EXPERIMENTAL

Sample Preparation. Hydrous melt samples of Ca(NO₃)₂·RH₂O, where the mole ratio of water, RH₂O moles of water per mole salt, was between 2.8 and 16 were prepared in 5 mm NMR tubes. The melts were prepared from anhydrous salt which had been dehydrated in a desiccator containing Mg(ClO₄)₂ under vacuum (less than 50Pa) at ambient temperature for
at least a week (9). The desired composition was prepared by the addition of a calculated amount of triply distilled water to a weighed amount of the anhydrous salt (ca. 10 g) in a stoppered 25 or 50 ml Erlenmeyer flask. The salt-water mixture was then melted to a clear solution. The 5 mm NMR tubes were loaded with approximately 0.5 ml of the hydrous melt. Loading the tubes with the more concentrated hydrous melts, \( R = 2.8 \) or 4.0, required the melt, tube and delivery tube to be heated. Prior to sealing, oxygen was removed by repeated evacuation of the samples frozen in a trichloroethylene-dry ice mixture (liquid nitrogen provided too great a thermal shock and led to breakage of the tubes).

**Instrument.** NMR measurements were carried out with a Varian XL-100 NMR spectrometer with the Nicolet TT-100 Fourier Transform Accessory, with a magnetic field of 23.490 Kgauss and a frequency of 100 MHz. Spectra were obtained at temperatures ranging from -20°C to 120°C by using the variable temperature accessory for the XL-100. Spin lattice relaxation times, \( T_1 \), were obtained from pulsed measurements with a 180°-\( \tau \)-90° pulse sequence (10). Spin-spin relaxation times, \( T_2 \), were obtained from measurements of the width at half height of continuous wave (CW) measurements (11). It is estimated the uncertainties in \( T_1 \) and \( T_2 \) are ±10% and ±20% respectively. Temperatures were determined from the separation of the hydrogen resonances, in ethylene glycol above 35°C, and in methanol below 35°C. It is estimated that the uncertainty in temperature is ±1°C.

**RESULTS**

**Relaxation Times.** Values of the proton spin-lattice relaxation time, \( T_1 \), and of the spin-spin relaxation time, \( T_2 \), are listed in Table I for the melt of composition \( R_{H_2O} = 2.8 \) at temperatures between -4°C and 120°C. Measurements at temperatures between 35°C and 100°C were made also on melts of composition \( R_{H_2O} = 4.0, 8.0 \) and 16.0.

The values of \( T_1 \) were obtained from the spectrometer's computer evaluation of the free induction decay of the signal amplitude in the 180°-\( \tau \)-90° pulse sequence (10,11). With decreasing temperature (or decreasing water content) the relaxation times decreased, and line broadening led to a decrease in sensitivity. In this region values of the spin-spin relaxation time, \( T_2 \), were calculated from the width at half height of the continuous wave resonance peaks, a typical one being shown in Fig. 1. In this initial study, unfortunately, values of both \( T_1 \) and \( T_2 \) were not determined at the same temperatures. Nevertheless, as will be seen, the indications are that \( T_1 \) and \( T_2 \) are very nearly equal in the high temperature (long relaxation time) region.

**Composition Variations.** Although the composition dependence of the relaxation times will be dealt with in more detail in a subsequent paper, the general character of the composition dependence is indicated...
in a plot of the mean Arrhenius energies, in the temperature range 35-100°C shown in Fig. 2 in comparison with: the water concentration dependence of the diffusion coefficient (logarithmic) of dilute massive solute ions, Cd^{2+} (12); the enthalpy of vaporization of water from hydrous melts, and the free energy of association of dilute solute ions in hydrous melt solvents (9). Although a quantitative relation between the concentration dependences of the thermodynamic and transport properties may not yet be available, both reflect the change of behavior in the range of concentration between aqueous solution and molten salt. The transport properties, however, appear to show a greater variation with composition than the thermodynamic properties.

Temperature Dependence. Fig. 3 shows the variation of T_{1} with temperature in the melt Ca(NO_{3})_{2}·4H_{2}O along with values of the fluidity (3), cadmium ion diffusivity (12), and equivalent conductance (13). The striking parallel between the behavior of the relaxation times and the macroscopic transport coefficients suggests that the same mechanism applies.

Although the Arrhenius equation can be fitted to the data over a limited range of temperature to provide mean activation energies for relaxation, measurements over an extended temperature range show marked deviations from Arrhenius behavior, as is the case for the macroscopic transport coefficients. A Fulcher-type equation was fitted to the combined spin-lattice and spin-spin relaxation times for samples with RH_{2}O = 2.8 at temperatures between -4 and 120°C

\[
\{T_{1}, T_{2}\} = A T^{-1/2} e^{\frac{-k}{T-T_{0}}}
\]

in which the parameter T_{0} represents a hypothetical "zero-mobility temperature" (13). Because of the high degree of correlation of the parameter values, it is convenient to fix either k or T_{0} in comparing values of the other among differing systems or differing properties. The value k = 649.5 obtained for diffusion data in Ca(NO_{3})_{2}·4.09 H_{2}O (14) leads to the values A = 661.3 ± 59 and T_{0} = 224.9 ± 0.9 with a standard error of fit of 21.3%. This error is due in part to a slight mismatch in the joining of the high temperature T_{1} data with the low temperature T_{2} data as well as the possible start of low temperature levelling off of the T_{2} data, as seen in Fig. 4. The data point at the lowest temperature (and smallest T_{2}) was excluded from the computer fit, as were the T_{1} data at temperatures below 70°C.

Because of the experimental uncertainty in the lower temperature T_{1} data, it is not certain whether the minimum and upturn indicated by the dashed line are real or an artifact, but both a minimum in T_{1} and a levelling of of T_{2} with increasing viscosity (decreasing temperature) would be expected from the elementary theory of nuclear magnetic relaxation via dipolar coupling, and has been observed for proton magnetic relaxation in glycerol (15). It may be seen also that, the temperature dependence of the relaxation times is very close to that estimated for
the viscosities. Experimental values of the viscosity of the melt \( \text{Ca(NO}_3\text{)}_2 \cdot 2.8 \text{ H}_2\text{O} \) are not available, but the lower curve in Fig. 4 was calculated from a short extrapolation of viscosity data in melts with \( R_{\text{H}_2\text{O}} = 4.0, 6.0, 8.0 \) and 10.0 to which a Fulcher equation had been fitted over the viscosity range \( 10^{-1} \) to 10 poise (3). Smooth curvilinear extrapolation of the pre-exponential factor (\( A \)) and of \( T_0 \), and linear extrapolation of the exponential parameter (\( k \)) led to the equation from which the lower curve was calculated

\[
\eta_{R_{\text{H}_2\text{O}}=2.8} = 0.00365 e^{-650/\left(T-223\right)}.
\]

The parameter values (except for the pre-exponential factor, which is a scale factor) are thus quite close to the values representing the temperature dependence of the relaxation times, and also to the values of the parameters describing the temperature dependence of cadmium ion diffusivity (12) in this melt, \( T_0(D_{\text{Cd}}) = 231.1 \), \( k = 650 \).

**DISCUSSION**

A quantitative test of models with these preliminary results may be premature in view of some experimental uncertainty in the behavior for the shortest relaxation times and the absence of needed information on water diffusivity in the melts (as well, perhaps, as direct experimental measurements of the viscosities). Nevertheless, a number of qualitative conclusions may be drawn, and the application of some proposed models of relaxation may be instructive.

**Grotthus Mechanism.** First, the results demonstrate clearly parallel behavior of the proton relaxation times and the macroscopic transport properties. To the extent that the proton spin-lattice relaxation may be governed by the same mechanisms governing diffusion of more massive solute metal ions (such as \( \text{Cd}^{2+} \)) in the solution, the results suggest that the Grotthus chain mechanism for the anomalously high proton mobilities in aqueous solutions is not operative. This is not unreasonable since, as the water content of a solution decreases, proton transfer could be expected to become less significant than water molecule diffusion as a mode of proton transport. Polarographic measurements of limiting currents for hydrogen reduction as compared to dilute solute metal ion reduction in concentrated lithium halide solutions are consistent with this (16). Experiments with hydrous melts "doped" with nitric acid (at concentrations of about 0.01 molar) showed little difference in the relaxation times. However as pointed out by McCall and Douglass (17), the Grotthus mechanism applies to the mobility of excess protons over those "bound" in the water structure in dilute solutions. Since the measured relaxation time is an average for all the protons, bound and unbound, the number of excess protons may have been insufficient in our measurements to distinguish "excess" protons. Spin-echo measurements of proton diffusion coefficients in pure water
are in essential agreement with tracer diffusion coefficients, but are lower than the "excess proton" diffusion coefficients calculated by application of the Nernst-Einstein equation to the limiting ionic conductance of hydrogen ions in solution. The same may occur in hydrous melts, with the added complication that, in the absence of a hydrogen bonded structure, a larger concentration of excess protons may be required before a Grotthus mechanism can occur.

BPP. A model of spin-lattice relaxation has been proposed by Bloembergen, Purcell and Pound (15) for the dipole-dipole coupling mechanism for relaxation, based on a single correlation time, $\tau_c$, proportional to the macroscopic transport properties such as the temperature reduced viscosity, $\eta/T$, or by the reciprocal diffusivity, $1/D$. This model, which is oversimplified (18) in that it assumes the Stokes-Einstein equation and neglects the possibility of a distribution of correlation times, corresponding to a cooperative rather than to a single-event transport mechanism (19) leads to the relation for the rotational or intramolecular part of the relaxation rate

$$\frac{1}{T_{1\text{rot}}} = K_1 \left[ \frac{\tau_c}{1 + 4\pi^2 \omega_0^2 \tau_c^2} + \frac{2 \tau_c}{1 + 16\pi^2 \omega_0^2 \tau_c^2} \right]$$

where $K_1$ is a constant comprised of the nuclear spin, gyromagnetic ratio and "molecular size" constant $\omega_0$ is the radiofrequency, and $\tau_c$ is the correlation time, $\tau_c \propto \eta/T \propto 1/T$. For nuclei of spin $1/2$, like the proton in water, the dipole-dipole relaxation mechanism predominates over other modes of relaxation such as those arising from quadrupole or spin-rotational coupling, and paramagnetic impurities. In deoxygenated calcium nitrate hydrous melts, only nitrogen (besides the water protons and isotopes of H, Ca and O) has a nuclear spin and is therefore capable of interacting with the proton nuclear spins. Equation 3, as well as a treatment of the translational or intermolecular contribution to the relaxation rate, predicts that a plot of the logarithm of the spin-lattice relaxation time versus the logarithm of the correlation time ($\eta/T$, $1/D$) should have a negative slope of unity at short correlation times (high temperature, high fluidity) and a positive slope at long correlation times (low temperature, low fluidity). Figures 5 and 6 show plots of $\log T_1$ vs. $\log 1/D_{Ca}$, and of $\log T_1$ vs. $\eta/T$ for Ca(NO$_3$)$_2$-2.8 H$_2$O. Lines of unit slope are drawn through the high temperature points. The rise at low temperatures is not well defined because of the loss of sensitivity, but the minimum appears to occur at a relaxation time of about 0.1 sec. This is comparable with the relaxation time at the minimum in the classical measurements of proton relaxation time in glycerol by Bloembergen (when the difference of frequency is accounted for).

According to BPP (15), the minimum occurs when $\omega_0 \tau_c = 1/\sqrt{2}$ and the ratio of $T_1/T_2$ at this minimum is 1.6. The intersection of the $T_2$ slope ($45^\circ$) with the $T_2$ plateau ($0^\circ$) should occur at $\tau_c = T_2^{45^\circ} / \sqrt{2}$. 

549
If, as is likely, there is distribution of correlation times resulting from the different molecular environments experienced by the nucleus during relaxation then the minimum value of $T_1$ will increase with decreasing sharpness of the curve at the minimum point with an increasing ratio of $T_1/T_2$. It would thus be desirable to extend the low temperature measurements in this system to ascertain with greater accuracy the position of the minimum of $T_1$ and the levelling off of $T_2$.

Resolution of Intramolecular and Intermolecular Motion. Hertz (20) has discussed the application of nuclear magnetic relaxation measurements to the evaluation of hydration numbers in ionic solution. In hydrous melts such as Ca(NO$_3$)$_2$-2.8 H$_2$O, where there is less than one water molecule per ion, the significance of the concept of hydration number is questionable. It is of interest however, to consider the contribution to the measured relaxation rates of intramolecular (rotational) and intermolecular (rotational and translational motion).

The BPP treatment (15) provides a starting point, but their treatment of the intermolecular relaxation can be regarded as only semi-quantitative (21), and important modifications have been made by Torrey (21) using the theory of random walk, and modified or extended further by Hubbard (22), Kubo and Tomita (23), Kruger (24), Harmon and Muller (25) and others, as discussed by Fiorito and Meister (26). The BPP treatment is further complicated by the variety of intra and intermolecular hydrogen distances used in the theoretical calculations and the lack of direct experimental evidence on the magnitude of the intra and intermolecular relaxation processes (26). Fiorito and Meister (26) concluded from their studies on hydrogen-bonded liquids that the intramolecular contributions to $T_1$ and $T_2$ can be neglected. A plot of experimental $T_1$ and $T_2$ in Ca(NO$_3$)$_2$-2.8 H$_2$O melts at various temperatures versus estimated correlation times is shown in Fig. 7 for several different estimates of $\tau_c$.

The rotational correlation times, $\tau_{rot}$, were calculated from the rotational relaxation rate

$$\frac{1}{T_1}_{\text{rot}} = \frac{3}{2} \frac{\gamma^4 \mu^2}{b^6} \tau_{rot}$$

after subtracting the estimated intermolecular relaxation rate from the total relaxation rate $1/T_1$ (15). In Eq. (4) $\gamma$ is the gyromagnetic ratio of the proton, $\mu$ is Planck's constant and $b$ is the distance between spins (protons) in the water molecule, taken as 1.52 Å. $\tau_{rot}$ also was estimated from the viscosity with Debye's equation for dielectric dispersion in polar liquids (15)

$$\tau_{rot} = \frac{1}{3} \tau_{\text{Debye}} = \frac{4}{3} \pi \eta a^3/k T$$

assuming an H$_2$O molecular radius, $a$, of 1.38 Å, using viscosities extrapolated from the data of Ambrus, Moynihan and Macedo (3); and finally from $\tau_c = a^2/6 D$, assuming $a = 1.38$ Å for H$_2$O and approximating
the rotational self-diffusion coefficients $D_{\text{r}}$ by the Cd$^{2+}$ diffusion coefficients obtained for Ca(NO$_3$)$_2$-2.8 H$_2$O melts (12). The Kruger equations (24) for the diffusive limit (mean jump length $<<$ distance of closest approach), as given in (26) and shown in figure 7, were used to estimate $(1/T_1)_{\text{inter}}$ for the two limiting cases $\omega T << 1$ and $\omega T >> 1$; and, in the absence of water diffusion coefficients in Ca(NO$_3$)$_2$-2.8 H$_2$O, $D$ was taken as the Cd$^{2+}$ diffusion coefficient (12). Equation (4) is the limiting relation for the regime $\omega T << 1$, i.e., for short correlation times (low viscosity, high temperature, long relaxation times), and thus provides no information on the minimum.

Application of the BPP theory and its modifications to water at 30°C yields intramolecular correlation time estimates of $0.25 \times 10^{-11}$ sec. to $0.263 \times 10^{-11}$ sec. and intermolecular correlation times of $0.23 \times 10^{-11}$ sec. to $0.64 \times 10^{-11}$ sec. Application to the spin-lattice relaxation times in the Ca(NO$_3$)$_2$-2.8 H$_2$O melts at 121°C yields intramolecular correlation times in the range $0.318 \times 10^{-11}$ to $0.802 \times 10^{-11}$ sec. and intermolecular correlation times of $3.62 \times 10^{-11}$ sec. to $18.4 \times 10^{-11}$ sec. These preliminary results indicate that the intermolecular correlation times are greater than the intramolecular correlation times by a factor of approximately ten in Ca(NO$_3$)$_2$-2.8 H$_2$O melts. Although the calculations are based in part on the application of macroscopic concepts of viscosity and diffusion to motion on a molecular scale, and although the correlation times for translation (motion over a distance of the order of a molecular diameter) and rotation (rotation through $180^\circ$) are not directly comparable, the order of magnitude difference, as compared to liquid water, would appear to have at least qualitative significance. The greater freedom for rotation than for translation in melts of such high charge density suggests that the effect of electrostriction is analogous to the effect of high pressure on relaxation in liquids (27).

CONCLUSIONS

Spin-lattice and spin-spin relaxation times have been measured for hydrous melts Ca(NO$_3$)$_2$-RH$_2$O, and show concentration and temperature dependences similar to those for the macroscopic transport properties. Estimates of rotational and translational correlation times, based on models for magnetic dipolar relaxation, suggest an order of magnitude greater degree of freedom for rotation than for translation in Ca(NO$_3$)$_2$-2.8 H$_2$O at 120°C ($\omega \tau \ll 1$). Low temperature results suggest that the region $\omega \tau \approx 1$ is accessible to measurement in hydrous melts, and our new techniques should provide higher precision. Additional relaxation measurements over a wide range of water contents, together with spin-echo measurements of water diffusivities, measurements with paramagnetic ions to provide shorter relaxation times, and with
quadrupolar nuclei should prove useful in resolving intermolecular and intramolecular motions of water molecules in hydrous melts.

ACKNOWLEDGMENT

One of us (JB) would like to acknowledge useful suggestions by Dr. D. Harold-Smith.
Table I. Temperature Dependence of Proton Spin-Lattice ($T_1$) and Spin-Spin ($T_2$) Relaxation Times in Ca(NO$_3$)$_2$-2.$\bar{8}$ H$_2$O$^*$

| $t/°C$ | $1000 K^{-1}$ | $T_1/s$ | $t/°C$ | $1000 K^{-1}$ | $T_2/s$ |
|--------|---------------|---------|--------|---------------|---------|
| 120.4  | 2.54          | 0.71    | 44.5   | 3.15          | 0.0315  |
| 101.2  | 2.67          | 0.43    | 34.7   | 3.25          | 0.0188  |
| 90.6   | 2.75          | 0.30    | 33.7   | 3.26          | 0.0105  |
| 84.1   | 2.80          | 0.243   | 27.0   | 3.33          | 0.0046  |
| 79.1   | 2.84          | 0.22    | 21.1   | 3.40          | 0.0047  |
| 77.9   | 2.85          | 0.21    | 19.4   | 3.42          | 0.0031  |
| 71.8   | 2.90          | 0.165   | 12.7   | 3.50          | 0.00113 |
| 69.5   | 2.92          | 0.17    | 12.7   | 3.50          | 0.00078 |
| 66.0   | 2.95          | 0.153   | 4.0    | 3.61          | 0.0003  |
| 64.8   | 2.96          | 0.125   | 4.0    | 3.77          | 0.00013 |
| 61.4   | 2.99          | 0.125   | 4.0    | 3.77          | 0.00013 |
| 60.3   | 3.00          | 0.110   | 4.0    | 3.77          | 0.00013 |
| 54.9   | 3.05          | 0.110   | 4.0    | 3.77          | 0.00013 |
| 49.6   | 3.10          | 0.100   | 4.0    | 3.77          | 0.00013 |
| 47.5   | 3.12          | 0.100   | 4.0    | 3.77          | 0.00013 |
| 31.9   | 3.28          | 0.12    | 4.0    | 3.77          | 0.00013 |
| 28.4   | 3.32          | 0.09    | 4.0    | 3.77          | 0.00013 |
| 21.1   | 3.40          | 0.143   | 4.0    | 3.77          | 0.00013 |

*The concentrations of salt and water in moles/liter at 50°C are $[\text{Ca(NO}_3\text{)}_2 = 8.57$ and $[\text{H}_2\text{O} = 24.00$.†

†Ref. 28.
REFERENCES

1. J. Braunstein in "Ionic Interactions," Vol. 1, Ed., S. Petrucci, Academic Press, New York, 1971, pp. 180-260.

2. (a) M. Telkes, "Solar Energy Storage," ASHRAE Journal, September 1974, pp. 38-44; (b) A. J. Ellis, "Quantitative Interpretation of Chemical Characteristics of Hydrothermal Systems," Proc. U. N. Symposium on the Development and Utilization of Geothermal Resources, Pisa, Italy, Sept. 22 - Oct. 1, 1970, Geothermics, Special Issue 2, pp. 516-528 (1970); (c) J. Millet and R. Buvet, "A Molten Carbonate Fuel Cell with Water Injection," in Hydrocarbon Fuel Cell Technology, Ed., B. S. Baker, Academic Press, New York (1965) pp. 285-292.

3. J. Ambrus, C. T. Moynihan and P. B. Macedo, J. Electrochem. Soc. 119, 192 (1972).

4. J. Braunstein, L. Orr, A. R. Alvarez-Funes and H. Braunstein, J. Electroanal. Chem. 15, 337 (1967).

5. C. T. Moynihan, C. R. Smalley, C. A. Angell and E. J. Sare, J. Phys. Chem. 23, 2237 (1969).

6. B. F. Fabricand and S. Goldberg, Mol. Phys. 13, 323 (1967).

7. L. C. Siew and B. R. Sundheim, J. Phys. Chem. 73, 4135 (1969).

8. D. Harold-Smith, J. Chem. Phys. 60, 1405-9 (1974); 59, 4771 (1973).

9. H. Braunstein, J. Braunstein and P. T. Hardesty, J. Phys. Chem. 77, 1907 (1973).

10. H. Y. Carr and E. M. Purcell, Phys. Rev., 94, 630 (1954).

11. T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, 1971.

12. A. L. Bacarella and J. Braunstein, Chem. Div. Annual Progr. Rep., February 1976, ORNL 5111, p. 15; A. L. Bacarella, D. Brown and J. Braunstein, Chem. Div. Annual Progr. Rep., May 20, 1974, ORNL 4976, p. 132.

13. C. A. Angell, J. Phys. Chem., 70, 3988 (1966).

14. C. T. Moynihan and C. A. Angell, J. Phys. Chem. 4, 736 (1970).

15. N. Bloembergen, "Nuclear Magnetic Relaxation": A reprint volume, W. A. Benjamin, Inc., New York, 1961; N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948); A. Abragam, "The

554
16. N. K. Roberts and H. L. Northey, J. Chem. Soc. (A) (1971), p. 2572.
17. D. W. McCall and D. C. Douglass, J. Phys. Chem. 69, 2001 (1965).
18. F. Noack, "Nuclear Magnetic Relaxation Spectroscopy in NMR, volume 3, Ed., P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, New York (1971) pp. 83-144.
19. L. V. Woodcock, "Molecular Dynamics Calculations of Molten Ionic Salts," in Advances in Molten Salt Chemistry, vol. 3, Eds., J. Braunstein, G. Mamantov and G. P. Smith, Plenum, New York (1975).
20. H. G. Hertz, "Nuclear Magnetic Relaxation Spectroscopy," Ch. 7 in Water, vol. 3, Ed., F. Franks, Plenum, New York (1973).
21. H. C. Torrey, Phys. Rev. 92, 962 (1953).
22. P. Hubbard, Phys. Rev. 131, 275 (1963).
23. R. Kubo and K. Tomita, J. Phys. Soc. Japan 2, 888 (1954).
24. G. J. Kruger, Z. Naturforsch. 24a, 560 (1969).
25. J. F. Harmon and B. H. Muller, Phys. Rev. 182, 400 (1969).
26. R. B. Fiorito and R. Meister, J. Chem. Phys. 56, 4605 (1972).
27. J. Jonas, "NMR Studies in Liquids at High Pressure," pp. 73-139 in Advances in Magnetic Resonance, V. 6, Ed., J. S. Waugh, Academic Press, New York (1973).
28. W. Ewing and R. J. Mikovsky, J. Amer. Chem. Soc. 72, 1390 (1950).
TYPICAL PROTON NMR CW SPECTRUM IN CALCIUM NITRATE-WATER MIXTURES, Ca(NO$_3$)$_2$·2.82 H$_2$O, AT 287.5 K.

Fig. 1

ENTHALPY OF VAPORIZATION OF WATER, SOLUTE ASSOCIATION FREE ENERGY, SOLUTE DIFFUSION COEFFICIENT AND ARRHENIUS ACTIVATION ENERGY OF THE SPIN-LATTICE RELAXATION TIME ($T_1$) IN HYDROUS MELTS OF Ca(NO$_3$)$_2$.

Fig. 2
DIFFUSION COEFFICIENT ($D$) OF DILUTE Cd$^{2+}$, PROTON SPIN-LATTICE RELAXATION TIME ($T_1$), EQUIVALENT CONDUCTANCE ($\Delta$) AND FLUIDITY ($1/\eta$) IN Ca(NO$_3$)$_2$·4.00 H$_2$O, 35-100°C. *(Ca(NO$_3$)$_2$·4.09 H$_2$O)

**Fig. 3**

THE TEMPERATURE DEPENDENCE OF THE PROTON RELAXATION TIMES ($T_1$ and $T_2$) AND THE TEMPERATURE-VISCOSITY RATIO ($1/\eta$) IN CALCIUM NITRATE-WATER MIXTURES, Ca(NO$_3$)$_2$·2.8 H$_2$O.

**Fig. 4**
SPIN-LATTICE RELAXATION TIME ($T_1$) AND SPIN-SPIN RELAXATION TIME ($T_2$) AS A FUNCTION OF THE RECIPROCAL OF THE DIFFUSION COEFFICIENT OF DILUTE Cd$^{2+}$ IN CALCIUM NITRATE-WATER MIXTURES, Ca(NO$_3$)$_2$ · 2.8 H$_2$O.

Fig. 5

SPIN-LATTICE RELAXATION TIME ($T_1$) AND SPIN-SPIN RELAXATION TIME ($T_2$) AS A FUNCTION OF THE VISCOSITY TEMPERATURE RATIO ($\gamma/T$) IN CALCIUM NITRATE-WATER MIXTURES, Ca(NO$_3$)$_2$ · 2.8 H$_2$O.

Fig. 6
SPIN-LATTICE ($T_1$) AND SPIN-SPIN ($T_2$) RELAXATION TIMES AS A FUNCTION OF CORRELATION TIME ($\tau_C$) IN CALCIUM NITRATE WATER MIXTURES ($\text{Ca(NO}_3\text{)}_2 \cdot 2.8 \text{H}_2\text{O}$).

Fig. 7