

A Neutron Scattering Study of the Kinetics of Diffusion and the Relation to the Structures of Ionic Solutions

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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ABSTRACT

The frequencies characteristic of H_2O molecules in hydration complexes and the associated diffusive kinetics were investigated by neutron scattering to determine (a) the dependence of the diffusive motions of ion-water complexes on temperature, on cation, and on anion, and to study their relationship to glass formation; (b) the changes in the hydration of ions and the diffusive kinetics which occur upon mixing in ternary solutions. For concentrated solutions of a series of lithium salts, of chromium salts, and of calcium nitrate with decreasing temperature, it has been shown that relaxation times characteristic of individual primary waters of hydration increase and exceed interaction time. Hence, only contributions from a classical diffusion of cation-water hydration complexes were observed. The self-diffusion coefficients for such complexes decreased rapidly with temperature; with both increasing mass of the cation and the number of waters in its hydration sphere; and with both increasing mass of the anions and their bonding to the primary waters which increases both the "effective mass" and the "friction coefficient" of the complex. The formation of glasses upon supercooling of such solutions appears associated with the restriction of the thermal motions of such complexes and the reduction of free volume. In addition, measurements have shown that in ternary solutions, upon mixing, significant changes occur in the bonding and ordering of water molecules in the hydration spheres of the component cations; in the associated diffusive kinetics of the water molecules; and in the distribution of anions relative to the cations. The results of these measurements are shown to correlate with the "structure-making" and "structure-breaking" characteristic of the ions and are compared with recent theory and with thermodynamic NMR and dielectric measurements for ternary solutions.

I. INTRODUCTION

The results of neutron inelastic scattering (NIS) investigations to date on the influence of ionic solutes on the intermolecular vibrations and the diffusive kinetics of the solvent molecules in binary aqueous solution, on the diffusive motions of hydrated ions in concentrated binary solutions, and on ternary solutions have been reported in the literature(1-4) or in previous annual reports(5,6). Hence, only a brief review of the results in these three areas is given below.

1) Summary of Previous Results

A. Binary Solutions:

Neutron inelastic scattering studies(1-4) have provided information on the changes relative to water that occur both in the intermolecular frequencies below 900 cm^{-1} and in the diffusive kinetics for H_2O molecules in ionic solutions as functions of cations, anions, concentration, and temperature. With increasing concentration, any spectral correspondence to water in the inelastic region is rapidly lost, and frequencies characteristic of ion-water complexes appear and intensify. These frequencies are specific to the ions involved and correspond in general to the rocking, twisting and wagging vibrational modes of water molecules and to the cooperative metal oxygen stretching and bending modes characteristic of the ion-water hydration complexes(1-4,7-10). For strongly hydrating ions (such as Cr^{+3} , Mg^{+2} , and Li^{+1}) these frequencies closely approach those observed for the corresponding solid salt hydrates and are in agreement with reported ion-water frequencies from optical spectroscopy(1-4). For certain strongly hydrating ions it has been shown(7) from infrared results and theory that the primary cation-water coordinations may involve a partial degree of covalency. Such a similarity of the orderings and coordinations of ion-water complexes in liquids to those in crystalline hydrates is not unexpected. Indeed, x-ray diffraction results, for example(11-14) on a number of magnesium salt hydrates show the local octahedral ordering of water molecules about the magnesium ion is a common characteristic.

In solutions of small and/or multiply charged cations the inelastic frequencies are primarily determined by the cation and only secondarily affected by -1 anions (e.g., Cl^- and NO_3^-)(1,2). These frequencies gradually broaden with increased temperature, reflecting the thermal disruption of the primary ion-water complexes. Ion-water frequencies also appear in the inelastic spectra of solutions of larger, singly charged ions (e.g., Cs^+ , K^+ , Na^+), but now depend both

on the cation and anion present. In addition, as the primary water coordinations are in general weaker than those for the small or highly charged cations, the frequencies initially sharpen with increasing temperature as a result of solvent coordinations being thermally disrupted more rapidly than the primary ion-water coordinations. Similar behaviors with temperature have been reported in the literature (15-21) from results of other measurements.

Neutron spectra have also been measured and compared for concentrated solutions of $\text{La}(\text{NO}_3)_3$ and CrCl_3 at 1°C for supercooled viscous solutions just above their respective glass transitions, and for the solid glasses. Near identities were observed in the inelastic frequencies of ion-water complexes for the solutions at 273°C and for the supercooled solutions with those in the solid glasses. The correspondence of solution frequencies to those of solid glass was more pronounced than to those in the solid hydrates where coupling of the hydration complexes to the crystalline lattice appears to broaden frequencies relative to the supercooled liquids and glasses.

In correspondence to the above changes in the inelastic spectra, changes specific to ions, to the concentration, and to the temperature are observed in the widths and the intensities of the diffusively broadened "quasi-elastic" components (1,2). With the increasing concentration of small and/or highly charged ions, at a given scattering angle, the quasi-elastic components are observed to rapidly narrow and intensify relative to water. In contrast, as the concentration is initially increased for solutions containing large singly charged anions, the quasi-elastic maxima appear to broaden and decrease in intensity relative to water. At lower temperatures (typically below 25°C) the angular and temperature dependences for the observed widths of the quasi-elastic distributions and their areas were in accord with the delayed diffusion of individual water molecules (22). Thus, for solutions containing small or multiply charged ions, a decrease in the self-diffusion coefficient, D , and an increase in the residence time, τ_0 , relative to water occurs (a "positive hydration" behavior). The values of D and τ_0 for positively hydrating ions decrease and increase respectively with increasing concentration and are primarily determined by the cations and only secondarily influenced by -1 anions. Larger, singly charged ions at lower temperatures, initially increase D and decrease τ_0 relative to water (a "negative hydration" behavior). The division of the Γ vs. K^2 curves into "positive and negative hydration" groups, the specific dependences on ions within a group, and (within experimental error) the values of self-diffusion constants obtained are in agreement with the trends and values of self-diffusion coefficients reported from NMR and other techniques (2). As for the inelastic frequencies, the curves of Γ vs. K^2 for small or highly charged cations are only secondarily affected by -1 anions, while, in contrast, the curves for the larger singly charged cations are

strongly dependent on the anion.

B. Diffusive Motions of Hydrated Ions in Concentrated Solutions and Their Relationship to Glass Formation:

More recently, the above studies of binary solutions were extended to concentrated ionic solutions known to form glasses in order to determine both the different components that contribute to the diffusive kinetics in ionic solutions, their dependences on cations, on anions, and on temperature, and relationship to glass formation. Upon supercooling, aqueous solutions of many multivalent ions become increasingly viscous and, below a characteristic temperature (T_g), form solid glasses(23). It has been suggested that with decreasing temperature, "liquid-like" diffusive motions become damped as T_g is approached, and a behavior akin to a harmonic solid is approached. It has been suggested(9) that the formation of strongly coordinated, centrosymmetric, cation-water complexes might in part inhibit the formation of ice and favor glass formation. In addition, it had been proposed that the formation of a glass at a characteristic T_g (which is dependent upon the cation, anion and concentration for a solution) may result from the fact that with decreasing temperature liquid-like diffusive motions become damped and a behavior akin to a harmonic solid is approached. Thus, Angell and Sore(23) studied the dependences of T_g on cation, on anion, and on concentration, and found that, for a given concentration and anion, the value of T_g increased with cationic charge, while for a given cation the variations in T_g with anion are large. Indeed, T_g decreases in the progression acetate > sulfate > nitrate > chloride (approximately with the basicity of the anion). However, in general, quasi-spherical, singly charged anions gave rise to lower T_g 's, while those containing asymmetric anions gave rise to higher T_g (23). It was suggested that this dependence could be attributed to the bonding of anions to H_2O molecules in the primary cation hydration sheaths and that the anions may order their environment, reduce the configurational entropy, and thus raise T_g .

In NIS investigations, the spectra for solutions, glasses and solid salt hydrates were measured by neutron inelastic scattering in order to provide information at a molecular level to complement the measurements on T_g discussed above. In addition, it might be expected that any ordering involving the ion-water complexes could be similar in the glass and in the supercooled liquid, and any effects arising from the coupling of such complexes to a lattice (as for the solid salt hydrates) would be absent. Also, in the supercooled liquid, relaxational broadening would be reduced relative to temperature above $1^\circ C$ (where most previous measurements on water and ionic solutions have been made), which should facilitate comparisons between the spectra of the supercooled solutions and the

glasses.

Initially, neutron spectra for concentrated solutions LiCl , LiNO_3 , CrCl_3 , $\text{Cr}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3$ have been measured and intercompared in the hope of first distinguishing contributions to the diffusive kinetics which involve ions moving together with waters of hydration and then to relate such motions, if possible, to the mechanism of glass formation. These salts were selected for the following reasons:

a) The concentrated CrCl_3 and $\text{La}(\text{NO}_3)_3$ solutions could be held in the supercooled state so that spectral comparisons could be made just above and below the glass transition.

b) Their high solubility allowed concentrations to be reached so that the majority of the waters present would be in the primary or secondary hydration layers of strongly hydrating cations. From NMR measurements(24-31) it would be expected that the exchange times for water molecules in the primary hydration layers of the cations could exceed the neutron interaction time (e.g., 10^{-11} - 10^{-13} sec). Hence, such motions should not contribute as strongly to the quasi-elastic components as they do for more dilute concentrations.

c) From O^{17} NMR measurements for chromium(25) and lithium chloride(27) solutions, evidence has been cited to indicate that Li^{+1} and Cr^{+3} cations may undergo diffusional motions together with their primary hydration spheres.

d) In keeping with the observed dependences of the glass transitions(23), the restriction of motions of the hydrated cation of Li^{+1} would be expected to decrease with anion in the progression nitrate > chloride.

Direct evidence has been obtained for the contribution of diffusive motions other than the activated jumps of individual H_2O molecules to the transport in ionic solutions and their fundamental relationship to the formation of glasses upon supercooling. The studies of concentrated lithium and chromium solutions have shown that, in addition to jump reorientations of individual water molecules, motions involving cations moving together with waters of hydration contribute to the overall diffusion process. At these high concentrations, departures from a delayed diffusion behavior involving individual H_2O molecules were observed and the diffusive kinetics were in accord with the "classical" diffusion involving heavy masses and low values of D . For such strongly hydrating cations, the exchange times for primary H_2O 's exceed the neutron interaction time, and so such motions would not contribute to spectra. The restriction of such diffusive motions of hydrated

cations upon "supercooling" may in part appear responsible for the formation of solid glasses. At temperatures near the T_g 's of the solutions, the relaxation times associated with the diffusive motions of both the individual H_2O 's and the hydration complexes are longer than the neutron interaction time, and these motions no longer contribute to the spectra. These results have been compared with reported glass transition temperature measurements. It is suggested that the formation of a solid glass at low temperatures could be primarily associated with the restriction of the diffusive motions involving hydrated cations by "bridging" anions. Thus, higher glass transition temperatures would be associated with anions of higher basicity.

In summary, these results show correspondence in the coordinations of local orderings of hydrated cations in concentrated solutions with those of the corresponding glasses and supercooled viscous solutions. The presence of such large centrosymmetric complexes may in part be responsible for inhibiting the formation of hexagonal ice. The increased restriction of their diffusive motions with decreasing temperature, and with increasing anion basicity may be responsible for the formation of the glass and for determining the characteristic glass transition temperatures. Further, these results also emphasize the complex role of anions at these high concentrations.

C. Ternary Solutions:

The type of neutron spectroscopic investigations described above have extended to studies of ternary salt solutions. It was the purpose of these measurements to determine, at a molecular level, the changes in ion hydration, in solvent structure, and in the diffusive kinetics of H_2O molecules that occur upon mixing in ternary solution and the extent to which such changes constitute departures from a simple additive of these properties for the individual component solutions. These results were also compared with reported thermodynamic and heat of mixing data (32-44). Initial measurements were made for 4.6 m NaCl - 4.6 m LiCl, 4.6 m NaCl - 1.0 m $MgCl_2$, 4.6 m NaCl - 2.2 m $MgSO_4$, 4.6 m NaCl - 1.0 m Na_2SO_4 and 4.6 m NaCl + 4.6 m CsCl solutions.

From measurements of the thermodynamics, of viscosity, and of "salting-out" it has been argued that in solutions containing more than one salt the combined structure-making and -breaking effects of ions are not additive. Further, both experiment and theory have implied that, upon mixing, significant changes in the hydration of the ions present, in the diffusive kinetics and in the structure of the solvent, can occur. Thus, Wood et al() have studied the heats of mixing for aqueous ternary solutions and have concluded that:

a) The orientations of the water molecules about the ions and the changes that result upon mixing are important in determining whether the heat of mixing is endothermic or exothermic. The heat of mixing appears to depend upon the detailed hydration structure and the electrostrictive properties of the ion which, in turn, depend simultaneously upon ionic size, charge and concentration.

b) For consideration of the heats of mixing, it was convenient to divide ions into the "structure-making" or "positively hydrating" ions (e.g., Li^+ , Na^+ , Mg^{+2} , Ca^{+2} , Ba^{+2} , F^-) and the "structure-breaking" or "negatively hydrating" ions (e.g., K^+ , Rb^+ , Cs^+ , Br^- , and Cl^-). The heat of mixing is endothermic within the same group and exothermic between different groups.

Recently, based upon his previous theory of the hydration of ions in solution, Samoilov(43,44) has proposed a semiquantitative theory which attempts to account for observed changes and trends in ion hydration in mixed salt solutions, and for salting-out phenomena at a molecular level. While, as yet, this theory is largely qualitative, it does appear to correlate with many of the observed dependences of the heats of solution and of mixing upon the changes in the hydration of individual ions that occur upon mixing, the cation and anion sizes and charges, concentration, and temperature. Such predictions of this theory can also be tested directly at a molecular level by measurements such as NIS that provide information concerning changes in the bonding and orientation of H_2O molecules in the hydration sheaths of ions, and corresponding changes in the diffusive kinetics and mobility of H_2O molecules that would occur upon mixing.

Relative to additive composites, both the cation-water frequencies in the inelastic spectra and the diffusive broadening of the incident neutron energy distribution show significant and pronounced changes for the ternary solutions. This behavior emphasizes that, upon mixing, significant changes occur in the hydration coordinations of the ions present and in the diffusive mobility of the individual water molecules. These direct observations support the arguments of Wood et al(36-41) and others who, from thermodynamic data, have proposed that the mutual interactions of ions in ternary solutions result in significant changes in their primary hydration layer regions.

Ternary solutions(5) of 4.6 m NaCl with a 1.0 m MgCl_2 and with 4.6 m LiCl (mixtures of two structure-making salts) showed changes in the inelastic frequencies of cation-water hydration complexes and in the self-diffusion coefficients in keeping with the occurrence of a net "dehydration" of cations upon mixing. Thus, for these solutions, frequencies characteristic of $\text{Mg-H}_2\text{O}$, $\text{Li-H}_2\text{O}$, and $\text{Na-H}_2\text{O}$ primary coordinations appeared both broadened and reduced in

intensity relative to either a simple additive composite or the spectra of the single salt solutions. Further, the self-diffusion coefficients for the average H_2O 's had increased relative to simple additivity, indicating that an additional increase in the diffusive mobility had occurred on mixing. These results should be considered as follows.

Upon mixing, cation- H_2O 's in the primary hydration layers of both cations become weakened, and a redistribution from the vicinity of the more weakly hydrating Na^+ ion toward the more strongly hydrating Mg^{+2} or Li^+ ions occurs. This, in turn, forces the anions away from the Li^+ and Mg^{+2} ions and toward the sodium ions. Thus, they serve to enhance the stability of the remaining water molecules around the sodium. After this, the majority of water molecules would be in the outer coordination spheres of Mg^{+2} or Li^+ , and, at best, would be weakly bound. Thus, the Li^+ or Mg^{+2} ions may be considered to be surrounded (at larger distances) by loosely bonded layers of mobile waters. The sodium would be left at best with all or part of its primary hydration waters surrounded more closely by the anions which stabilize these remaining waters. As a result, in the spectra, the frequencies characteristic of the lithium and magnesium primary water coordinations would have de-intensified and broadened as these ions are increasingly surrounded by waters with looser bonding, and the weak coordinations of the majority of waters around the outer layers of these hydrated ions would have effectively increased their diffusional mobility relative to the single salt solutions.

For a 4.6 m CsCl + 4.6 m NaCl solution at 1°C (mixtures of "structure-making" and "structure-breaking" salts), a net "hydration effect" was observed. Cation-water frequencies are enhanced and a decrease in the self-diffusion coefficient, relative to simple additivity, occurs. Indeed, the frequencies characteristic of the $\text{Cs-H}_2\text{O}$ coordinations appear strongly enhanced in the ternary NaCl + CsCl solution relative to the spectrum of an additive composite. Further, such frequencies for cesium chloride primary coordinations in the ternary solutions show a greater similarity to those observed for a binary CsCl solution at higher temperatures than either to those in the composite spectrum or in a cesium chloride single salt solution at 1°C . In these solutions, the Na^+ cation is a stronger hydrator than the Cs^+ . Indeed, NIS results show that the cesium ion sterically disrupts large numbers of water molecules around it and acts as a "structure-breaking" ion, increasing the diffusive mobility of such waters. Thus, a net migration of such waters from around the vicinity of the Cs ion toward the sodium would be favored. In turn, anions could be forced toward the cesium. This would continue until the weak bonding that a water molecule could find in an outer layer around the sodium or magnesium ion would be about equivalent in strength to the bonding in the primary layers of the cesium ion further stabilized by the chloride. In these ternary solutions, the hydration of

the cesium would approach that for a concentrated cesium-chloride solution which would explain the enhancement of the inelastic frequencies characteristic of cesium-water complexes. Simultaneously, the water molecules, now in the outer layers of the sodium ion, would be on the average more strongly bonded than they originally were in the structure-broken region surrounding the cesium prior to mixing. The result would be as noted, one of a net hydration, and on the average a stronger bonding of the water molecules which would give rise to the observed decreases in the self-diffusion coefficient relative to additivity. The effects of strong anions was determined by the comparisons of the spectra of ternary solutions of $\text{NaCl} + \text{Na}_2\text{SO}_4$ and $\text{MgSO}_4 + \text{NaCl}$ with equivalent solutions having a common (Cl^-) anion. In both the ternary solutions containing SO_4^{2-} anions, frequencies characteristic of cation-water coordinations do not appear as strongly broadened upon mixing as in the corresponding ternary chloride solutions. Thus, frequencies characteristic of $\text{Mg-H}_2\text{O}$ coordinations are enhanced relative to the chloride solutions, indicating that the strong sulfate-anions were able to strengthen the hydration of the cations. Thus, it appeared that relative to the dehydration effect observed for $\text{MgCl}_2 + \text{NaCl}$ solutions, as discussed above, the degree of dehydration may have been reduced by the presence of the SO_4^{2-} anions. The observed changes that occur in hydration and in the associated diffusive kinetics upon mixing solutions are in agreement with reported results for heats of mixing. Consequently, upon mixing, two "structure-making" or two "structure-breaking" salts, a net dehydration occurs. In contrast, upon mixing a "structure-making" and a "structure-breaking" salt, a net hydration takes place.

2) Description of Recent Investigations

During the 1970-1971 contract year, measurements have been made to extend the above studies of the kinetics of hydrated ions and of ternary solutions and the effects of mixing. Emphasis has been placed on the following areas:

a) To complement previous studies and to further investigate both the effects of temperature and of anions on the diffusive motions of hydrated cations in concentrated solutions and their relationship to glass transitions, measurements were made during this quarter on a 15 m LiCl solution at 15°C , a 7.2 m CD_3COOLi solution at 75°C , a 16.2 m LiNO_2 solution at 25°C , and on a 6.0 m $\text{Ca}(\text{NO}_3)_2$ solution at 25° , 1° , and -20°C . In addition, as will be detailed below, it was found that the neutron scattering data for the diffusive motions of hydrated ions and H_2O 's, in concentrated solutions, as well as the effects of anion basicity and temperature on such motions, could be interpreted in terms of an extended jump diffusion model by Larsson and Bergsted(45).

b) Previous studies of ternary solutions primarily involved a common anion but different combinations of "structure-making" or "-breaking" cations. However, recent emphasis has been placed upon the role of anions. Thus, measurements were made on ternary solutions with a single cation but in which Cl^- anions were mixed with a strong "structure-breaking" anion (I^-) or a "structure-making" anion (SO_4^{2-}).

c) To further systematically study the effects of mixing solutions of two salts and to allow a comparison of existing theories, the following measurements were made:

1. For salts with a common anion (Cl^-), the effect upon mixing a solution of a strongly hydrating cation (Mg^{+2}) were investigated as a function of +1 cations in the second solution (Li^+ , Na^+ , Cs^+).

2. To investigate changes that occur upon mixing as a function of concentration, measurements were made on a dilute solution of $\text{LiCl} + \text{NaCl}$ to compare with previous measurements on a 4.6 m $\text{NaCl} - 4.6$ m LiCl solution.

3. To investigate the dependences of the changes that occur upon mixing on temperature, measurements were made on a $\text{NaCl} + \text{LiCl}$ solution at 50°C to compare with measurements made at 1°C .

4. For salts with a common cation ($\text{MgCl}_2 + \text{MgSO}_4$, $\text{KCl} + \text{KI}$, $\text{LiCl} + \text{LiI}$), the effect of mixing different anions was investigated.

II. EXPERIMENTAL

1) Instrumental

The measurements were made using the beryllium-filtered incident beam and a time-of-flight spectrometer described in detail previously (1-4). The solutions were prepared from reagent grade materials and deionized water. The solution samples were 0.42 mm in average thickness and were contained in an aluminum sample holder, appropriately shielded so that the neutrons could only be scattered from the liquid. A thin layer of an inert polymer film (2 μ in thickness), plated on the cell and the aluminum windows, afforded protection against corrosion without significantly contributing to background. As detailed previously (46), measurements have shown that the above sample thickness yielded negligible spectral distortions due to multiple scattering. For spectra measured below 0° , the samples were cooled by flowing liquid nitrogen or liquid nitrogen

boil-off gas through a channel in the sample holder and the temperature was controlled to $\pm 2^\circ$. Care was taken to prevent condensation on the scattering surface of the sample. For spectra taken at $+1^\circ$, the sample was cooled by circulating water from an ice bath and was shielded to avoid scattering of neutrons by the coolant. The glass transitions for the glass forming solutions investigated here were determined by differential thermal analysis, and measurements had shown that when these solutions were held above their glass transitions in the supercooled state for the periods over which the spectra were measured (typically 6 hr), no significant degree of crystallization had occurred. In addition, the high glass transition temperatures allowed the samples to be cooled to the vicinity of the glass transition directly in the sample holder at a sufficiently rapid rate so that crystallization did not occur.

2) Analysis of Data

The spectra were corrected for background, for counter efficiency, and for chopper transmission. The background corrections were made by a channel-by-channel subtraction of the spectra obtained for the empty sample holder, and were found to be predominantly a flat component upon which was superimposed a weaker broad distribution, centering at about channel 146. This latter component, which varied with rotor speed, is ascribed to the 180° burst. Statistical uncertainties were calculated from the total number of background counts and the number of observed counts per channel. Further, the reproducibility and reliability of spectral features were checked by comparisons of spectra remeasured at different times with new solutions; comparisons of data collected from four independent counter banks, electronics, and memory banks from the time-of-flight analyzer; and a comparison with background spectra for the empty cell to show that no spectral features or maxima arose from the sample holder or the aluminum window. The solid curves in Figures to were averaged through the data points with regard to statistical uncertainties. The half-width at half-maximum, Γ , for the Lorentzian function associated with a diffusively broadened incident energy distribution was determined in a manner described in detail previously(1-4). Specifically, Γ 's were selected by comparing the observed quasi-elastic component with the measured incident-energy distribution which had been further broadened by a series of Lorentzian functions of varying half-widths at half-maxima.

III. RESULTS AND DISCUSSION

The NIS measurements made during the 1970-1971 year (as outlined in Section I) will be discussed below both for the motions of hydrated ions in concentrated solutions as well as for ternary solutions. For both areas the current results will be considered and discussed together with previous results of NIS investigations and results of other techniques including x-ray diffraction, Raman and infrared spectroscopy, and NMR and PMR investigations. Thus in the following, prior to the discussion of the current results, a review of pertinent background information and theory will be given.

1) Motions of Hydrated Ions and H₂O Molecules in Concentrated Ionic Solutions

A. Review of Background Information

a) Cation Hydration Complexes. X-ray diffraction(12,47,49), NIS(1-6), Raman(8-10), and NMR(50-58,27) results have shown that in solutions containing strongly hydrating or multiply charged cations, "hydration complexes," which include the cation together with first and, in certain cases, higher layers of water molecules, have identities as structural and kinetic entities. Thus, neutron(1-6), infrared(7), and Raman(8-10) results have reported frequencies characteristic of the internal vibrational modes of such a complex; such modes involve metal-oxygen stretching and bending motions and torsional oscillations of H₂O molecules which depend on the coordination, strength and geometries of primary hydration water molecules about a cation. Further, it has been argued(8,50,7) that such coordinations may, in a number of cases, involve a partial degree of covalency resulting from the sharing of electrons between the cation and the neighboring waters. From NMR measurements, Fratiello, et al(52,53) and Matwiyoff and Taube(51) have argued that Al, Be, Ba, In, Mg hydrated cations in solution exist as kinetic units and contribute to diffusive transport. The ordering and the definition of such units(51,52) improve with decreasing solution temperature below 0°C. Further, it has been argued, that such complexes and their identities persist even in dilute solutions. Stronger cations (e.g., In⁺³ and Mg⁺²) show no evidence in the presence of weaker -1 anions (e.g., ClO₄⁻, Cl⁻ and NO₃⁻) for replacement of a solvent molecule by an anion in the first coordination sphere. However, these authors do note on the basis of line widths that ion-pairing of the solvated cations to anions may occur which could affect the effective mass of the kinetic unit.

Both the x-ray work of Brady(48) on ErCl₃, ErI₃ and LiCl solutions and the small angle x-ray scattering studies of Dorosh and Skryshevskii(12) on MgCl₂, CaCl₂, CoCl₃, NiCl₂, CuCl₂, CdCl₂

solutions indicate that water molecules take up specific geometrical orientations about the cations in the primary hydration layer, with the Cl^- anions taking up positions outside the primary layer. Indeed, in the presence of weaker anions (e.g., Cl^-), it appears that "true hydration" is associated with the cations which specifically orient the water molecules. Then, in turn, at higher concentrations, such hydration complexes may pack around the anions. From x-ray studies of LiCl solutions, Brady(47) concluded that the four water molecules coordinate around the Li^+ ion in a tetrahedral coordination. Similarly, Yagil(58) has argued that the lithium ion can share four free electron pairs in the first vacant "L" shell and has a hydration number of four. Woessner(55,56) has also argued for a tetrahedral coordination of high symmetry on the basis of quadrupole relaxation measurements. Indeed, Woessner and coworkers(55) conclude that there is bonding between the lithium ion and the primary water molecules, and the lithium oxygen nuclear separation is about 1.74 Å. This number is less than the sum of the lithium ion crystallographic radius and the Van der Waal radius of the oxygen atom, but is larger than the sum of the lithium ion crystallographic radius and the single bond radius of the oxygen atoms. Brady(47) concluded that at higher concentrations the hydration sheaths around the cation are oriented with positive dipole ends pointing out and the hydrated lithiums then pack around the chloride ions. Indeed, in like manner, the magnesium ion has been shown to be octahedrally coordinated both in ionic solutions and in solid salt hydrates. Thus, in such solid hydrates, even though the crystal symmetry may vary, the magnesium ion is always surrounded by six water oxygens having an average Mg-O distance of 2.6 Å. Such behavior has been observed for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Of course, in the presence of stronger anions, small distortions of the octahedral symmetry occur(11). More recently, more complete ligand field calculations by Breitschwerdt(59) show that, at least for transition metal ions, it is possible to treat the cation together with its first coordination sphere as isolated units in terms of crystal field theory.

b) Motions of Hydration Complexes and Their Relationship to Motions of H_2O Molecules in Primary Hydration Layers.

With regard to the cation-water complexes discussed, the following three general types of motions involving H_2O 's can, in principle, occur: motions of the center of mass of the hydration complex; the exchange of the primary waters from the hydration layers; and hindered reorientations of waters bound in the hydration layers of the cation. Any interpretation of neutron data should consider these three types of motions as well as the effect that temperature and different anions have on each.

Experimental evidence for motions involving cations together with their waters of hydrations have been reported by Olson et al(25) for chromium, by O'Reilly and Peterson(27) by Hertz(60) and by Weiss and Nothnagel(61) for lithium, by Matwiyoff and Taube(51) for magnesium, and by Fratiello et al(52,53) for Al, Be, Ca, In, and Mg ions. Further, Angell and Sare(23) have noted that the formation of solid glasses upon the supercooling solutions of multivalent ions may involve the restrictions of such motions of hydrated cations due both to decreasing temperature and to anions. In like manner, Hester and Grossman(9) have noted that the presence of such centrosymmetric hydration complexes and their enhanced ordering upon supercooling may favor the formation of glasses. As discussed by Angell et al(23), as the characteristic glass transition of a solution is approached, the viscosity of solutions typically approaches 10^{13} P and the self-diffusion coefficients typically approach 10^{-15} cm²/sec, and its total configurational entropy is reduced as the excess free volume (over that for random packed spheres) approaches zero. Near the glass transition point, motions of such hydration complexes and, hence, corresponding transport processes in solution would only occur through a cooperative rearrangement of many particles. Further, anions would bind to protons of H₂O's associated with the cation sheaths so as to further restrict their motions -- the more basic anions producing the greater restriction.

When considering the possible motions of such complexes, two additional types of motions, known to occur experimentally, must also be considered. NMR relaxation measurements(29,30,31) for the exchange times of the primary water molecules on such hydration complexes have shown that for certain ions (e.g., Al⁺³, Ga⁺³, Be⁺² and Cr⁺³) such times exceeded 10^{-4} sec. with regard to such motions. Zaitseva and Fisher(62,63) have argued that the exchange rate of primary water molecules from a cation in turn influence the diffusive motions of the cation as follows. When the primary cation-water coordinations become weaker and the exchange rate increases for primary waters, both the effective mass of the hydration complex and the forces restricting its motion (hence, the friction coefficient) decrease and its diffusive mobility strongly increases.

In addition to the above two types of relaxation motions, Connick and Wüthrich(64) from O¹⁷ NMR relaxation measurements have shown that waters in the primary hydration layer of cations rotate about the metal-oxygen axes in times short compared to the characteristic times for translations or tumblings of the hydration complex. Indeed, in certain cases, they note that such rotational relaxation of individual H₂O's in the hydration sphere of the ion may involve both primary and secondary waters. The word "reorientation" must be considered with regard to the time scales of a particular experiment. Thus, in neutron spectra well defined maxima occur corresponding to a

strongly hindered oscillation of water molecules in the primary hydration spheres. This indicates that a water molecule makes many rotational oscillations within the NIS interaction time prior to breaking a bond and reorienting. Thus, such motions would appear to be strongly hindered on the time scale of neutron scattering experiments, but might appear nearly freely reorienting on the longer time scale of NMR experiments. In this regard, the results of permittivity, dielectric, and PMR measurements of solutions of alkaline halides by Giese et al(65) should be noted. In particular, these authors have argued that in LiCl solutions the tetrahedrally coordinated primary waters are sufficiently rigidly oriented by the cation so that their dipole moments are rigid. However, such water molecules still undergo restricted rotation about their dipole axes around the MO bond.

In addition to the exchange of individual H₂O's from hydration layers, such rotational orientations of water molecules in the hydration layers of cations may also significantly influence the diffusive motion of the center of mass of a hydration complex and affect both its average effective mass and its coupling to the rest of the solution. This would be particularly true as a solution were supercooled toward the glass transition. Thus, Hester and Grossman(9) from Raman measurements have argued that with decreasing temperature the centrosymmetric ordering of H₂O's about a strong cation becomes more stable and the tendency for such anion-cation pairing is reduced. Moynihan and Fratiello() from PMR measurements on salt hydrate melts have argued for an increased stabilization of H₂O in the primary hydration layer of Ca⁺² with decreasing temperature. They note that, as the temperature is increased, the thermal energy of H₂O molecules in primary hydration layers would cause deviations from the minimum energy H₂O-ion orientation and decrease the proton deshielding. Thus, decreasing temperature could increase the internal bondings of hydration complexes and, hence, their effective diffusional masses by stabilizing waters about them, reducing the exchange rate of primary waters, reducing direct cation-anion pairing, and restricting thermally induced reorientation of the primary waters which would increase their time average bonding to other solvent molecules or to anions. Indeed, the "coupling" of such hydrated cations with decreasing temperature can strongly effect both the diffusive motions of the complex and the glass transition temperature of the solution.

c) Effects of Anions on the Motions Characteristic of Hydrated Cations.

The effects of anion and anion basicity on the motions of units and the glass transition temperature of solutions have been considered by Angell and Sare(23). They suggest that anions may "contact" the protons associated with cation hydration sheaths and thereby order their environment, reduce the total configurational

entropy and, hence, raise T_g . In general, spherical, singly charged anions correspond to lower T_g 's, while asymmetric anions or more strongly basic anions such as an NO_3^- , an SO_4^{2-} , and an acetate ion, give rise to high values of T_g . In accord, Weiss and Nothnagel(61), from a comparison of self-diffusion coefficients of H_2O 's, and ions for LiCl and Li_2SiF_6 argued that the diffusion of the hydrated Li^+ 's were more strongly restricted by SiF_6^- anions than by interactions with Cl^- . Thus, with increasing basicity an anion may interact more strongly with H_2O 's in primary hydration spheres, restrict their reorientations, and couple more strongly on a time average to the hydrated cation. Thus, in essence, for observation times short relative to the exchange times of the H_2O 's or the average reorientational relaxation times of the primary H_2O 's, the hydrated cation, together with the anion, may be the effective diffusing unit. However, the effects of anion interactions on the exchange rates of primary water molecules as well as of their ability to restrict the rotational reorientation of H_2O in the primary hydration layers must also be considered. Plane and Taube(26) have shown that anions decrease in their effectiveness in promoting the exchange of primary water molecules from the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ complex in the sequence $\text{NO}_3^- > \text{ClO}_4^- > \text{Cl}^- > \text{Br}^-$. Thus, anions may have two effects. With increasing basicity they could enhance the exchange of primary water molecules but also increasingly restrict the reorientation in the primary hydration layers, in the manner discussed above. However, in the presence of a strongly hydrating cation such as Cr^{+3} while different anions have a marked effect on the exchange rate, in the above sequence the overall change is about a factor of two. Thus, while such times are decreased by stronger ions they may still be long ($>10^{-4}$ sec for $\text{Cr}(\text{H}_2\text{O})_6^{+3}$) relative to both the internal vibrational periods of the complex and to neutron interaction times (typically $10^{-11} - 10^{-13}$ sec) that increasing anion basicity may perturb the energy levels of the chromic ion sufficiently so as to lower the activation energy necessary for water molecules to exchange from primary hydration layers.

In like manner, Olson et al(25) noted that anions can accelerate the exchange rate of primary water molecules either by a "medium" effect or by the formation of cation-anion complexes which in turn exchange waters more readily than the isolated hydrated cation. From NMR studies of rare earth ions and their complexes, Reuben and Fiat(66,67) argued that the formation of a metal ligand bond between the lanthanide cation and primary H_2O oxygens may be partially shielded by outer shells. Thus, NO_3^- , acetate, and sulfate ions can form inner sphere complexes and enhance the exchange rate of primary water molecules more readily than in the case of ions for which the primary initial cation-water bonds are stronger. Thus, for the lanthanide elements an acetate ion can replace more than one water molecule in a primary layer through bidentate binding

to the cation and reduce the residence times for the remaining waters. Such ion-pairing should be regarded as "dynamic" or "time-average." Thus, as argued from Raman(9) and NMR(54) results, SO_4^{-2} or NO_3^- anions may approach cations briefly and disrupt the primary ion-water by a fluctuating field gradient. Woessner et al(55,56), Bryant(68), and Weiss and Nothnagel(61) have argued from NMR measurements that, with increasing concentration as an anion approaches the hydration layer about a cation, abrupt changes in the symmetry of H_2O 's about Li^+ ions occur which alter both the relaxations of the ions and of the primary H_2O 's. Thus, Woessner et al note that above concentrations of 4.4 m (corresponding to a first and second hydration layer) such distortions from symmetry result in the Li^+ ions being less effective in showing the motions of the average waters with increasing concentration than they were below 4.4 m. In contrast, the Li ion becomes more rapidly restricted in its motions above 4.4 m. If it is assumed that Cl^- - H_2O bonds were weaker than H_2O - H_2O bonds for the primary waters, then the approach of the Cl^- may have increased the reorientational freedom of the H_2O 's but the time average coupling of the hydrated Li^+ to the heavy Cl^- may have restricted its motion. A stronger anion such as an SO_4^{-2} or an acetate may enhance the distortion of the hydration complex but may form stronger anion- H_2O coordinations than the original solvent-solvent coordinations and, hence, increasingly show the motions of the H_2O 's.

It has been argued(9,69) also that at lower temperatures such inner sphere anion contacts are increasingly displaced by H_2O 's and the probability of ion-pairing is reduced. As the temperature of a solution is lowered toward the glass transition, anions would be "repelled" out and the probability of ion-pairing would be decreased. The exchange rate for the primary hydration waters would be decreased, and the anions would more effectively bridge the protons of the primary hydration waters, and thus both restrict their rotational motions and restrict the diffusion of the hydrated cations. In this regard, Reuben and Fiat(66,67) have noted there may in essence exist two types of water molecules with regard to rotational freedom in the hydration layers of the lanthanides: a water molecule which is hydrogen-bonded to a strong anion may be strongly inhibited in exchanging from the primary layer; one bonded to other water molecules could more readily exchange. Thus, there is effectively a competition depending upon the relative strengths of the primary cation-water and anion-water bonds. If the characteristic time that a molecule remains bonded to a cation, were sufficiently decreased by a basic anion, ion-pairing would be more probable. The cation would be only partially primarily hydrated during most of its motions and its diffusive mobility might correlate with the exchange rate of primary waters rather than with the reorientational freedom of such waters.

B. Theoretical Relationships Between Motions of Hydrated Cations and Quasi-Elastic Neutron Scattering.

To correlate the above types of motions with the current results of neutron scattering measurements, it is useful to consider a model for the "quasi-elastic" scattering of slow neutrons in hydrogenous liquids formulated by K. E. Larsson and L. Bergstedt⁽⁴⁵⁾. This model is a generalization of the Singwi-Sjölander⁽²²⁾ model previously used to describe the jump diffusion of individual water molecules in pure water and in more dilute solutions. It assumes that the center of mass of a molecule in a liquid can vibrate for a period of time, τ_0' , and then undergo classical diffusion in a period, τ_1' . In addition, a protonic group of the molecule may vibrate about the center of mass for a period of time, τ_0 , and then during the time, τ_1 , jump over a characteristic average length, l . The general expression for the differential scattering cross section in terms of the above four parameters is complex. However, simplifications occur in four limiting cases (depending upon the relative magnitudes of these four characteristic times). These cases are both particularly useful and applicable in quantitatively interpreting the neutron scattering data for concentrated ionic solutions being supercooled.

As previously reported⁽³⁾ for concentrated chromium and lithium salt solutions, when the temperature is lowered the half-width at half-maxima, Γ 's, of the Lorentzian broadened incident energy distribution (as a function of the momentum transfer (K^2)) undergoes a variation in functional form. This corresponds to a change from a case where both reorientations of individual water molecules and motions of hydrated ions contribute to a case where motions of hydrated ions dominate. Quantitatively, this change in functional form can be described in terms of the above four parameters by assuming that τ_1' and $\tau_0 \gg \tau_0'$. Equivalently, this assumes the center of mass of the hydrated ion is undergoing a classical diffusion type behavior and, in contrast, an individual water molecule in the primary layer remains bonded for a time, τ_0 , prior to undergoing rotational reorientation or jump exchange. However, once any one of such primary hydration waters have broken a bond it allows the center of mass to displace. Hence, τ_0' is much less than τ_0 , and the ion would spend the majority of the time diffusing with a result that $\tau_1' \gg \tau_0'$. If it is further assumed that well above the glass transition temperatures both τ_1' and τ_0 are within the neutron interaction time, then both of the motions of the center of masses and of jump reorientations of individual water molecules would contribute to a spectrum. For small values of K^2 , Γ is given by

$$\Gamma \rightarrow n \left[D_{CM} + \frac{\langle l^2 \rangle}{2\tau_0} + \langle r_i \rangle^2 (1/\tau_0 + 2/\tau_1') \right] K^2$$

while for large values of K^2 , Γ is given by

$$\Gamma \rightarrow \pi D_{CM} K^2 + h (1/\tau_0 + 1/\tau_1').$$

This is shown pictorially in Figure 1 by Curve II.

It is seen that Γ rises linearly from the origin and its slope depends upon D_{CM} (the self-diffusion coefficient for the center of mass), upon effective diffusion coefficient for the individual water molecule motions given ($l^2/2\tau_0$), and a term depending upon the average vibrational amplitude of the individual water molecule, r_i^2 . However, at higher values of K^2 (unlike the case for the simple jump diffusion - Curve I, Figure 1), the curve does not approach a constant value but rather rises with a slope which now depends only upon the self-diffusion coefficient of the hydrated ion.

If the temperature were to be further lowered in the process of supercooling then, in accord with the above discussion, the exchange rates and reorientation rates of individual water molecules would decrease rapidly; τ_0 could become longer than the maximum neutron interaction time experimentally accessible. Also, l^2 and r_i^2 would reduce in magnitude. In this limit, Γ then should rise linearly with K^2 with a slope given by πD_{CM} (curve III of Figure 1), and the motions contributing to the broadened incident energy distribution are the diffusion of the center of masses of the hydrated ions. As discussed in the following section, just such a functional transition behavior with temperature has been observed, as noted above for both chromium and lithium salts.

It should be further noted that in this case the integrated area in the diffusively broadened incident line is directly proportional to the Debye-Waller factor

$$e^{-2W_i} = e^{-K^2 l^2/6} < u_i^2 >$$

corresponding to the mean square vibrational amplitudes $< u_i^2 >$ of the water molecules in the primary layers. It would be expected, with decreasing temperature, that this amplitude would continuously decrease in correspondence to a "rigidification" of the primary water molecules, as will be discussed in the following section. In correspondence, the inelastic frequencies corresponding to torsional oscillations of water molecules in the primary hydration layers and the metal oxygen stretching and bending frequencies gradually sharpen with decreasing temperature.

As the temperature is fully decreased to the vicinity of the glass transition and as τ_0 is increasing, τ_0' could eventually become larger than τ_1' . Such behavior would be in accord with a reduction

in "free volume" and a continuous increased hindrance of the reorientation of individual water molecules in the primary hydration layer. Then, close to the glass transition, the probability of breaking any bonds of hydration waters would become so small that the center of mass of the cation could be fixed for periods sufficiently long so that it might oscillate a number of times prior to reorienting. Any motions of the center of mass at temperatures close to the glass transition as a result of a strong reduction in free volume could correspond to a highly cooperative rearrangement of particles and, therefore, be strongly restricted. The model of Larsson can also theoretically account for and predict the behavior of Γ vs. K^2 in this low temperature region, as is shown in Figure 1 by Curve I. Thus, when τ_0' and $\tau_0 \gg \tau_1'$ for small K^2 the width is given by

$$\Gamma \rightarrow \pi [D_{CM} \frac{\tau_1'}{\tau_1' + \tau_0'} + \frac{\langle \ell^2 \rangle}{2\tau_0} + \frac{\langle r_i^2 \rangle}{6} (1/\tau_0 + 2/\tau_0')] K^2$$

while at high K^2 the width is given by

$$\Gamma \rightarrow \pi (1/\tau_0' + 1/\tau_0)$$

Γ vs. K^2 again rises linearly from the origin but not approaching a constant value at high values of K^2 . The initial slope is primarily dependent on ℓ^2/τ_0 (as the value of $D \cdot \tau_1'/\tau_0$ is small). However, for this case, from an experimental standpoint, the values of the Γ 's involved may be so small so as not to be resolvable. Indeed, as previously reported(3), measurements made on lanthanum nitrate and chromium chloride solutions at temperatures just above and below the glass transitions, show no resolvable broadening. In contrast to the case discussed above, the area under diffusively broadened incident energy distribution would now depend upon the product of two Debye-Waller factors

$$\sim e^{-1/6(\langle u_i^2 \rangle + \langle u_{CM}^2 \rangle)K^2}$$

where $\langle u_i \rangle$ is an average Debye-Waller amplitude corresponding to the vibrations of H_2O in the primary hydration layer and $\langle u_{CM} \rangle$ is the amplitude corresponding to the vibrations of the center of mass for hydrated ions. However, because of the larger mass, the exponent for the center of mass vibration involved might be considerably smaller than that corresponding to individual water molecules.

The point to be emphasized is that while the widths and small changes in the area of the quasi-elastic maximum may lie outside of experimental resolution at temperatures near the glass transition, the above model is still, in principle, capable of accounting for the entire change in temperature behavior from temperatures near 25°C down through the glass transition in a plausible and quantitative

manner. In addition, in terms of this model, the effect of increasing anion basicity at a given temperature would be to strongly increase τ_0 due to a strong restriction of rotational freedom of the primary H_2O 's. Such an increase could result in τ_0 passing from a time shorter to a time longer than the neutron interaction time. This would then have two effects, as will be discussed in the next section, which have been observed.

(a) The curve of Γ vs. K^2 would pass from a behavior where it has one slope at the origin and another slope at higher values of K^2 (Curve II, Figure 1) to a behavior where it is linear through the origin for all K^2 's (Curve III, Figure 1).

(b) As a result of the increase in τ_0 , corresponding to an increased restriction in the rotational freedom of the individual water molecules in the primary hydration layer, the motion of the center of mass for the hydrated cation would also be restricted and the self-diffusion coefficient would strongly decrease (Curve II vs. Curve III).

As concentrated solutions were heated to higher temperatures (e.g., $25^\circ C$ to $75^\circ C$) the residence times for the primary H_2O 's would decrease and the diffusive kinetics would be dominated by individual water molecules undergoing jump diffusion (as has been used previously to describe the behavior in more dilute solutions of ionic salts). Larsson's model in the limit of $\tau_1 \gg \tau_0$ and τ_0 indeed passes to this limit. Water molecules would exchange rapidly from the primary hydration layer which would effectively dehydrate the cation and allow it to move more freely. However, it should be kept in mind that because of the larger scattering cross section for hydrogen, small, if any, contributions to the scattered intensity would arise from the nearly bare cations and the diffusive broadening would arise from the individual water molecules. In this case (as shown by Curve I, Figure 1), Γ at small K^2 , is given by

$$\Gamma = \hbar [D_{CM} + D_i] K^2$$

It rises linearly from the origin with a slope which depends on the sum of the self-diffusion coefficient for the center of mass of the ion and the self-diffusion coefficient for jump reorientations of individual water molecules. As the former would not contribute much, it would be expected that experimentally Γ would depend only upon the diffusion coefficient for the jump reorientation of the individual water molecules. For large values of K^2 , Γ would again rise linearly with a slope given by the $\hbar D_{CM}$ and an intercept given by \hbar/τ_0 (τ_0 being the residence time for the individual water molecules). Again, as the bare ions would not contribute effectively, Γ would approach a constant value of \hbar/τ_0 . Thus, the expression reduces to that for the simple jump diffusion model for Singwi and Sjölander (22)

applied previously to the description of diffusive motions in less concentrated solutions at higher temperatures. Indeed, an evolution for such a jump diffusion behavior at higher temperatures has been observed for such solutions as described in the next section.

In summary, it should be re-emphasized that the model of Larsson and Bergsted accounts for the observed behavior of the diffusively broadened quasi-elastic component in concentrated solutions of multivalent ions in a nearly continuous manner from high temperatures to temperatures close to the glass transition. The assumptions made with regard to the four characteristic time constants are physically plausible and in accord with proposed mechanisms for the glass transition temperature, as well as with the types of motions including exchange of water molecules, diffusion of hydrated ions, and reorientations of water molecules in the primary layer of the type discussed above and observed by spectroscopic and relaxation measurements. However, from a theoretical standpoint, this model should not be taken as capable of yielding a complete description of such liquids over a wide range of interaction times. Indeed, it is an approximation valid for longer periods of time and is not valid for very short interaction times (e.g., very large K^2 values) where any correct model must continually pass to a free particle limit. However, it does appear to represent a valid approximation within the range of interaction times of these experiments (e.g., range of K^2 of these experiments) and at the lower temperatures involved.

In the NIS measurements, to be discussed below, when with decreasing temperature or increasing concentration the curve of Γ vs. K^2 has evolved to shape III in Figure 1, its slope $d\Gamma/dK^2$ should primarily reflect the diffusive motions of the hydrated ions as discussed above. Moynihan and Angell(70) have treated the diffusion of hydrated cations in terms of the Stokes-Einstein relationship, $D = kT/M\xi$, where M is the effective mass of the hydration complex and ξ is the Langevin friction coefficient. Recently, Zitseva and Fisher(62,63) have proposed a hydrodynamic theory in an attempt to account for the motions of ions in solutions, taking into account also the effects of ion hydration.

The reciprocal of the friction coefficient (e.g., $1/\xi$) may be considered as a short delay time before diffusion sets in and a measure of the collision time itself. From the self-diffusion coefficients obtained in this work, as discussed below, from the Γ vs. K^2 curves the masses of the hydration complexes and known temperatures, values for $1/\xi$, typically of about $10^{-14} \times 10^{-15}$ sec., are obtained for the lithium and chromium solutions. An observation time for the neutron may be defined(71) as $\tau^{obs} = M/K^2kT$, and if the neutron is to observe a classical behavior, $1/\xi/\tau^{obs}$ must be less than unity. Using the above values for $1/\xi$, the masses M and the temperatures,

and inserting the largest experimental available values of K^2 , it is indeed found that this ratio is less than unity throughout the entire observation range of K^2 . Hence, a classical diffusion behavior, as observed, would indeed be consistently expected. Further, a NMR correlation time of the order $\sim 10^{-10}$ sec. has been reported(27) for reorientations involving the hydrated lithium ion in aqueous solutions and is related to the viscosity, η , the effective volume of the hydrated ion, V_m , and temperature through the relation $\tau_c = \eta V_m / kT$. This can also be written in terms of the Stokes-Einstein friction coefficient, the volume of the hydrated ion, the effective radius of the hydrated ion, its effective mass and temperature as

$$\tau_c = \frac{M V_m \xi}{2 R_g k T}$$

If values of the friction coefficient, as given above, are used, values of the correlation time (typically 10^{-10} sec) are obtained in reasonable agreement with the NMR correlation time for rotation of the complex.

In the following discussion of the neutron data, the motions of the hydrated ions will be treated in terms of a Langevin equation. Egelstaff and Schoefield(72) have given the solution for the scattering law for the Langevin equation which is in accord with the fluctuation dissipation theory. They show that there exists a parameter, $K^2 \cdot D/\xi$ such that for K^2 values where this parameter is $\ll 1$, a classical diffusion behavior is approached. Where K^2 values, corresponding to this parameter are $\gg 1$, the width rises linearly proportionately to K . Equivalently, one can define a value(72) of $K_c \equiv (kT/MD^2)^{1/2}$ such that when $K \ll K_c$, a contribution from a recoil term, is negligible; while, for $K \gg K_c$, recoil terms predominate. In the present experiments the range of K^2 was such that $0 \leq K^2 \leq 5$ (\AA^{-2}), the smallest mass of the hydration complexes involved, was approximately 80 AMU (for 15.0 m LiCl), and the values of D were of the order of 10^{-5} cm^2/sec . Hence, the experimental range of K^2 is much less than K_c^2 , and recoil effects should be negligible. Indeed, Vineyard(72) has noted that, typically for atoms having atomic masses below 20 AMU, recoil effects are not negligible except in cases of abnormally small momentum changes.

C. Diffusive Motions of Hydrated Ions - Results and Discussion

The dependences of the inelastic spectra corresponding to the characteristic frequencies of hydration complexes and the corresponding curves of Γ vs. K^2 and their dependences on temperature, concentration, anion-basicity, and on cation are shown in Figures 2 through 7. These results are shown and compared for LiSCN, LiI, LiCl, LiNO₃, LiNO₂, and CD₃COOLi; for MgCl₂, MgSO₄, and Mg(CD₃COO)₂;

for $\text{Ca}(\text{NO}_3)_2$; and for $\text{Cr}(\text{NO}_3)_3$ and CrCl_3 . In particular, the dependences of the curves of Γ vs. K^2 on temperature and the influence of anions of different basicity on these dependences will be interpreted and compared with the model of Larsson and Bergsted(45) (as discussed above).

a) Diffusive Broadening of the Quasi-Elastic Components. In Figure 2 the temperature dependences of the Lorentzian half-widths at half-maxima, Γ , for the diffusively broadened incident energy distributions are shown as a function of the momentum transfer, K^2 , for 4.6 m and 15 m LiCl, for 16.3 m LiNO_2 , and for 7.2 m CD_3COOLi . With decreasing temperature the Γ vs. K^2 curves for 15 m LiCl, 16.3 m LiNO_2 , and 7.2 m CD_3COOLi evolve from Curve I of Figure 1 (characteristic of activated jumps of individual H_2O 's) and become linear through the origin. This functional behavior is in accord with Curve III, Figure 1, and primarily with the quasi-elastic broadening results from diffusive motions of the hydrated lithium complex; and, hence, τ_0 and $\tau_1' \gg \tau_0'$. Further, τ_0 is assumed to be long relative to the neutron interaction time such that contributions due from the exchange of individual water molecules in primary hydration layers do not significantly contribute to the neutron spectrum. Thus, for the three more concentrated solutions in Figure 2, the progression for Γ vs. K^2 with increasing temperature in the functional shapes are as expected on the basis of the model of Larsson and Bergsted(45), discussed previously and shown in Figure 1. Thus, at low temperatures the curves are linear and only the diffusive motions of the hydrated cations contribute (Curve III, Figure 1). With increasing temperature, an evolution in shape occurs whereby Γ rises linearly from the origin with one slope, and then, at higher values of K^2 , appears to be again rising linearly with a different slope. This is the behavior expected when τ_0 and $\tau_1' \gg \tau_0'$, but τ_0 is within the neutron interaction time so that both motions of the center of mass of the hydrated cation, as well as hindered reorientations of the primary water molecules, contribute (Curve II, Figure 1). At still higher temperatures, the curves show a delayed diffusion behavior rising linearly from the origin but then approaching a nearly constant value of \hbar/τ_0 at higher K^2 values (Curve I, Figure 1). In this case, the jump reorientations of the individual water molecules predominate.

In contrast to the concentrated 15.0 m LiCl and 16.3 m LiNO_2 solutions where most of the H_2O would be in the primary hydration layers of the Li^+ , the more dilute 10.0 m or 4.6 m LiCl and LiNO_3 solutions (Figures 2 and 3) still show significant contributions of delayed diffusion behavior at 274°K. The variation of the curves of Γ vs. K^2 with decreasing temperature corresponds to decreasing self-diffusion coefficients and increased residence times for the motions of the individual molecules. Thus, in LiCl and LiNO_3 solutions, H_2O 's beyond the primary layer are not sufficiently coordinated so that their

relaxation times exceed the neutron interaction time and the predominant contribution to the quasi-elastic broadening at 274°K results from the activated jumps of individual H₂O's rather than the overall motion of the hydration complexes as for 15.0 m LiCl, 16.3 m LiNO₂, and 7.2 m CD₃COOLi.

However, reference to the Γ vs. K^2 curves of Figures 2 and 3 shows that their temperature and concentration dependences show a pronounced dependence on anion "basicity." Thus, in Figure 4 it is seen that even at 4.6 m concentration, the curve of Γ vs. K^2 for a 4.6 m CD₃COOLi solution is linear through the origin in contrast to those for the other Li salts. Thus, the acetate anion appears to have stabilized the H₂O's in the hydration spheres of the Li cation so that the residence times exceed the neutron interaction time. Further, from Figures 2 and 5, a comparison of the linear Γ vs. K^2 curves at 274°K for 15.0 m LiCl, 16.3 m LiNO₂ and CD₃COOLi show their slopes, which are proportional to \bar{D} , decrease in the progression Cl⁻ > NO₂⁻ > CD₃COO⁻. Thus, the self-diffusion coefficients are decreasing with increasing anion basicity. Thus, progression is in accord with the arguments of Angell and Sore(23) that anions may contact waters in the primary hydration layers, order their environments, and restrict the diffusive motions of the hydrated cations. Such a restriction of the diffusive neutrons may in turn result from an increased restriction of the motions of water molecules in the primary layers with increasing anion basicity. As the frequency of breaking bonds is decreased for the primary water molecules due to their rotation about the metal oxygen axes becoming restricted, the motions of the center of mass of the hydrated cation in turn could become restricted. Additional evidence for such an anion dependency comes in comparing the changes in shape of the curves of Γ vs. K^2 with temperature for each of these three lithium salts. Up to 50°C, the curves for 7.2 m lithium acetate remain linear, and their slopes (and, hence, the corresponding self-diffusion coefficients) increase with increasing temperature. Thus, throughout this temperature range for the lithium acetate solution the motions that make the prime contributions to the quasi-elastic component are those of the hydrated lithium ions. Even though the mobility of the hydrated cations increases with temperature (as evidenced by the increase in the self-diffusion coefficient), not until 75°C have relaxation times for individual H₂O's in the primary layers decreased and entered the neutron interaction time scale. In contrast, for the 15.0 m LiCl solution, a departure from linearity and, hence, a change in functional form is observed at a lower temperature. Thus, at 1°C, the curve of Γ vs. K^2 is linear. However, with increasing temperature, the curve is observed to approach a behavior such that it rises linearly from the origin but approaches a nearly constant value at higher K^2 values, in accord with kinetics dominated by the jump diffusion of individual water molecules. Increasing temperature to 25°C in the lithium chloride

solution has decreased the τ_0 for jump reorientation of individual water molecules, and these motions have entered the neutron time scale. Thus, the more basic acetate ion has strongly retarded such motions relative to the chloride ion. A comparison of the curves for lithium nitrite with those for lithium acetate and lithium chloride shows an intermediate behavior for the NO_2^- anion in restricting the thermal disruption of the primary hydration layer and allowing the jump reorientations of H_2O 's to come into the neutron interaction time.

In addition to the data for the above lithium salts, the curves of Γ vs. K^2 , as a function of temperature, are shown for calcium nitrate, magnesium acetate, and magnesium chloride in Figure 6. The dependences of Γ vs. K^2 on temperature and anion basicity parallel those for the lithium salt discussed above. The curves for the 4.6 m MgCl_2 and 6.0 m $\text{Ca}(\text{NO}_3)_2$ remain in accord with a jump diffusion behavior as the temperature is decreased to 274°K. The slopes at the origin decrease and the approach to a constant value of Γ at high K^2 becomes more pronounced. This behavior is in keeping with a decrease in the self-diffusion coefficients and increases in the residence times with decreasing temperature. In contrast, it was found that for the supercooled solution at -20°C, Γ vs. K^2 is linear. Thus, the supercooling has resulted in a rapid restriction of the jump reorientations of individual water molecules. Both the exchange and the reorientation of such primary waters now occur with average relaxation times much longer than the neutron interaction time. In addition, at -20°C, the smaller slope of Γ vs. K^2 corresponds to a much smaller self-diffusion coefficient, as expected if contributions to the diffusive broadening arose almost exclusively from motions of the hydrated calcium cations. As shown in Figure 6, the more basic acetate ion in magnesium solution strongly hinders the reorientations of the primary waters in a manner similar to that noted above for the lithium salts. Indeed, a comparison of the Γ vs. K^2 curves for MgCl_2 and MgSO_4 of Figure 5 with those for $\text{Mg}(\text{CD}_3\text{COO})_2$ of Figure 6 emphasizes that even relative to the SO_4^{2-} anion which has served to increase the residence times of the H_2O relative to Cl^- , the acetate anion has increased such relaxation times beyond the NIS time scale and thus the Γ vs. K^2 curve is linear, reflecting the diffusive motion of the hydration complex. At 274°K, the slope is so small that the broadening is almost at the experimental limit of resolution. This low slope and, hence, small value of the diffusion coefficient undoubtedly reflect a high "effective mass" for hydration complex both relative to lithium acetate solutions. This, in turn, may reflect the heavier mass of the cation-water complex in magnesium relative to lithium and a stronger time average coupling to the acetate anion. Indeed, unlike the temperature behavior for the Γ vs. K^2 curve for 15.0 m LiCl , 16.0 m LiNO_2 , and 7.0 m CD_3COOLi , shown in Figure 2, the curves of Γ vs. K^2 for magnesium acetate increase in slope but remain linear to above 75°C. Hence, the acetate anion appears to have very effectively

hindered the reorientations of the primary waters so that their relaxation times exceed the neutron interaction time even at these high temperatures. Again, this behavior would be in accord with a strong association between the hydrated cation and the anion. In this regard it should also be noted(23) that the acetate anion strongly increases the glass transition temperature of magnesium solutions relative to other anions.

In addition to the above results, a number of the data previously reported should be recalled for comparison. As shown in Figure 5, CrCl_3 and $\text{Cr}(\text{NO}_3)_3$ solutions (at sufficiently high concentration so that the H_2O molecules present were strongly coordinated in the first or second hydration layers) also show curves of Γ vs. K^2 at 1°C having low slopes (hence, small values of the self-diffusion coefficient and are linear to the origin (Curve III, Figure 1)). In addition, measurements were reported(3) for solutions of 4.3 m $\text{La}(\text{NO}_3)_3$ and 4.23 m CrCl_3 at temperatures just above and below respective glass transition temperatures. The chromium and lanthanum salts were chosen as they could readily be held in a supercooled state for the extended periods of time necessary in order to perform the experiments. In general, with decreasing temperature, the diffusively broadened quasi-elastic component narrowed rapidly and, for the above two solutions, showed no abrupt change as the glass transition temperature was passed. However, the diffusive motions of the hydrated cations rapidly became restricted with decreasing temperature so that the broadening of the quasi-elastic maxima in turn rapidly decreased to within experimental resolution.

In summary, it should be re-emphasized that the variations in both functional form with decreasing temperature and increasing anion basicity of the Γ vs. K^2 curves and, hence, of the diffusive kinetics, strongly support the argument of Angell and Sare(23) for glass formation in ionic solutions. As the temperature is initially lowered, both exchange and rotational reorientations of individual primary water molecules become increasingly restricted. Then, as a result, "excess free volume" is reduced and motions of the hydrated ions increasingly involve cooperative rearrangements. The glass transition itself may be correlated to a near complete restriction of motions of hydrated cations. Further, the above results also emphasize that increasing anion basicity can (as argued by Angell and Sare(23)) restrict the motions of the hydrated cations and order their environment, thereby decreasing the configurational entropy.

b) Dependences on Temperature and Anions of the Quasi-Elastic Areas.
As discussed above, both for simple jump diffusion and for the extended model of Larsson and Bergsted(45), the areas of the quasi-elastic components depend on Debye-Waller factors. The Debye exponent is proportional to a mean square amplitude for the average vibrations. At

temperatures well above the glass transition, it would primarily correspond to the vibrational amplitudes of individual water molecules in primary hydration layers; while close to the glass transition temperature, it could correspond to vibrations both of primary water molecules and of vibrations involving the hydrated cations. In Figure 7, at the upper half, the natural logarithms of the quasi-elastic areas are plotted vs. K^2 for a series of more dilute solutions, and for water for which a simple jump diffusion model has been shown to be an adequate approximation. At such lower temperatures and higher concentrations, the area determined for the quasi-elastic maxima (relative to 25°C water) become simplified due to the intensification and narrowing of the components. As seen, the curves of $\ln A$ vs. K^2 are linear and functionally in accord with the behavior expected for a Debye-Waller factor. For water at 1°C, the mean square amplitude is reduced relative to 25°C, and small or multiply charged ions further reduce the mean square amplitudes. The parameter, α , proportioned to a mean square vibrational amplitude, reduces from about 0.14 Å² at 25°C to 0.10 Å² at 1°C. Small or multiply charged ions at 1°C cause a further amplitude reduction to a value of about 0.06 Å².

At the lower half of Figure 7, similar curves, as a function of temperature, are compared for lithium acetate, for lithium chloride, and for calcium nitrate solutions. The following features should be noticed.

(a) Again, $\ln A$ vs. K^2 are linear (the behavior expected on the basis of the Larsson and Bergsted model that the area of the quasi-elastic maxima should be proportional to a Debye-Waller factor). The curves for the lithium salts have shapes intermediate to that for water at 1°C (see upper half of the figure), and those for multiply charged cations at 1°C. Thus, the lithium cation does not reduce the average amplitude as strongly as the multiply-charged cations.

(b) As shown in the lower half of Figure 7, the slope for 15.0 m LiCl at 1°C is lower than that for the lithium acetate, corresponding to a stronger coordination of the primary waters in the more concentrated Li solution, relative to the acetate solution which would involve both primary and secondary hydration waters. However, with increasing temperature, it is seen that the slope increases more rapidly for the lithium chloride than for the acetate solution, again indicating that the acetate ion is more effective than the chloride ion in restricting an increase in vibrational amplitude with increasing temperature.

These results complement and support those discussed above for the diffusive motions and their changes with increasing temperature which showed that the reorientation and exchange of individual water molecules in the primary layers were more strongly restricted by the acetate ion than the chloride ion. The change in the curves

of $\ln A$ vs. K^2 for calcium nitrate, as a function of temperature, are also in keeping with a reduction of the vibrational amplitude for the primary hydration waters upon supercooling.

c) Inelastic Spectra. The inelastic spectra for a series of lithium salts with different -1 anions are shown in Figure 4. In Figures 7 and 3, the temperature dependences and concentration dependences of certain of these salts are shown. A comparison of these figures shows in the region typical of librational frequencies of water molecules coordinated to the cation and of metal-ion stretching and bending frequencies (in the region between 900 and 200 cm^{-1}) that the observed frequencies are common for all the lithium salts shown and are not observed in pure water or other ionic solutions. While, in general, these frequencies appear sharpened for certain salts than others and show some interplay in sharpness, in intensity and in their dispersion, they appear within resolution at nearly the same frequencies in all these lithium salts. The presence of these frequencies and their primary dependence on the Li^+ cation, suggest that in these solutions the majority of H_2O molecules are primarily oriented about and coordinated to the lithium ions. Indeed, the quasi-elastic measurements further support such a conclusion. The curves of Γ vs. K^2 for all the lithium solutions lie below that for water, including those for the normally strong "structure-breaking" anions, I^- and SCN^- . In the presence of weaker cations, e.g., K^+ or Cs^+ , such strong "structure-breaking" anions cause an increase in the self-diffusion coefficients and a decrease in the residence time relative to water in contrast to the results for the lithium solutions. Thus, it appears that even in the presence of an I^- or SCN^- ion the lithium is able to primarily control the orientation of water molecules and increase their relaxation times relative to water. In this regard, it is also of interest to note that even in the presence of a strong "structure-making" anion (the acetate anion), the Li^+ cation again appears to dominate and control the ordering of the waters. This is in contrast to the behavior observed for salts having a weak cation, e.g., Cs^+ or K^+ in the presence of a strong anion such as an F^- . In such cases, the orientation of water molecules and their characteristic frequencies appeared primarily determined by the anion, as has been previously reported and discussed.

Thus, it would appear in the above solutions of lithium salts that the water molecules are primarily oriented around the cation, and then these, in turn, are oriented or packed around the weaker anions. Of course, as will be discussed in detail below, the anions serve to perturb to varying degrees the ordering of water molecules around the cations and to strongly influence their ability to undergo rotational reorientations and to exchange from the vicinity of the cation. To further understand such effects, the following features of the spectra should be noted.

(1) In general, the inelastic frequencies appear characteristic of lithium ion coordinations and appear sharper and better defined in the lithium iodide and lithium acetate solutions relative to the lithium nitrate and lithium thiocyanate solutions. If such sharpening is associated with a more unique and less perturbed coordination of the water molecules about the lithium ion, it would appear that both a strong "structure-breaking" anion, I^- , and a strong "structure-making" ion acetate, both serve to aid the hydration of lithium relative to the more intermediate anions, such as Cl^- , SCN^- , NO_3^- . In turn, this suggests that more than one factor may be involved as to the role of anions and their effect upon water molecules distributed about hydrated cations. Thus, the large I^- ion can sterically disrupt any remnant of solvent structure which would favor the further ordering of water molecules about the lithium cations. In addition, water-iodide bonds would be expected to be weaker than any solvent-solvent coordinations which should again favor less competition between the lithium and solvent coordinations in orienting waters in the hydration spheres. It is seen in Figure 4 that the curves for Γ vs. K^2 for lithium iodide lie higher than that for the other salts. Thus, the sharpening of the inelastic frequencies reflects that even though the average residence time for water molecules has been reduced in the presence of the iodide ion, the ability of the iodide ion to break solvent coordinations and the fact that any anion-solvent coordinations would involve a weaker bonding than the original solvent-solvent coordinations has allowed more water molecules to assume a unique orientation about the cations and thereby decrease the dispersion of frequencies associated with such complexes. It might be expected that the strong acetate ion would tend to approach the lithium cation tending to ion-pair either directly or through hydration spheres, thereby displacing water from the coordination sphere of the lithium or strongly distorting the hydration sphere. It is seen in Figure 3 that the curve of Γ vs. K^2 for the lithium acetate shows a different shape at a 4.6 m concentration than those for the other salts being linear in K^2 rather than showing a typical jump diffusion behavior. This has been (as described above) attributed to the fact that the residence times for the individual H_2O molecules have now exceeded the neutron interaction time and thus the quasi-elastic broadening reflects diffusion or motion of the hydrated lithium ion. The corresponding sharpening of the inelastic frequencies in this spectrum for lithium acetate undoubtedly results from the stability of the basic acetate ion to strongly hinder the rotational reorientation and relaxation of the primary water molecules which in turn sharpens the inelastic frequencies. Undoubtedly distortions of the hydration complexes due to such interactions of hydrational waters with the acetate anion result. However, the closeness of the frequencies observed to those noted above in the case of a very weakly coordinating I^- ion suggests that, while present, such a distortion is not sufficiently large to completely disrupt

the characteristic lithium hydration complex and cause a drastic change in its characteristic modes. Thus, while the ordering in the hydration complexes would be expected to be more disturbed geometrically in the presence of an acetate ion than in the presence of the weak I^- ion, the acetate ions would have strongly restricted the reorientational motions of the waters about their dipolar axis (as also discussed in a paper by Protzel et al(65)) and any relaxational broadening of the inelastic spectrum would have been strongly reduced. It also appears that in addition to perturbing any geometrical orientation of water molecules about the lithium which would serve to weaken a directional type of bonding between the lithium and primary waters, strong water-acetate interaction may have served to polarize the water molecules which, in contrast, would serve again to strengthen cation-water coordinations. Such effect, in part, could explain that the water molecules about the lithium did not have their coordinations strongly disrupted by the strong acetate ion. The SCN^- and NO_3^- ions would be intermediate cases. From the curves of Γ vs. K^2 it is seen that these ions serve to disrupt solvent structure, increase the self-diffusion coefficients, and decrease the residence times for water molecules relative to lithium chloride and lithium acetate, but not as strongly as is observed for lithium iodide. Thus, such water molecules would favor a hydration and a geometrical ordering of water molecules around the lithium ion, in part disrupting the solvent-solvent complexes. However, they would not do this as effectively as the iodide ion and would still form stronger anion-water coordinations than would the iodide ion. Further, however, such coordinations would not be sufficiently strong as are water-acetate coordinations to strongly restrict the reorientational ability of water molecules and to, hence, decrease the relaxational broadening.

(2) For the lithium nitrate and chloride solutions, as the concentration is increased from 4.6 m toward 10.0 m (12 water molecules per ion-pair to 5 water molecules per ion-pair), the sharpening of the inelastic frequencies and the decrease in the self-diffusion coefficients reflect the stronger coordination of water molecules in the primary hydration layer. However, it still appears quite possible that the closer approach of the anion to the primary hydration layer has served to weaken the coordinations of the primary water molecules, as noted by Woessner et al(48,49) relative to their coordinations at lower concentrations. Thus, the closer approach of a chloride ion would involve an increased number of Cl^- - primary H_2O coordinations than at lower concentrations, and such coordinations could well be weaker than the normal primary H_2O-H_2O coordinations. This, in turn, is reflected by a less rapid increase with concentration of the relaxation times of the average water at higher relative to lower concentrations. In addition, the chloride ion might tend to disrupt any longer range ordering in the vicinity of the

lithium cation than may be present at lower concentrations, as discussed in previous reports. In the case of lithium chloride where solubility allows the concentration to be increased further above 10.0 m, it is interesting to note that as the concentration approaches 15.02 m the inelastic frequencies again broaden. Thus, as the anion now approaches the cation it is able to perturb the ordering of the water molecules in the first layer and thus give rise to a broadening of their characteristic modes. For a strong anion, such as the acetate, an increase in concentration broadens the inelastic frequencies corresponding to a distortion of the primary hydration layers which overcomes any sharpening effect on the inelastic frequencies due to the restriction of relaxational freedom by the anion-water coordinations. Thus, with concentration, as the cation-water lines broaden, the curves of Γ vs. K^2 show a further decrease in the self-diffusion coefficient associated with the hydrated cation. This indicates that the acetate ion has both a distortional effect due to its interactions with the primary waters but that, in addition, such interactions also serve to strongly limit the diffusional mobility of the hydrated cation, possibly by bridging such units together in the manner suggested by Angell et al(23).

(3) With increasing temperature, for a 4.6 m solution of lithium chloride (the primary and secondary hydration layers), the self-diffusion coefficient is observed to increase and the relaxation time for reorientation of the individual water molecules decreases. In correspondence, the inelastic frequencies are observed to broaden. This behavior reflects a thermal disruption of the hydration spheres. A similar behavior is observed for a 15.0 m lithium chloride solution, but the broadening is less rapid with increasing temperature as would be expected for the stronger coordinations of the primary hydration layer. In contrast, with increasing temperature, the inelastic frequencies for a lithium acetate solution are observed to sharpen. In like manner, in contrast to the lithium chloride solution, as has been discussed above, even at higher temperatures for the lithium acetate solution the curves of Γ vs. K^2 do not only show a jump diffusion behavior but the motion of a hydrated cation whose diffusional freedom is increasing with temperature. The sharpening with temperature indicates that distortion of water molecules in the primary hydration layer of the lithium ion is being reduced more rapidly than their thermal disruption is increasing. This probably results from the fact that anion-water coordinations are becoming weaker more rapidly than the cation-water coordinations as the temperature is increased. In addition, however, as the anion-water coordinations weaken, their ability to restrict the overall diffusive motion of the hydrated cation is rapidly decreased. It should be noted, however, that in the acetate solutions at these concentrations, both primary and secondary water molecules would be involved and that curves of Γ vs. K^2 even at the higher temperatures indicate that most of these water molecules have

residence times beyond the neutron interaction time. Thus, the acetate ion appears to have a very strong ability to hinder the re-orientation of water molecules and to enhance the bonding between primary and secondary hydration sphere waters, probably through a strong polarization effect. This, in turn, serves to stabilize the entire complex and increase the residence times of the individual water molecules with regard to reorientation strongly, even though the geometric ordering of this complex may have undergone some distortions from that which would be characteristic of the primary and secondary hydration spheres around the lithium ion in dilute solutions. In addition, if the acetate ion can bridge such hydrated lithium complexes thereby reducing the diffusional mobility, it may also to some extent at these high concentrations hinder the exchange of individual water molecules by effectively blocking their passage from the hydration sphere of one ion to the hydration of another more distant hydrated cation.

2) Ternary Solutions

A. Background Information

a) Summary of Thermodynamic Data and Theory. In recent years ion-ion interactions and ion solvent interactions in ternary solutions have been the subject of considerable theoretical investigation. There have been many discussions in the literature concerning both the nature of the specific ion interactions and the role of solvent and hydration structures. Friedman(32) applied Mayer's(33) ionic solution theory to electrolytic mixtures for solutions of pure electrolytes with a common ion. More recently, Ramanathan and Friedman(32) proposed a refined model for aqueous 1-1 electrolytes where a hypernetted chain integral equation is used to calculate ion-ion pair correlation functions and the thermodynamic properties of models for aqueous 1-1 electrolytes. The potential involves a coulomb term between the interacting ions, a repulsive core term, a term including the dielectric effect (in which an ion is considered as a cavity of characteristic radius in the dielectric), as well as a term involving cosphere overlap (in which it is assumed that an isolated ion is surrounded by a close sphere of solvent with different properties than the more distant pure solvent). In this model the molecular nature of the solvent enters in parameters such as the radius of a water molecule, the dielectric constant of the distant solvent, and the coefficient of the Gurney or cosphere portion of the potential. Friedman concluded that like-charge ions have specific interactions which may be more important than any triplet interactions, in contrast to the results of the theory of Bronsted(35). Further, Wood and his coworkers(36-41), using the theory of Friedman and measurements of heat of mixing, demonstrated that

(1) in the presence of cations such as Li^+ , Na^+ , K^+ , Mg^{+2} , and Ca^{+2} the heat of mixing is nearly independent of whether the anion is a chloride or a bromide,

(2) cations can be divided into two groups with regard to the heat of mixing -- a "structure-making" group (e.g., Li^+ , Na^+ , Mg^{+2} , Ca^{+2} , and Ba^{+2}), and a "structure-breaking" group (e.g., K^+ , Rb^+ , and Cs^+). The heats of mixing between ions of the same group are endothermic and between opposite groups, exothermic,

(3) for mixing of potassium salts with fluoride, chloride, bromide and acetate anions the heats of mixing for anions can be comparable in magnitude with those of cation heats of mixing,

(4) the detailed structure of the water about ions is a most important factor in determining the heat of mixing. If contributions due to interactions of oppositely charged ions are first estimated and subtracted from the heats of mixing, the interactions between ions of like charge are then the major contributors to the mixing which correlate the "structure-making" and "-breaking" behavior noted above; such interactions between ions of like charge may serve to perturb the ordering of water molecules in their hydration spheres.

The determination of excess thermodynamic properties of mixed aqueous electrolytic solutions has provided the means for studying the overall effects of specific ion interactions. Thus, when mixed aqueous solutions at constant ionic strength are investigated in the presence of a common ion, the effects of the ionic atmosphere cancel as to the effects of oppositely charged pairs and one observes phenomenon due only to like-charged pairs and higher order interactions. However, as noted by Anderson and Petree(42) such thermodynamic results still represent a summation over a number of variables. Thus, interactions between like-charged ions, distortions of hydration or cospheres occur, and changes in the structure of the pure solvent may simultaneously contribute nevertheless. By studying changes in heat of mixing parameters as a function of temperature, Anderson and Petree tentatively concluded that changes in the ordering and bonding of water molecules in the regions of primary hydration spheres of ions play a strong role in the heats of mixing.

To specifically account for changes in the bonding and the ordering of water molecules that occur upon mixing binary solutions and their relationship to "salting-in" and "salting-out" phenomena, Samoilov(43,44) has recently proposed a semiquantitative theory based upon his concept of "positive" and "negative" hydration. The effects of specific ion-pair interactions are not calculated directly. Rather, Samoilov considers the changes that occur upon mixing in terms

of two types of interactions. The first type assumes that the interaction between cations in solutions weakens the bonding of primary water molecules allowing them to be more readily reoriented. In contrast, the interactions between anions and cations "enhance the bonding" of water molecules in the primary layer of the cation and hinder the reorientation of H_2O 's. For such interactions no quantitative statement of the specific ion-ion interactions is explicitly provided. Rather, they are treated in terms of a "semi-empirical" parameter that expresses the rate with which primary water molecules can exchange from the vicinity of the first hydration layer of cations. The second term represents a specific dipole interaction between the average field of a neighboring ion and a water molecule which can reorient in the vicinity of a second ion. When the interaction is between two cations, the field of one cation tends to reorient water molecules which have exchanged from but are in the proximity of the primary hydration sphere of a second cation. In contrast, for a cation-anion interaction the anion tends to inhibit a reorientation of such water molecules. This theory has been correlated with a great deal of thermodynamic and "salting-out" data and predicts trends similar to those obtained by Wood and coworkers(36-41) in terms of the "structure-making" and "-breaking" properties of the ions.

B. N.M.R. and Dielectric Measurements

To date there have been only a limited number of measurements to directly determine, at a molecular level, the changes that occur upon mixing in ternary solutions in the bonding and ordering of water molecules in the hydration spheres of cations; the changes in the structure of the bulk solvent; the influence on such changes of anions of varied strengths; and the effect of temperature. The summation of such changes, of course, must and should be accounted for in any thermodynamic model. However, evidence to date indicates that it is difficult to get a unique understanding of such molecular processes from the thermodynamic data alone in view of the fact that a number of changes upon mixing may be simultaneously occurring and the thermodynamic results represent their net sum. The neutron scattering measurements made during the past year and a half are aimed specifically at determining the changes in the ordering of H_2O molecules and their diffusive kinetics relative to the individual unmixed solutions that occur upon mixing in ternary ionic solutions. As will be discussed below, such neutron measurements have shown that significant changes in both the ordering and bonding in primary hydration spheres and in the diffusive kinetics of H_2O molecules may occur upon mixing. In addition, when such results are considered together with previous neutron scattering results on binary solutions(2-6) and the classification of ions in the "structure-making" and "-breaking" classes, for roles of anions and cations in concentrated ionic solutions, and with NMR(74,75) and dielectric measurements(76) made on ternary

solutions, additional insight is gained in ternary solutions as to the relative roles and influences specific to cations and anions and solvent molecules. Ionov and coworkers (74) measured the spin lattice relaxation time, T_1 , for the "weakly hydrating" $^{23}\text{Na}^+$ ion in 0.2M solutions of sodium chloride mixed with solutions of CsCl, KCl, NaCl, LiCl, LiNO_3 , and $\text{Ca}(\text{NO}_3)_2$ as a function of concentration up to 5M. The T_1 is shown by the authors to be nearly inversely proportional to the correlation (τ_c) or residence time for waters in the hydration envelope of the sodium ion. The results show a number of interesting features. τ_c for the sodium ion decreases with the addition of a second salt as $\text{CaCl}_2 > \text{LiNO}_3 \cong \text{LiCl} > \text{NaCl} > \text{KCl} > \text{CsCl}$. Thus, the "structure-making" salts LiCl, LiNO_3 , and CaCl_2 enhance the stability of the hydration sphere of the sodium ion relative to sodium chloride, whereas, the "structure-breaking" salts (CsCl, KCl) decrease it. These results provide direct evidence at a molecular level that the correlation time associated with the ion being "salted out" (e.g., Na^+) is enhanced by "structure-making" salts and decreased by "structure-breaking" salts. Further, in the presence of strongly hydrating Li^+ , little difference is observed between Cl^- or NO_3^- anions when mixed with NaCl. However, interestingly these authors note that for a given "structure-making" cation, τ_c , for the sodium ion, increased more rapidly with the increasing concentration of the second component when the anion of the second component was varied from a chloride to an iodide. Thus, in the presence of a strongly hydrating cation for the second component the influence of a -1 anion was secondary but still a change occurs towards an increased hydration of the sodium, as the anion of the second component was varied more strongly towards a "structure-breaking" activity (e.g., Cl^- to I^-). Two additional interesting features of the data of Ionov and his coworkers (74) should be noted for "structure-makers" as the second component, τ_c 's for the sodium ion increased nearly linearly with increasing concentration from low concentrations where ions would be well separated. Secondly, for the "structure-breakers" as the second components (e.g., CsCl and KCl), the τ_c for the $^{23}\text{Na}^+$ initially decrease but then, at higher concentrations again increase. This indicated that at higher concentrations of CsCl and KCl these salts again act as "structure-makers." This secondary behavior for the "structure-breakers" with increasing concentration is analogous to that reported previously (2) for that observed for the concentration dependences of self-diffusion coefficients KCl and CsCl measured by neutron inelastic scattering investigations and spin-echo measurements. Specifically, at low concentrations both cesium and potassium increase the self-diffusion coefficient relative to pure water and act as "negative hydrators" or "structure-breakers." However, with increasing concentration, the self-diffusion coefficients approach a maximum value and then decrease. In like manner, it was noted that as the temperature increased the "structure-breaking" effect of these ions became less pronounced. The above behavior has been attributed (2)

to the fact that these ions in solution at low temperatures and concentrations tended to disrupt water around them but could not form cation-water hydration complexes in which the water molecules would be as strongly coordinated as in the pure solvent. Thus, in effect, the ions had to "compete" for their hydration with the structure of the solvent. However, at higher concentrations or temperatures where respectively there was either little solvent structure left or the solvent structure had been nearly totally thermally disrupted, the ions could then orient water molecules around them and build order hydration layers more readily than at lower temperatures where a competition for the solvents was involved.

To account for the above NMR results, Ionov and coworkers (74) postulate that when sodium chloride (which is only a weak "structure-making" salt) is mixed with a strong "structure-making" salt in dilute solution, a larger number of H_2O 's become oriented about the stronger cation. In turn, the chloride ions are "forced away" from the strongly hydrating cation and towards the sodium ion where they disrupt remnant solvent structures in outer hydration layers and form chloride water bonds which were weaker than the previous H_2O-H_2O bonds. Hence, a distribution of such water molecules from solvent structure to orientations about the sodium ion occurs. In contrast, when sodium chloride is mixed with a "structure-breaking" ion (e.g., Cs^+ or K^+), anions would be forced from the vicinity of the sodium (which is now the more strongly hydrating of the two ions) towards the Cs^+ or K^+ cation, tending to stabilize the latter and forcing the sodium ion to compete more strongly for waters of hydration with the solvent.

A similar argument has been used by Kokovina and his coworkers (76) to interpret measurements of the dielectric permeability of ternary aqueous solutions of alkali and alkaline earth chlorides. They argue that when monovalent, weakly positively hydrating Na^+ cations are mixed with more strongly hydrating divalent cations (Ba^{+2} , Sr^{+2} , Ca^{+2} and Mg^{+2}), a "squeezing out" of the Cl^- anion occurs which increases in going from Ba^{+2} to Ca^{+2} . The "squeezed out" Cl^- anions migrate to other parts of the solution, either to the farther surroundings of the monovalent cation, or to free water zones, depending on the character of the short range hydration of the monovalent cation. If the hydration of the monovalent cation (like that of sodium) is positive, the water molecules adjacent to it are less mobile than free water and the anions "squeezed out" from the divalent cations migrate to free water zones which they disrupt. Hence, they increase the re-orientation of water molecules in such zones and enhance the dielectric permeability. In contrast, if the monovalent cation is "negatively hydrated" (e.g., like potassium or cesium) adjacent water molecules are more mobile than in free water. Then, the Cl^- anions migrate not to free water zones but to the longer range or outer hydration layers of the monovalent cations where they cause a partial redistribution of

water molecules from the broken region into "free water" zones. Thus, water molecules pass into the "free water" regions whereby their mobility is reduced and, hence, the dielectric permeability is now diminished. However, these authors note that, for a strongly hydrating cation such as Mg^{+2} (for which it has been argued that partially covalent bonds may be formed in the primary hydration layer), the tendency to ion-pair through the primary hydration layer of the cations can inhibit the repulsion or the "squeezing out" of the Cl^- ion relative to Ba^{+2} and Sr^{+2} . While the above interpretations must be considered tentative, they do emphasize that, upon mixing, non-additive changes in the solvent structure and in the distributions of waters and anions around cations occur and correlate strongly with the "structure-making" or "-breaking" nature of the ions. Further, a number of the above observations and, in particular, the "squeezing out" of anions may be understood more closely when they are considered together with reported(1-6) results of neutron scattering observations on the hydration of ions and the relative influences of cation-water and anion-water interactions.

C. Summary of Previous Neutron Scattering Results on Binary Solutions and Their Implications for Ternary Salt Solutions

In previous reported(4) measurements for concentrated solution, it has been shown that strongly hydrated cations (e.g., Li^+ , Mg^{+2} , Cr^{+3}) may diffuse together with their waters of hydration. Indeed, the concept of a hydrated cation has a well defined meaning for such cases, and such hydration complexes give rise to characteristic frequencies in the infrared and have identities distinguishable in NMR measurements. It has been argued(8) that Mg^{+2} and Cr^{+3} may even involve a degree of covalency between the cations and the primary waters. At higher temperatures, as the coordination of waters about the cation become disrupted, the anions are drawn in and tend to ion-pair through the primary hydration layers. Anions (on a time-average) may approach the cation more closely and distort the symmetry of the primary-water coordinations. For less strongly hydrating cations and at low temperatures, the anions are "repelled" further from the hydration layers of the cation. However, with increasing concentration, the anion "draws in" and may perturb or distort the symmetry of the hydration layers. Thus, for less strongly hydrating cations such as a barium, a strontium, or a calcium, the anions could be readily displaced from the immediate vicinity of the primary hydration layers by the addition of water molecules upon mixing in ternary solutions. Weakly or negatively hydrating cations again form primary ion-water coordinations but at lower temperatures such water molecules are more mobile than those in pure water or those oriented about the multiply-charged cations noted above. Hence, such cations must compete strongly with solvent structure. In addition, even weaker anions can readily ion-pair with such cations and displace water molecules from their vicinity.

In addition to the above results, previous neutron studies (4) of the effects of anions on the diffusive mobility of hydrated cations have shown that the approach of an anion to a cation may influence the waters of hydration about a cation in a number of ways that depend specifically upon the relative strengths of cation-water anion-water coordinations. Thus, a weak anion, like Cl^- , with increasing concentration may disorient and disrupt H_2O in cation hydration layers thereby increasing the motional freedom both of the cation and of the waters. Such a behavior has been reported, for example, from NMR studies of LiCl solution (55,56,27). For more strongly hydrating cations, weak anions such as chlorides or nitrates may only produce a negligible distortion. In contrast, stronger anions such as sulfates or acetates will more closely approach cations, and tend, on a time-average, to ion-pair and to enhance the exchange of primary water molecules. In general, with increasing strength, anions will more closely approach a cation, but if the cation-water coordinations are sufficiently strong the anion may only distort the primary hydration layers. However, it may also hinder rotational reorientations of the primary water molecules, thus both effectively hindering the diffusive mobility of the hydrated cation and the reorientation of individual water molecules.

Such results from previous neutron scattering measurements extend and support an understanding of the results used from dielectric and NMR measurements for ternary ionic solutions. Thus, when two salts with a common anion are mixed and when both are "structure-makers" but one is a stronger "structure-maker" than the other, interactions between the different cations can perturb the hydration layers about both cations and weaken their bonding relative to their individual solutions. Further, an additional disruption of remnant solvent may occur due to such interactions relative to the individual solutions. Water molecules could then migrate from the region of the disrupted solvent and redistribute to the outer layers of cations with the majority going to the more strongly hydrating cation. The bonding of such water molecules in the outer layers of a cation would be stronger than that in the disrupted solvent, but weaker than they were in "free water" regions. For weak anions the H_2O - H_2O coordinations in higher hydration layers could be stronger than anion-water coordinations. Thus the anions would be forced away (from the stronger cations), a larger density of anions would appear around the weaker ones, and solvent structures in their vicinity would be further weakened, thus favoring an orientation of additional water molecules around the weaker cation. This additional hydration would in turn tend to stabilize the weaker cation and strengthen the coordination relative to its binary solution in keeping with the above NMR observations.

In contrast, if a weak positive hydrating salt, like NaCl, were mixed with a weaker "negatively hydrating" salt, like CsCl, the solvent structure around the Cs⁺ would be strongly disrupted. Upon mixing, anions would now be repelled from the region of sodium which would make it compete more strongly with any remnant solvent structure. The anions would migrate and tend to ion-pair with the Cs⁺ forcing waters from the broken regions in its vicinity to the solvent. Thus, an increase in ordering of the solvent structure would occur. The sodium ion would become more mobile and anions would tend to pair with the cesium.

If part of the weak chloride ions in such solutions were replaced with strong anions (e.g., SO₄⁻² anions) then the tendency to pair through primary hydration layers with the stronger of the two cations would inhibit the displacement of such anions toward the weaker cation upon mixing. Further, they could stabilize additional H₂O's in higher hydration layers about the stronger cation and enhance stabilization of H₂O's in the ternary solution (on an average) relative to those in component solutions.

In summary, most detailed theoretical considerations of mixing in aqueous solutions have involved specific ion-ion pair interactions. Thus, in the application of such theories to the interpretation of heat of mixing data, Wood and his coworkers (36-41) have compared the data for a mixed solution with that of the individual component. They have noted that many common ion-ion interactions effectively cancel out so that the resultant quantity primarily reflects interactions between the non-common ions together with any changes in solvent or hydration structures that may have occurred. Indeed, such results are observed empirically to correlate well with the "structure-making" or "-breaking" classifications of the original salts. However, it should be emphasized that redistributions of waters in hydration layers of common anions, as well as a disruption of the solvent structure, may occur as the result of such stronger, direct ion-ion interactions. Indeed, it may be the direct ion-ion interactions that account for the largest observable bulk energy changes that occur upon mixing, while changes in solvent and hydration structures are a secondary effect in terms of energy. Nevertheless, despite this secondary energetic effect, ion-solvent interactions and the resulting changes that occur upon mixing may strongly determine whether one or more components is salted out in the process. Thus, Samoilov has based his theory of "salting-in" and "salting-out" strongly on the basis of changes in hydration and solvent structure that occur upon mixing.

It is clear that the changes that occur upon mixing in ternary solution are indeed complex, involving changes in ion interactions, in solvent structure, in the distribution of anions and cations,

and the ordering of waters in hydration layers. The present neutron data serve to isolate and clarify one particular aspect of these changes; namely, the changes that occur in the waters in hydration layers, in the solvent structure, and their dependencies on the "structure-making" and "-breaking" characteristic of the ions involved.

The results and interpretations based upon the NMR and the dielectric measurements will also be shown to be in accord with the neutron scattering spectra discussed below for ternary solutions. However, it is to be emphasized that the neutron scattering spectra reflect only one type of the changes that occur upon mixing solutions, specifically the changes in the bonding through orientation and in the diffusive kinetics of water molecules in primary hydration layers and in the bulk solvent. They do not directly reflect specific ion-ion interactions per se. It is not the purpose of the present experiments or investigation to argue that specific ion-ion interactions may not be producing the most significant energy changes that occur upon mixing. Rather, they emphasize that redistributions of water molecules occur in hydration layers, changes in the solvent structure occur, and a redistribution of anions may also take place -- possibly as the result of such strong, direct cation-cation interactions. Such redistributions of water molecules strongly affect the degree to which one or another component is salted out upon mixing.

D. Results and Discussion

The results of the measurements are summarized briefly in Table I. In order to discuss trends, these are divided into the following categories:

CASE A: A salt with a weak "structure-making" cation (e.g., NaCl) is mixed with each of a series of salts having cations ranging from strong "structure-makers" to a "structure-breaker." Both component salts have a common, weakly hydrating anion (e.g., Cl^-).

CASE B: A salt with a strongly hydrating cation (e.g., MgCl_2) is mixed with a series of salts whose cations vary from strong "structure-makers" to "structure-breakers." This series, when compared with (A) above, illustrates the difference when the fixed component salt (e.g., magnesium chloride) is a strong "structure-maker" as opposed to when the fixed component salt is a weak "structure-maker" (e.g., NaCl). Again, the anion is common (Figures 9 - 12).

CASE C: The effects of replacing in part weak anions (e.g., Cl^-) by strongly hydrating anions (e.g., SO_4^{2-}) in the presence of a common "weakly" hydrating cation, Na^+ , and a common strongly hydrating cation, Mg^{+2} , are illustrated (Figures 1 and 2).

CASE D: These data correlate Case (C) and illustrate the effect of replacing in part a weak anion, Cl^{-1} , by a stronger "structure-breaking" anion, I^{-1} , in the presence of a common "structure-breaking" cation, K^{+} (Figures 3 and 4) and of a common "structure-making" cation, Li^{+} (Figures 5 and 6).

At the right in Table I are shown the trends observed for the ternary solution relative to "additivity" of the individual components both for the self-diffusion coefficients and for the inelastic frequencies. The inelastic frequencies observed for the ternary solution are compared with those obtained by adding spectra for the individual component solutions. In essence, such a composite spectra would be obtained by running simultaneously the two components separated by a partition that would prevent mixing and would not contribute to the neutron spectrum. In like manner, an effective self-diffusion coefficient for the composite was obtained on the basis that the diffusion process at these concentrations is dominated by activated jumps of individual water molecules. Then additivity of the average activation energies corresponding to the component solutions was assumed. Previous results have demonstrated that for the individual salt solutions the observed angular, temperature, and shape dependences of the diffusively broadened incident energy distribution (the quasi-elastic component) were in accord with an activated jump diffusion mechanism(1-6). In Table I changes in the self-diffusion coefficient corresponding to either increases or decreases of D_M for the ternary solution relative to the D_{comp} , are observed. In correspondence, the curves of Γ vs. K^2 for the ternary solution lie systematically above or below those corresponding to the additive composite. The values of D were obtained by noting that the curves of Γ vs. K^2 rise linearly from the origin with a slope at the origin given by $\hbar D$. In general, the observed variation in the values of D due to mixing are small, but are real and systematic. D reflects small non-additive changes in the average activation energies of the solvent molecules. Thus, any increase in D reflects a decrease in the average activation energy of the water molecules present, while a decrease reflects an increase in the average activation energy of the water molecules present. Thus, the changes in the self-diffusion coefficients, listed in Table I, provide information on whether the mixing process increased or decreased the net average activation energy of the water molecules present.

In contrast to the diffusive kinetics, a comparison of the inelastic portions of the spectra with those for a composite and the individual solutions does not provide direct information on changes in the average activation energies of water molecules present. Rather, primarily they reflect the changes in the ordering and in the coordination of molecules around the cations that have resulted from the mixing process. As indicated in Table I and discussed in

detail below, significant changes in the ordering of the hydration layers about one or both cations in ternary solutions are observed to occur in a manner peculiar to the combination of "structure-making" and "-breaking" ions present. The results for the specific cases listed in Table I will now be considered individually and they will also be related to the possible redistributions of water molecules in hydration layers and the effects of anions as discussed in the previous section with regard to the data of Ionov and coworkers(74) in their NMR measurements and the results of dielectric measurements on ternary solutions.

A number of the more general trends in Table I should be noted. Initially, in most cases (with certain exceptions), the mixing of two "structure-making" cations in the presence of a common weak anion such as Cl^- results in an increase in the self-diffusion coefficient or equivalently a decrease in the activation energy for the average H_2O relative to additivity. An exception, the mixing of MgCl_2 and LiCl , will be discussed below. At the concentrations involved, typically 4.6 m, there are 12 water molecules per ion pair. Hence, most of the water molecules would be expected to be in primary or secondary hydration layers or in the general vicinity of the cations involved. Thus, it appears that the ion interactions that occur upon mixing two "structure-making" cations disrupt the ordering of water molecules on the average. When a "structure-making" and a "structure-breaking" cation are mixed, the activation energy for the average water molecules is increased relative to the composite. Thus, with the exception noted above, the observed increases and decreases in diffusion coefficients that occur upon mixing correlate respectively with the mixing of two "structure-making" cations or a "structure-making" and "structure-breaking" cation.

The data in Table I for Case C, however, emphasizes that in the presence of a common positively hydrating cation (e.g., either Mg^{+2} or Na^{+1}) the replacement of chloride anions in part by the more strongly hydrating SO_4^{-2} anions decreases the self-diffusion coefficient relative to an additive composite in accord with an increased stabilization of the average water molecule. A similar behavior is observed for mixtures containing a common "structure-breaking" cation, K^+ , or a common "structure-making" cation, Li^+ , when the Cl^- ions are in part replaced by the more strongly "structure-breaking" anion, I^- ; again decreases in the self-diffusion coefficients relative to simple additivity are observed which are more pronounced in the presence of the "positively hydrating" Li^+ than in the presence of K^+ . Thus, both stronger "structure-making" anions and stronger "structure-breaking" anions (relative to Cl^-) enhance the stability of the average H_2O . The more strongly hydrating SO_4^{-2} anion may stabilize waters around it or in the hydration layer of the cations such that any dehydration effect due to cation-cation interactions is compensated.

However, this cannot be the case for the I^- ion for which the disruption of the solvent and the further weakening of anion-water interactions relative to Cl^- have allowed the H_2O molecules to enhance their ordering about the cations. Such an effect being more pronounced for K^+ than for Li^+ as lithium hydrates more strongly and therefore does not change the competition with H_2O - H_2O coordinations as much as the change from the weaker K^+ .

The above results can be understood and related to the NMR and dielectric measurements discussed above, as follows. For the solutions of Case A, upon mixing, remnant "free water" or solvent zones and outer hydration layers of both cations become weakened or disrupted and a redistribution of H_2O 's occurs. Water molecules migrate primarily toward the outer hydration layers of the more strongly positive hydrating ion (thus primarily towards Mg^{+2} or Li^{+1}) for $NaCl$ - $MgCl_2$ and $NaCl$ - $LiCl$ solutions. In turn, anions are forced toward the Na^+ cation, disrupt water-water bonds in its vicinity, and aid in stabilization of the hydration as seen in NMR measurements. However, the majority of water molecules have migrated toward the outer hydration layers of the stronger Mg^{+2} or Li^{+1} ions. There they have weaker coordinations than in the solvent prior to its disruption by cation-cation interactions. Thus the net bonding of water molecules in the solution decreased. This displacement of anions toward the Na^+ would be less pronounced for magnesium than for lithium, as a result of the tendency for magnesium (as discussed above) to ion-pair through the primary layer.

A similar redistribution would be expected when $NaCl$ is mixed with $CsCl$, except that the larger "structure-breaking" cesium would already have a large number of waters around more loosely coordinated than for normal water. Upon mixing, such disrupted H_2O 's would migrate towards the Na^+ cation and become more strongly bonded than they were in the vicinity of the Cs^+ . This, in turn, would drive the chloride anions from the vicinity of the sodium, and the anions would tend to ion-pair with the cesium in the manner similar to that previously observed in more concentrated cesium chloride solutions. Thus, in essence, the sodium cation will become "diluted" while the cesium cation would become "concentrated." The net result would be a decrease in the self-diffusion coefficient relative to the composite. The H_2O 's around the Na^+ due to the repulsion of the Cl^- anions would be less strongly coordinated than for a pure $NaCl$ solution. Hence, τ_c for the Na^+ ion would decrease in accord with NMR results. However, now the majority of H_2O 's on the average would be more strongly coordinated in the solvent or about the Na^+ than they were formerly in broken regions about the Cs^+ cations. Hence, D would decrease as observed.

A similar progression would apply to the mixtures shown in

Table I for Case B. The one exception, as noted above, would be the mixture of MgCl_2 and LiCl . This mixture would be expected to be unusual for two reasons. Upon mixing it would be more difficult to drive the Cl^- anion from the vicinity of the Mg^{+2} toward the Li^+ due to the tendency of magnesium to ion-pair through its hydration layer as noted above. Further, as previously reported(1-6), lithium may form not only first but second and possibly third hydration layers. Evidence for such hydration layers has come from the NMR results of Hinman(57), the work of Woessner and coworkers(55,56), and, more recently, from neutron scattering results on concentrated ionic solutions(4) showing that the lithium ion may diffuse together with the two hydration layers. Thus, upon mixing, the arrangements of anions about the magnesium may be nearly unaffected and H_2O 's normally beyond the primary layer or in solvent regions of a pure MgCl_2 solution would migrate to the lithium, complete its outer hydration layers and become, on the average, more strongly bonded than in the outer layers of the magnesium. In turn, this would force the chloride ion away from the lithium, further aiding the stabilization of the Li hydration complex. In this regard, the results of Woessner(55,56) have shown that, for lithium chloride solutions with increasing concentration as the chloride anions approach the water molecules in the second or in the first hydration layers, abrupt increases in the reorientational freedom of the lithium ion occur, corresponding to a weakening of its hydration layers. Thus, in the LiCl-MgCl_2 ternary solution the indirect ion-pairing between the Mg^{+2} 's and Cl^- 's in the redistributions of H_2O 's from the outer layers of the Mg^{+2} cations to complete the hydration layers of the Li^+ cations and the repulsion of Cl^- anions from the Li^+ toward the Mg^{+2} where they may enhance the self-shielding are all factors that can enhance the stability of H_2O upon mixing. The summation of these factors for the $\text{MgCl}_2\text{-LiCl}$ system, unlike the NaCl-LiCl system, appears sufficient to compensate for any additional cation-cation interactions tending to weaken the cation-water coordinations.

Trends and changes in the inelastic frequencies are observed which both show that water molecules are redistributed between cations and support the above picture. Before considering such results, certain features and characteristics of the inelastic spectra should be noted. In general, frequencies characteristic of cation-water coordinations become more pronounced both as the coordinations grow stronger and with increasing concentration so that the number of water molecules involved in the solution are more uniquely oriented geometrically about the cation. Thus, for example, if the hydration spheres of one or more cations became distorted due to ion interactions, the characteristic cation-water frequencies would be expected to broaden. In like manner, if additional waters were to migrate toward the outer hydration spheres of a cation (thus effectively diluting it), the characteristic ion-water frequencies tend to broaden and become less intense. In

contrast, if the water molecules in the outer layers of a cation were removed (thereby effectively concentrating it) or become strongly stabilized, the frequencies corresponding to such water-cation interactions would appear enhanced.

The most pronounced changes in the inelastic frequencies for the mixtures shown in Table I for Case A and Case B occur when NaCl or MgCl₂ are mixed with the "structure-breaking" salt, CsCl. For such Mixtures, Cs-H₂O frequencies (similar to those observed at higher concentrations and temperatures in pure cesium-chloride solutions(2)) appear enhanced and intensified while Na-H₂O frequencies are suppressed relative to the composite. This would be in keeping with the above picture. The redistribution of water molecules would have effectively diluted the sodium ion, thereby deintensifying and broadening characteristic Na-H₂O frequencies. However, the migration of Cl⁻ anions to the region of broken structure around the Cs⁺ cations would enhance the number of weaker Cl⁻-H₂O bonds relative to H₂O-H₂O bonds. In turn, this would allow the weak Cs⁺ ion to orient H₂O around them more readily in a similar manner to that when the H₂O-H₂O bonding was thermally disrupted as noted above(2). Thus, the cesium-water coordinations present would be similar to those that are observed to persist in the cesium at higher concentrations and high temperatures and would be competing with cesium chloride ion-pair formation.

In Case B where magnesium chloride is mixed with lithium and sodium chloride, only relatively small deviations are seen in the inelastic frequencies of the ternary solution relative to those of the composite. There is a slight tendency for magnesium water frequencies to be more pronounced than lithium water or sodium water frequencies in the spectra of the ternary solutions than in the composite spectra. This could reflect a stronger coordination of the water molecules around the magnesium relative to those around the lithium and the sodium as well as a lower degree of stabilization of the hydration waters around the latter two monovalent cations because the ion-pairing through the first hydration layer characteristic of magnesium in hydration complexes would inhibit the repulsion of chlorine ions from the vicinity of the magnesium which would enhance the stabilization of waters around +1 cations. Even smaller deviations are seen in Case A where sodium chloride is mixed with lithium chloride relative to the composite spectrum. In general, frequencies of the hydration complexes of both component cations appear broadened relative to the composite spectra which may in part reflect both the cation-cation interactions that perturb primary hydration layers. The above interpretations of the inelastic spectra, while tentative, do correlate in a plausible manner with the results of the dielectric, the NMR, and the quasi-elastic measurements discussed above. In addition, the fact that the changes of this type

are observed and appear real and reproducible, though small in certain cases, clearly indicates that redistributions of water molecules and perturbations of hydration layers about the cations are occurring. They strongly support the arguments of Anderson and Petree() that significant changes occurred upon mixing in ternary solutions that are associated with water molecules in the regions of the primary hydration layers of the cations.

For the solutions shown under Case C in Table I, for which there is a common cation but for which chloride anions have been replaced either by more strongly hydrating SO_4^{2-} ions or more strongly "structure-breaking" I^- ions, two features of the inelastic spectra of the ternary solutions should be noted and considered together with previous results obtained when chloride ions were replaced entirely by sulfate or by iodide ions in binary aqueous solutions. The ternary solutions show only frequencies characteristic of cation-water coordinations and such coordinations appear intensified relative to an additive composite in the inelastic spectra. When chloride ions are replaced by sulfates and when chloride ions are replaced by iodide ions, there is no indication of prominent new frequencies characteristic of a strong reordering of H_2O 's by the anions. Rather, the effect has been to enhance and sharpen existing cation-water frequencies. Thus, it would appear that both the sulfate and iodide ions have served to stabilize water molecules around the existing cations to a larger extent on the average than expected on the basis of simple additivity of the two component solutions. Indeed, this behavior is in keeping with the decrease in self-diffusion coefficients discussed above and may represent the fact that, while a disruption of hydration layers has occurred on mixing, the additional stabilization of waters around the cations that were originally associated with the chloride component solutions which occurred upon mixing more than compensated for any disruption. Similar effects of such ions have been noted even in binary solutions. Thus, upon comparing a magnesium chloride and a magnesium sulfate solution of equivalent concentrations where most of the waters would be in the hydration layers of the magnesium, the sulfate ion has served both to enhance magnesium-water frequencies and to strongly decrease the self-diffusion coefficient for these waters. A similar behavior has been reported previously for a comparison of a sodium chloride and a sodium sulfate solution.

Such a behavior (as previously reported(4) and discussed in connection with the influence of strongly hydrating cations on the diffusive motions of hydrated cations) can result from the ability of strong anions to hydrogen-bond to protons of water molecules in the primary hydration layers about cations. In doing so, a tendency to ion-pair might be strong enough to slightly distort such coordinations but would not be strong enough to displace water molecules from the

hydration layers to a significant degree. Thus, in the ternary solutions, sodiums, formerly surrounded by chloride ions, would now be bridged to other sodiums through the strong sulfate ions and the chlorides would be squeezed out. The sulfate ions, while partially distorting cation-water coordinations, would strongly restrict the ability of water molecules in the primary layer to break hydrogen bonds and reorient relative to other water molecules or to water-chloride coordinations.

In contrast to the behavior of the sulfate ion, the iodide ion could only form coordinations with water molecules which would be weaker than water-water coordinations or chloride-water coordinations. Its primary effect would be to disrupt the solvent sterically and weaken existing water-water coordinations. Upon the disruption of such solvent structure, water molecules could then orient more readily about a weakly hydrating cation like potassium which would be originally competing for waters of hydration with existing solvent coordinations. A similar result would occur if chloride ions were replaced by iodide ions in the presence of a lithium cation; however, the effect would be less as the strongly hydrating lithium could itself disrupt and reorient water molecules more readily than the weaker potassium and, therefore, the iodide effect in breaking any small amount of the remaining solvent structure would be much more secondary. Indeed, precisely this trend has been observed previously and reported (2) for binary solutions: A replacement of chloride by iodide ions for potassium salts enhances the potassium-water coordinations more strongly than does the replacement of chloride by iodide-ions for lithium salts. It is also of interest to note that a similar trend in the presence of a "structure-breaking" cation was observed in comparing the cesium bromide and cesium chloride. The bromide ion would disrupt solvent structure more readily than the chloride ion and, further, would not ion-pair as strongly as the chloride ion. Thus, in the inelastic spectra, the presence of the bromide ions serves to enhance cesium-H₂O frequencies relative to the cesium chloride solutions and, with increasing concentration, the initial increase in the self-diffusion characteristic of the "structure-breaking" ion levels off at a lower concentration for the cesium bromide and the cesium chloride solution because the bromide ion breaks solvent structure more rapidly than the chloride ion; therefore additional cesium ions are not needed to compensate.

In summary, the neutron scattering measurements, discussed above, have provided direct information at a molecular level upon one aspect of the changes that occur upon mixing two binary aqueous ionic solutions. They serve to show that changes do occur in the hydration spheres of cations in the solvent structure and in the distribution of anions relative to the cations as a result of the mixing

process. They further emphasize that these changes are strongly correlated to the "structure-making" and "-breaking" characteristics of the cations present. It should be emphasized that these measurements serve to provide data that complement and possibly extend existing models and theories of ternary solutions by providing information both on the types of changes occurring in activation or bonding energies of water molecules and in their distributions in cospheres of ions. Most theories to date have been concerned with the ion-ion interactions and correlation functions characteristic of the ternary solutions. Admittedly, such interactions may account for the more significant energy changes that occur upon mixing. However, the water structures and hydration structure are generally included in such theories in terms of dielectric coefficients, sizes of ions, or holes imbedded in dielectrics and in the Gurney cosphere terms. The present data show, however, that a secondary effect of such interactions between ions is the redistribution of water molecules and anions between cospheres as well as perturbation of existing cosphere structures. Thus, the simple concept of accounting for changes in hydration structures of ions upon cosphere overlap and the "squeezing out" of water back to the original solvent may represent a first approximation often used for calculational convenience to a more complex redistribution of water molecules and anions that is occurring at a molecular level and which, in part, is strongly determined by the so-called "structure-making" and "-breaking" classifications of the original ions.

APPENDIX A

Application of Langevin Equation to Motions of Hydrated Ions

It is necessary to consider the conditions for the validity of the Langevin equation

$$M\ddot{\vec{r}} + M\dot{\vec{r}} = F(t) \quad (1)$$

and their possible relationship to the properties of concentrated ionic solutions to better justify its use in the interpretation of the neutron data. In this equation, the term

$$M\dot{\vec{r}}$$

is a frictional force proportional to the velocity and $F(t)$ is a stoichiostatic force which is assumed to vary rapidly relative to the correlated frictional force. $F(t)$ serves to impart a mean thermal energy to the Brownian particle. These conditions imply that only small momenta changes between the bath and the Brownian particles occur, and that the coupling of the particle to the bath is weak. Thus, the velocity correlation of the Brownian particle would be expected to vary slowly over the relaxation time for any auto-correlation

of the stoichiastic forces if the Langevin equation is to be valid for the system. In contrast, if the correlation functions of the forces were to be slow, compared to the relaxation of the velocity auto-correlation or $1/\xi$, the behavior of the particle would approach that of a bound oscillator. Hence, in general, it can be said that, with regard to high frequency motions, a liquid would behave like a solid whereas, for low frequency motions, diffusion of a Brownian type (described by a Langevin equation) should play the dominant role. In treating the concentrated ionic solutions, in terms of the Langevin equation, it is assumed that the hydrated ion complex can make well defined intramolecular vibrations and that its lifetime is long compared to its overall diffusional motions. In such aggregate, a reference molecule may have a velocity correlation function which weakly oscillates, but, as is pointed out by Hertz(60), such oscillation should not contribute much to the diffusional motion. Thus, only the weak interaction or zero frequency parts of the velocity correlation function which correspond to motions of the center of mass of the aggregates, will be considered to contribute to the diffusive motions.

The above conditions may be formulated more precisely as follows. Oppenheim and coworkers(77,78) have noted that for the Langevin equation to be valid it is required (a) $m/M \ll 1$, where m is the mass of the bath particle, and M is the mass of the Brownian particle; (b) momentum of the Brownian particle must be large compared to that of the bath particle; and (c) the velocity of the heavy mass must be small compared to the magnitude of a typical velocity of a bath particle. It can be shown(79) that the friction coefficient, ξ , is related to the velocity auto-correlation function as

$$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{3kT}{M} e^{-\xi t} \quad (2)$$

It is related to the self-diffusion coefficient as

$$D = 1/3 \int_0^{\infty} \vec{v}(0) \cdot \vec{v}(t) dt = \frac{kT}{M\xi} \quad (3)$$

Thus, $1/\xi$ represents a relaxation time over which any auto-correlation in velocity would be lost. The more viscous the liquid, the more rapid would be this loss in correlation. In terms of the mean square amplitude of the stoichiastic force,

$$\langle F(t)^2 \rangle$$

and an average correlated time interval, Δt , which is the order of the auto-correlation time of $F(t)$, then the expressions for the self-diffusion coefficients and friction coefficients can be written, respectively, as

$$D = 1/3 \frac{1}{M \xi} \langle F^2 \rangle \Delta t \quad (4)$$

$$\xi = \frac{1}{3kTM} \langle F^2 \rangle \Delta t \quad (5)$$

Alternatively, these quantities can be written in terms of an ensemble average of the Laplacian of the intermolecular potential, V , at a given Brownian particle due to the bath

$$D = kT \left(\frac{2}{3\pi} m \langle \nabla^2 V \rangle \right)^{-1/2} \quad (6)$$

$$\xi = \left(2/3 \frac{m}{M} \langle \nabla^2 V \rangle \right)^{1/2} \quad (7)$$

The above equations have often been modified by using the Stokes Law expression

$$\xi = 6\pi\eta a \quad (8)$$

where a is the radius of the Brownian particle, and η is a sheer viscosity for the fluid. However, the validity of the use of such a Stokes Law expression, originally derived from flow around a macroscopic sphere, has been questioned when applied at a molecular level; in addition, in ionic solutions, where cation-water interactions may affect both the effective mass of the Brownian particle and the coupling between such an aggregate and the bath. Thus, Zeitseva and Fisher(62,63) treated the motions of the hydrated ions in solutions in terms of a hydrodynamic theory with allowance for ion hydration. The ions force fields are assumed to have a spherical symmetry and the characteristic length that enters the calculations is an effective radius of the hydrated ion. The effect of the hydration is manifested as a local change in the solvent density and an average self-consistent potential which takes into account both the direct and indirect forces acting on the solvent molecules. The resulting friction coefficient depends on this potential, its depth and functional form. However, if a simple potential of radius, R , and depth, ϵ , is assumed, the friction coefficient will be given by

$$\frac{8\pi}{9} \left(\frac{\epsilon}{kT} \right)^2 [4/3 \eta \omega_1 (\epsilon/kT) + \xi \omega_2 (\epsilon/kT)] \quad (9)$$

It should be noted that, unlike the usual Stokes formula, this expression depends both upon the sheer viscosity, η , and on the volume viscosity, ξ .

More importantly, it also depends strongly on the ratio of $\epsilon/k \cdot T$, and, hence, on the depth of the potential orienting the water molecules about the ions relative to the thermal excitation energy, kT . Thus, it would be expected that as ion-water coordinations and hydration strengths increased, the friction coefficients and the effective masses of the hydrated particles would increase. For example, Zaitseva and Fisher have estimated that the weakly hydrated ions (e.g., K^+ , Cs^+ , Cl^- , Br^- , and I^-) that the effective masses would approximately correspond to those of the ions together with, at most, two to three water molecules. Thus, in general, the effective masses of the ions would be low and waters could exchange readily from their coordination sphere. In contrast, for stronger hydrating or structure-making cations or anions (e.g., Li^+ , Ca^{+2} , Mg^{+2}) the effective masses of the kinetic entities could include the cations together with as many as ten water molecules.

In interpreting the neutron data in terms of hydrated ions and their motions according to a Langevin equation, a number of features of the spectra together with information on the ability of such concentrated solutions to form glasses (which will be discussed in detail below) should be noted simultaneously. The inelastic spectra show frequencies characteristic of well-defined cation-water coordinations which are determined primarily by the cation and only secondarily affected by the anion. With decreasing temperature, as the glass transition is approached, no large changes occur in such frequencies, rather they gradually sharpen and become better defined in correspondence with a reduction of thermal amplitudes and any relaxational broadening. Further, the evolution of the Γ vs. K^2 's with decreasing temperature from a jump diffusion behavior to a behavior characteristic to a straight-line behavior strongly indicates that both the exchange of individual water molecules from the hydration spheres and reorientations of water molecules on the hydration sphere which would involve the breaking of a bond have passed outside the neutron time scale. Indeed, the curves of Γ vs. K^2 at such low temperatures appear linear throughout the entire range of K^2 values. If any delay time were to be encountered it would have to occur at K^2 values larger than those experimentally available. However, such a delay time would then be small and comparable to the average period expected for the vibration of a heavy mass such as a hydration complex. In turn, this would mean that if the center of mass of such a complex tried to execute a vibration it would relax before many oscillations were completed and that, in essence, its residence time in a potential would be so short as to make any degree of bonding questionable. Thus, it would appear that the complex that one is dealing with that would contribute the linear behavior in the curves of Γ vs. K^2 as obtained from the quasi-elastic components would be a hydrated cation coordinated to an anion and that such a complex could be defined as stable at least for times exceeding the maximum neutron interaction time currently available (e.g., 10^{-11} ,

10^{-12} secs.). It should be emphasized, however, that when measurements would be made by techniques that measure over longer interaction times such as spin echo measurements, reorientation or activated jumps of primary water molecules or dissociation between the hydrated cation and the anion could contribute to an observed diffusional process. Further, it would be assumed that during the interaction time such an ion-water complex would undergo weak interactions with its surroundings which might then involve weak electrostatic forces and/or steric constraints, as determined by the free volume present. In addition, the present experiments indicate that as the anion basicity or strength is increased, the effective lifetime or stability of the hydrated cation-anion complex is correspondingly increased. Thus, relative to lithium chloride, the straight-line behavior for the curves of τ vs. K^2 and the onset of contributions from reorientations of individual water molecules is delayed for lithium acetate to a much higher temperature. A stronger anion, like acetate, may distort the cation-water complex and even decrease the exchange times for the individual water molecules relative to either a more dilute solution or a solution containing a weaker anion. However, simultaneously, it may more strongly restrict the reorientation of motions of water molecules about their dipole axes which would normally break water-anion coordinations. So long as the exchange times and the reorientation times are long compared to 10^{-11} - 10^{-12} secs, they do not contribute to the quasi-elastic component. It should also be noted that the behavior in the curves of τ vs. K^2 both with temperature and anion parallel those observed by Angell and coworkers for measured glass transition temperatures and their dependence on concentration and on cation and anion. Thus, for a given multivalent cation, the glass transition increases both with concentration and with anion basicity. Angell and coworkers (23) have argued that the glass transition could be primarily associated with a rapid decrease in the free volume available for the motion of the hydrated ions which would give rise to a rapid decrease in the self-diffusion coefficient, increase in the solution viscosity, and require an ever-increasing cooperative rearrangement for a motion of a hydrated unit to occur. In addition, they argue that the stronger or more basic anions tend to more strongly interact with the protons of the waters about the hydrated cations and to restrict their Brownian motion. Such observations are in complete accord with the results of the present neutron investigation. It must be questioned, as the glass transition is closely approached in temperature, whether the coupling between such units, as the free volume is reduced, would become sufficiently strong so that vibratory motions of such complexes would have to be considered and the Langevin equation and its applicability would be questionable. The present quasi-elastic measurements do not provide direct information on this question, as in this temperature range the broadening due to the motions of the hydrated complexes, becomes sufficiently small so that it is within experimental resolution, and thus information on the temperature dependence of the self-diffusion coefficient in this range is not

available. However, the inelastic spectra by frequencies characteristic of local ion-water coordinations of the complexes show no abrupt changes between 1°C and temperatures at which the solution has become a glass. There is no evidence at low frequency of the presence of new modes or of distributions of frequencies which might indicate the presence of contributions from the intermolecular "vibrations" of large mass hydrated ion aggregates, nor is there any indication at the glass transition of an abrupt change in the area of the quasi-elastic component which, in turn, would correlate with the change in the mean square of the vibrational amplitude.

It is clear from the plots of the self-diffusion coefficient divided by kT that within the available temperature range that if the motions of the complexes are treated in terms of a Langevin equation then the experimentally determined friction coefficient shows a pronounced temperature behavior and rapidly increases in an approximately linear manner with decreasing temperature. In view of the tendency of such solutions to form glasses and the nearly continuous behavior of both inelastic frequencies and the self-diffusion coefficient as the temperature is decreased toward the glass transition, it would undoubtedly be more realistic to consider the self-diffusion coefficient in terms of a model such as that of Cohen and Turnbull(80) developed to explain the self-diffusion coefficient for liquids that form glasses. From this theory the self-diffusion coefficient would be given by

$$D = CT^{1/2} \exp - \left[\frac{C}{T-T_0} \right] \quad (10)$$

or by

$$\ln D = \ln C + 1/2 \ln T - \frac{C}{T-T_0} \quad (11)$$

In view of the relatively small temperature interval, in which the present studies have been concentrated, it could be difficult to differentiate a nearly linear behavior for D/kT from any slow changes in the above exponential behavior predicted by the theory of Cohen and Turnbull. Hence, such an expression can neither be confirmed or negated by the present data. Indeed, Equation 11 above indicates that if such diffusion data are plotted arbitrarily in terms of $\ln D$ vs. $1/kT$, care must be taken to conclude that simply because a linear behavior is observed that an activated jump mechanism for the ions can occur unless a sufficiently wide temperature region has been studied and, in particular, temperatures close to the glass transition have been explored.

It is of interest to note that the results of this present experiment agree in certain aspects with results reported for the studies of self-diffusion liquids by recent spin-echo measurements. Thus, Hertz has noted that for a number of solutions, including lithium

chloride, as a concentration is approached where most water molecules are in the primary hydration layer the self-diffusion coefficient for water at 25° approaches closely that for the lithium ion. Under these conditions, within the time duration of the experiment, the majority of water molecules in the hydration sphere he considers to be tightly coupled and moving with the ion. Thus, the water molecules are bonded to the ion for a time much longer than the decay time characteristic of the velocity correlation function of the lithium ion and for periods typically equal to or longer than 10^{-11} secs. Recently, similar measurements have been made by Weiss and Nothnagel(61) as a function of both temperature and concentration for both LiCl and Li_2SiF_6 solutions. For LiCl, the authors have measured the self-diffusion coefficients corresponding to the water molecules and of the lithium ions. These authors have argued that the water molecules around the lithium cations are well ordered by the lithium, but that at both higher temperatures (e.g., $t > 40^\circ\text{C}$) and higher concentrations (e.g., above 4.4 moles/liter) a perturbation of the symmetrical structure occurs, resulting in an increase in the mobility of the water molecules and a slight decrease in the self-diffusion coefficients. Further, they argue that the bonding between the cation and the water molecules in this primary hydration sphere is sufficiently stronger than that of the bonding characteristic of pure water for the solvent so that this water effectively diffuses with the hydrated ion. Unfortunately, in these measurements no self-diffusion values of the chloride anion were obtained so that it would be possible to determine whether there were a tendency for it also to move with the lithium-water complex. However, these authors have also made measurements on Li_2SiF_6 solutions and determined the self-diffusion coefficients for the lithium ions, for the SiF_6^- anions, and for the water molecules. The authors note, not only is the self-diffusion of H_2O small when compared with normal water in a corresponding solution of lithium chloride, but that the self-diffusion coefficient of the lithium $+$ ion is also reduced. They note that the self-diffusion coefficient of the larger SiF_6^{--2} anion would be expected to be slower than that of the Cl^{-1} ion. They argue that, due to interactions between the hydrated lithium and its larger anions, has in turn slowed down the Li^+ ion. Thus, at the higher concentrations and lower temperatures there may be a tendency of this anion in part on a time-average to diffuse together with a cation-water complex. This is analogous to the effect noted in the neutron measurements for a comparison of lithium acetate and lithium chloride in that the lithium acetate has strongly stabilized the waters such that their relaxation times do not enter the neutron interaction time range until much higher temperatures to those associated with lithium chloride. In addition it has given rise to a large decrease in the self-diffusion coefficient relative to lithium chloride.

These findings also, as noted above, are in accord with the

interpretation of spin-echo measurements by Hertz; namely, that the more strongly hydrated ions such as Ca^{+2} , Li^{+1} , and F^{-1} , the motion of the ion can be tightly coupled to waters in the first hydration spheres for times much longer than the decay time of the velocity correlation function of the ion. In contrast, for ions such as K^{+} or I^{-} which are normally negatively hydrating, the water is not sufficiently tightly coupled so that a dynamic complex has a meaning. Further, Hertz notes that any coupling of such complexes or be it weak to other network particles serves to strongly decrease the self-diffusion coefficient.

I. TERNARY SOLUTIONS

				$\frac{D_M}{D_{\text{composite}}}$	Type of Variations Observed in the Cation-Water Frequencies That Occur on Mixing Relative to Additivity	Proposed Changes in Cation Hydration and in the Distributions of H ₂ O's and Anions to Account for Changes in Frequencies and Self-Diffusion Coefficients
CASE A (CATION EFFECTS)						
Mixing of a Weak Structure-Making Salt With a Series of Structure-Making and -Breaking Salts Having Common Anions						
4.6 m NaCl } (Na ⁺ weak structure-maker)	+ }	1.0 m MgCl ₂ } structure-makers	↓ decreasing cation hydration	> 1	Only small variations in cation-water frequencies observed relative to additive composite (see text)	Upon mixing, H ₂ O coordinations in hydration layers or cospheres of cations are weakened. H ₂ O's redistribute from vicinity of weaker cation, Na ⁺ , toward Mg ⁺² or Li ⁺¹ . In turn, Cl ⁻ anions repelled from Li ⁺¹ (and to a lesser degree from Mg ⁺²) toward Na ⁺ where they disrupt H ₂ O-H ₂ O coordinations that formerly "competed" with the formation of Na ⁺ -H ₂ O coordinations and enhance Na hydration. However, a majority of H ₂ O's transferred to the vicinity of Li ⁺ and Mg ⁺² where they are more weakly bonded on an average than H ₂ O's in the unmixed component solutions.
		4.6 m LiCl } ↓		> 1		
		4.6 m NaCl } ↓		< 1		
		4.6 m CsCl } structure-breaker		< 1		
CASE B						
Mixing of a Strong Structure-Making Salt With a Series of Structure-Making and -Breaking Common Anions						
4.6 m MgCl ₂ } (Mg ⁺ strong structure-maker)	+ }	4.6 m MgCl ₂ } structure-makers	↓ decreasing cation hydration	< 1	Only small variations from composite spectra (see text)	Solvent molecules from the strongly disrupted solvent region about the "structure-breaker," Cs ⁺ , redistribute toward the stronger cations, Na ⁺ or Mg ⁺² . Anions in turn are distributed toward the Cs ⁺ . The anions further disrupt H ₂ O-H ₂ O coordinations near the Cs ⁺ and favor orientation of H ₂ O's about the Cs ⁺ . The strong enhancement of H ₂ O's about cesium gives rise to a net increase in the average activation energy for H ₂ O and a decrease in D.
		4.6 m LiCl } ↓		< 1		
		4.6 m NaCl } ↓		> 1		
		4.6 m CsCl } structure-breaker		< 1		
CASE C (ANION EFFECTS)						
4.6 m MgCl ₂ + 2.3 m MgSO ₄		Combination of weak (Cl ⁻) and strong (SO ₄ ⁻²) anions in presence of weakly hydrating Na or strongly hydrating Mg cations		< 1	Frequencies of Mg-H ₂ O and Na-H ₂ O coordinations are observed and are enhanced relative to the composite spectra	The SO ₄ ⁻² anions hydrogen bond to H ₂ O's in the primary hydration layers of the Na ⁺ and Mg ⁺² cations and thus restrict their orientational freedom.
4.6 m NaCl + 1.0 m Na ₂ SO ₄				< 1		
CASE D						
3.2 m KCl + 4.6 m KI		Mixture of weak (Cl ⁻) and strong (I ⁻) "structure-breaking" anions in presence of common strong (Li) and weak (K ⁺) "structure-making" cations		< 1	Frequencies of K ⁺ -H ₂ O are strongly enhanced and those of Li ⁺ -H ₂ O coordinations more weakly enhanced relative to composite spectra	I ⁻ ions disrupt H ₂ O-H ₂ O coordinations more effectively and form weaker anion-H ₂ O coordinations than Cl ⁻ anions. This in turn favors the enhancement of cation hydration due to a reduction in the competition between cation-water and solvent-solvent interactions. The enhanced cation hydration is thus more pronounced in the presence of the weakly hydrating K ⁺ cation than of the stronger Li ⁺ cation.
4.6 m LiCl + 4.6 m LiI				1		

57

FIGURE 1

The theoretical dependences of the Lorentzian half-width at half-maxima, Γ , for the diffusively broadened incident energy distribution are shown as a function of the momentum transfer, K^2 , for the four limiting cases of the Larsson-Bergstedt theory, as discussed in the text. The progression, as shown in going from Curve I to Curve IV, should be compared with the data shown in Figures 2 and 3 as the temperature is decreased for concentrated ionic solutions. In terms of the four characteristic times, τ_1' , τ_0' , τ_0 , and τ_1 , discussed in the text, Curve I corresponds to $\tau_1' \gg \tau_0'$ and τ_0 , and coincides with the jump diffusion limit previously used to describe the diffusive motions arising from reorientations of individual molecules in water and less concentrated ionic solutions.

Curve II and Curve III correspond to the limit where τ_1' and $\tau_0 \gg \tau_0'$. However, for Curve II, it is assumed that both τ_1' and τ_0 are within neutron interaction time, while, in contrast, for Curve III, which would correspond to lower temperatures, τ_0 now exceeds neutron interaction time.

Curve IV corresponds to the case expected theoretically at temperatures close to the glass transition where τ_0' and τ_0 would now be much greater than τ_1' . However, as discussed in the text, the values of Γ for this case might well be sufficiently small so as not to be experimentally resolvable for most solutions studied.

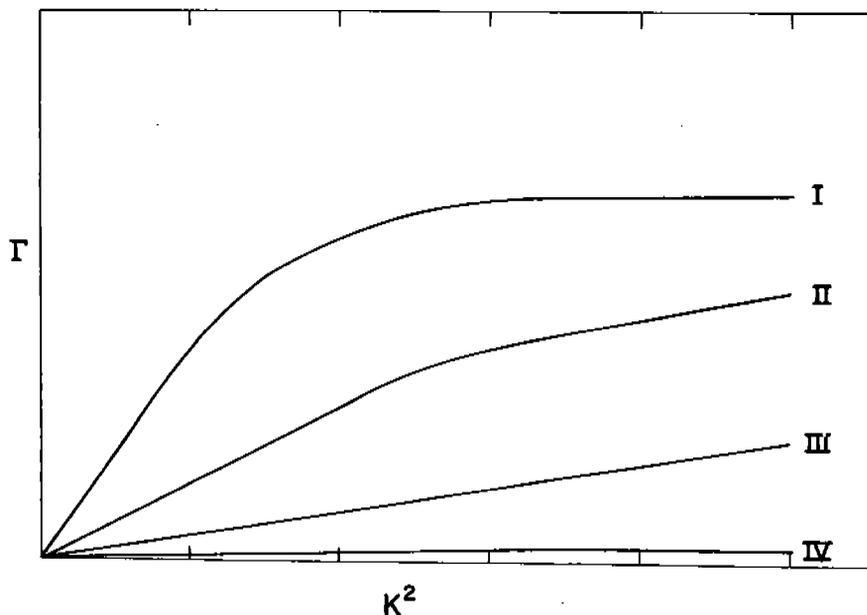


FIGURE 2

The observed dependence of the half-width at half-maxima (Γ) of the Lorentzian broadened, quasi-elastic maxima on K^2 are shown, at various temperatures, for 15.0 m LiCl, 4.6 m LiCl, 16.3 m LiNO₂ and 7.2 m CD₃COOLi.

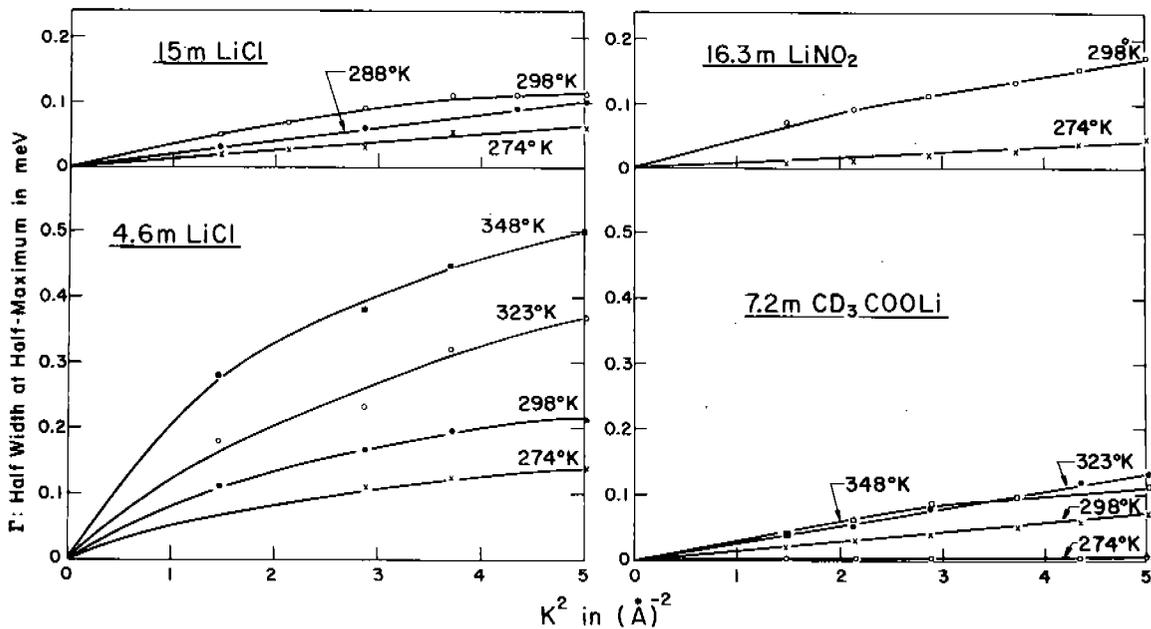


FIGURE 3

In the upper half of the figure, the spectra of neutrons scattered at an angle of 45° are compared for 4.6 m and 10.0 m LiCl; 4.6 m and 10.0 m LiNO₃; and 4.6 m and 7.2 m CD₃COOLi. In the lower half, the corresponding Γ vs. K^2 curves are shown.

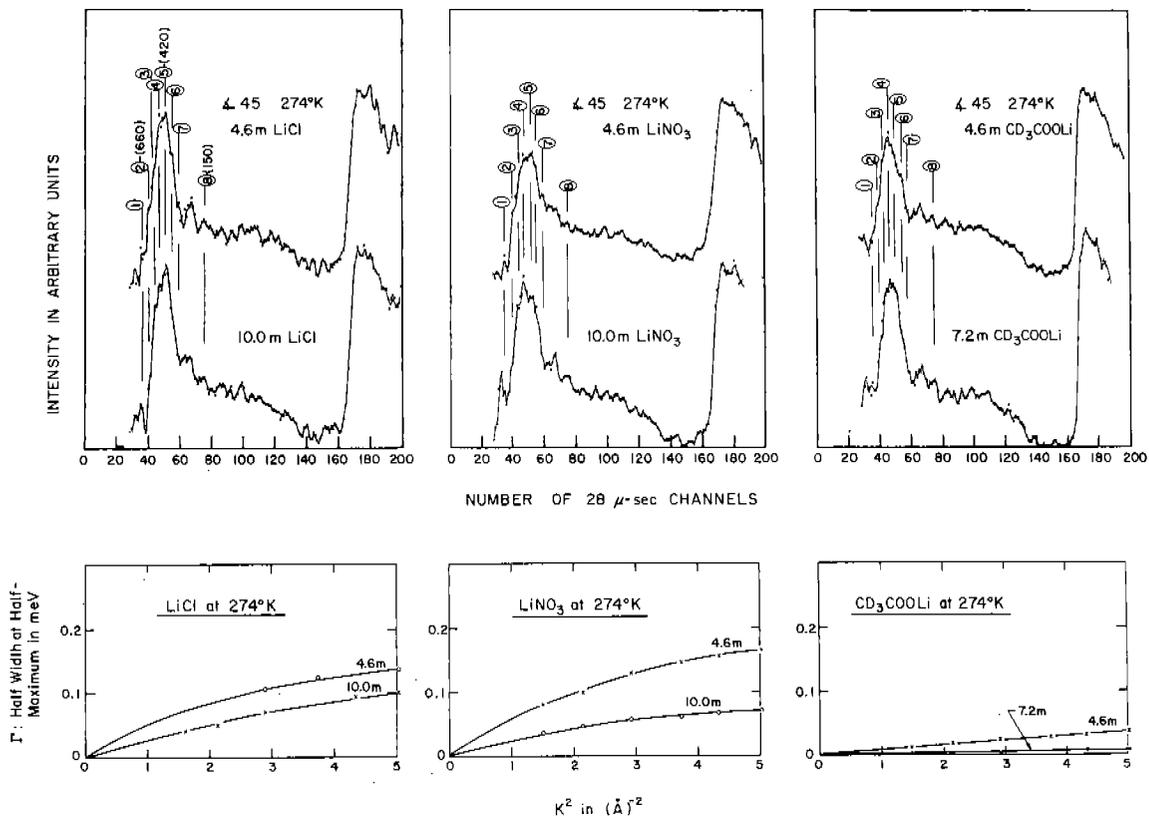


FIGURE 4

The neutron spectra of 4.6 m solutions of several lithium salts are compared with H₂O in the upper half of the figure. The corresponding Γ vs. K^2 curves are compared in the lower half.

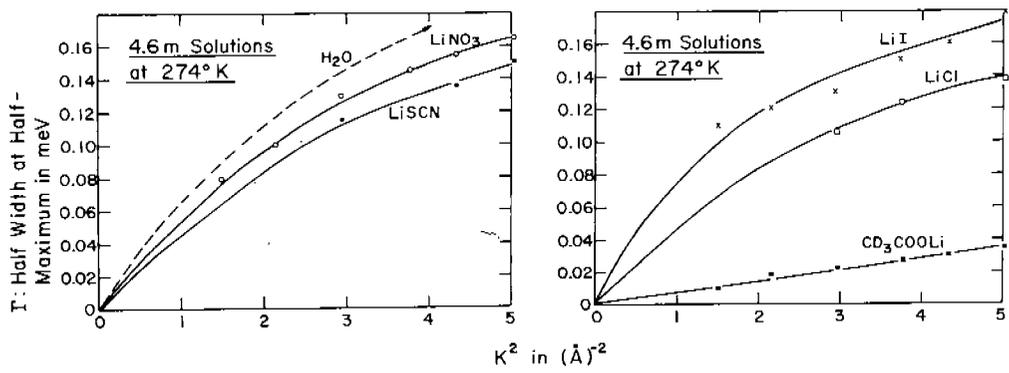
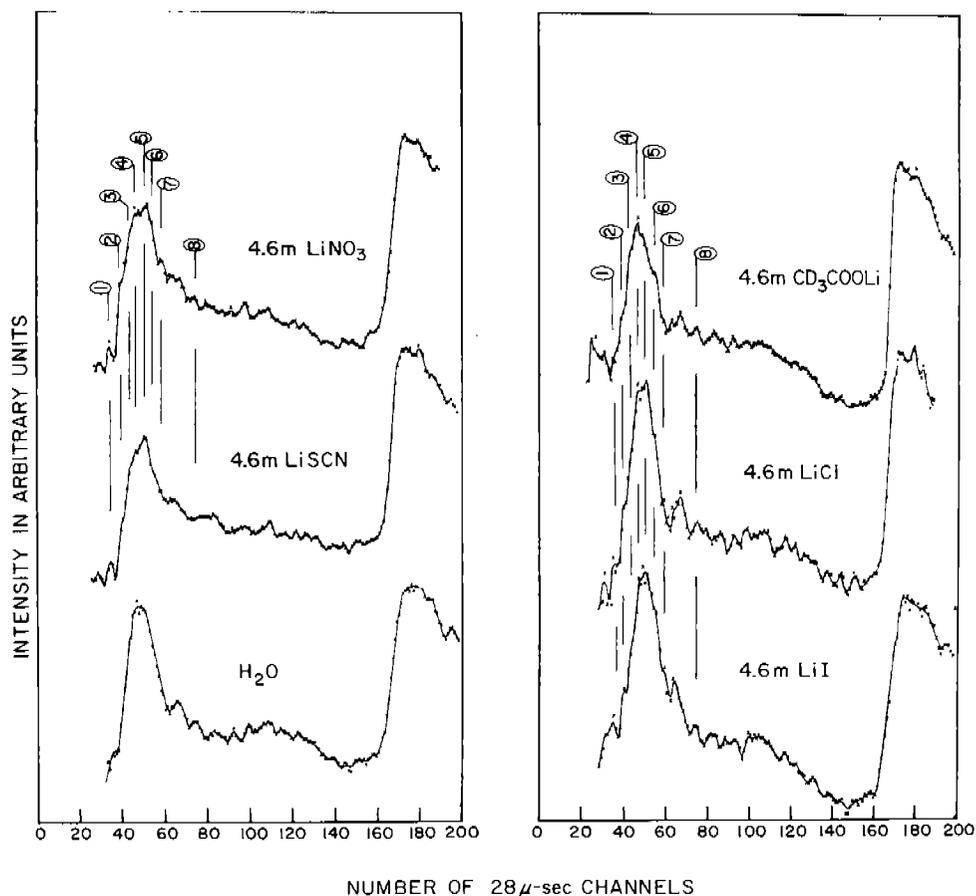


FIGURE 5

The values and the functional dependence (see Figure 1) of the Γ vs. K^2 curves for solutions of several cations and Li salts of different anions are shown.

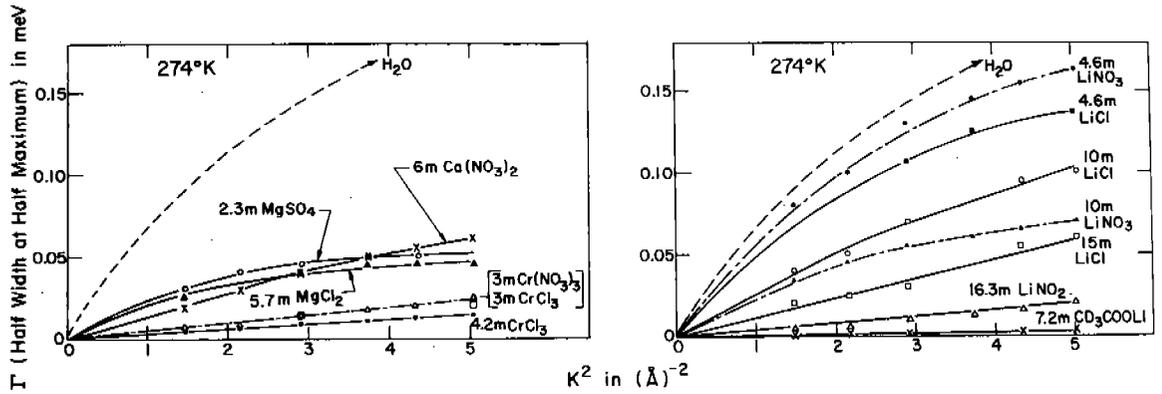


FIGURE 6

The inelastic spectra and Γ vs. K^2 curves are compared for $MgCl_2$ and $MgSO_4$ and also for their temperature dependence of 5.7 m $(CD_3COO)_2Mg$ and 6.0 m $Ca(NO_3)_2$.

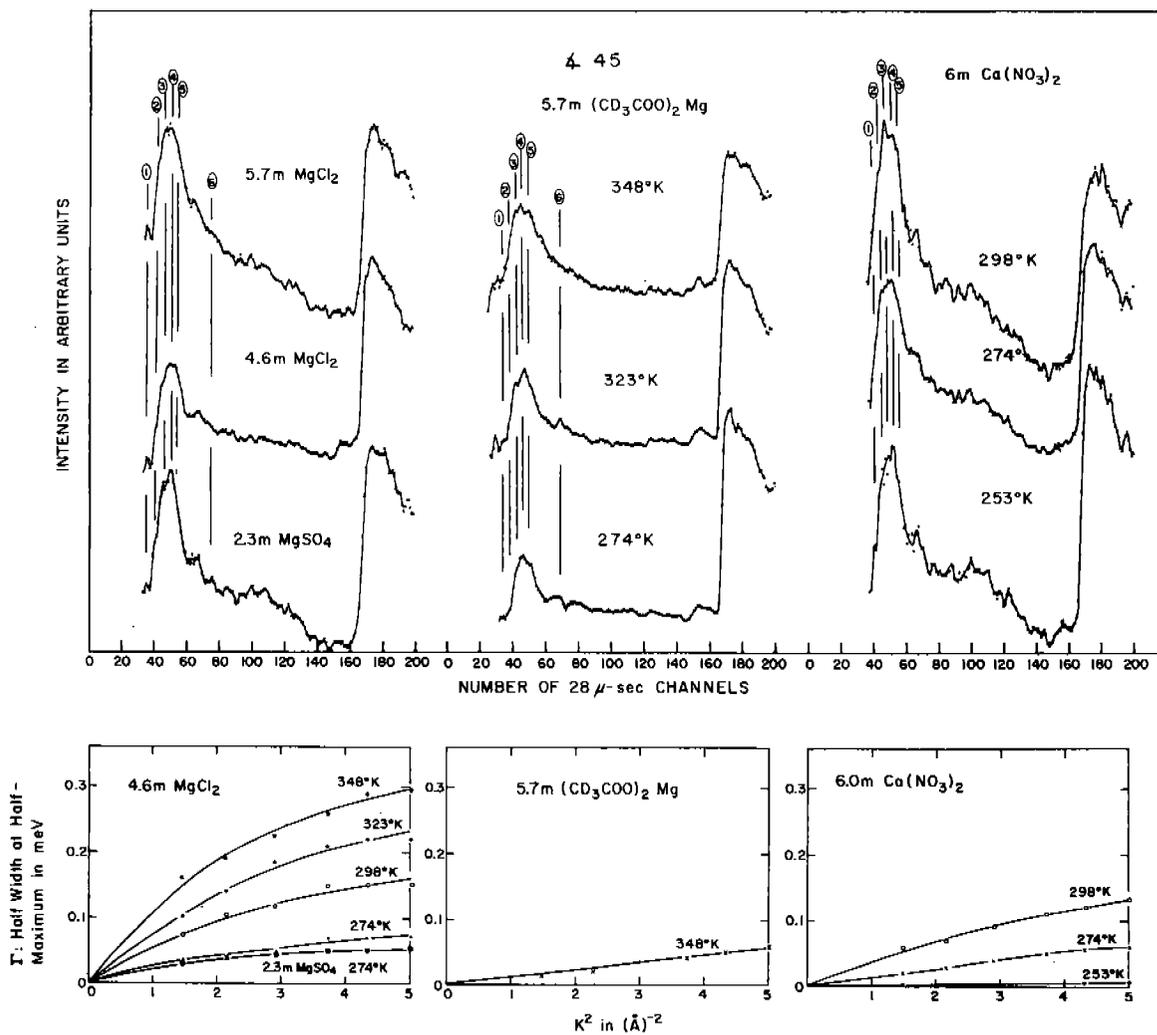


FIGURE 7

The logs of the areas of the quasi-elastic maximum, as a function of K^2 , are shown for different salt solutions as a function of temperature. These plots are observed to be linear as would be expected for an area of the quasi-elastic maximum proportional to a Debye-Waller factor. The lines, for graphical purposes, have been displaced with regard to the ordinates to prevent overlap.

As noted at the top of the figure, it is observed that a reduction in the Debye-Waller exponent occurs in going from 25°C to 1°C and, at small or highly charged ions, causes an additional reduction in this exponent relative to pure water. Within a given shaded band the lines for the indicated salts fall within errors indicated by the width of the band. Similar curves are compared in the bottom half of the figure for solutions of lithium and of calcium salts, as a function of temperature.

In addition, it is observed that, with increasing temperature, the slope increases more rapidly for the lithium chloride solution than for the lithium acetate solution, emphasizing the ability of the acetate ion relative to the chloride ion to stabilize the primary waters of hydration.

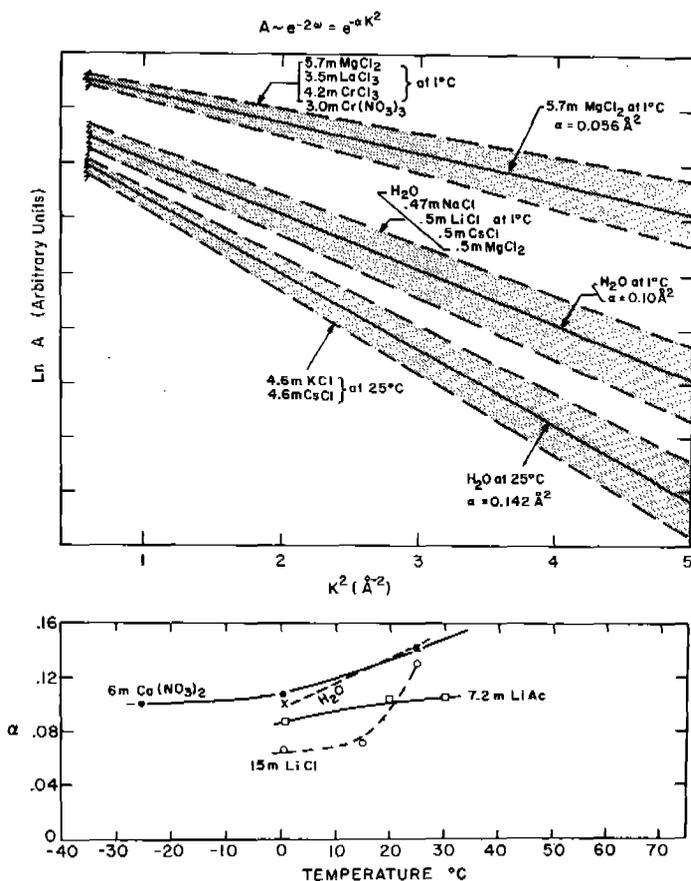


FIGURE 8

The inelastic neutron spectra are compared at various temperatures for 4.6 m LiCl, 15.0 m LiCl, and 7.2 m CD₃COOLi.

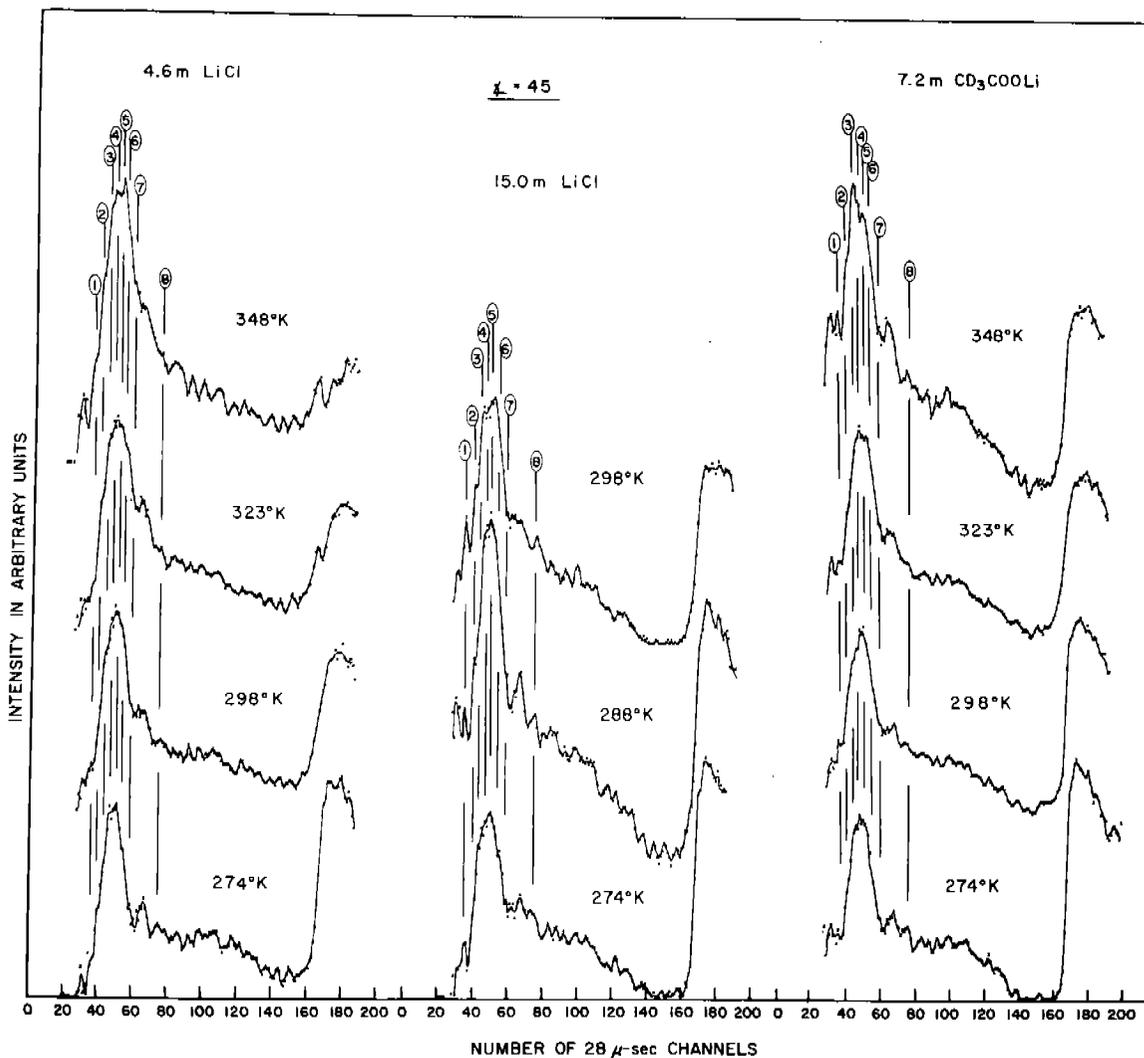


FIGURE 9

The spectra of neutrons scattered at an angle of 45° are compared for a 4.6 m MgCl_2 solution, a composite spectra of a 4.6 m MgCl_2 solution, and a 4.6 m LiCl solution (assuming simple additivity), a mixture of 4.6 m MgCl_2 and 4.6 m LiCl solutions, and a 4.6 m LiCl solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid lines.

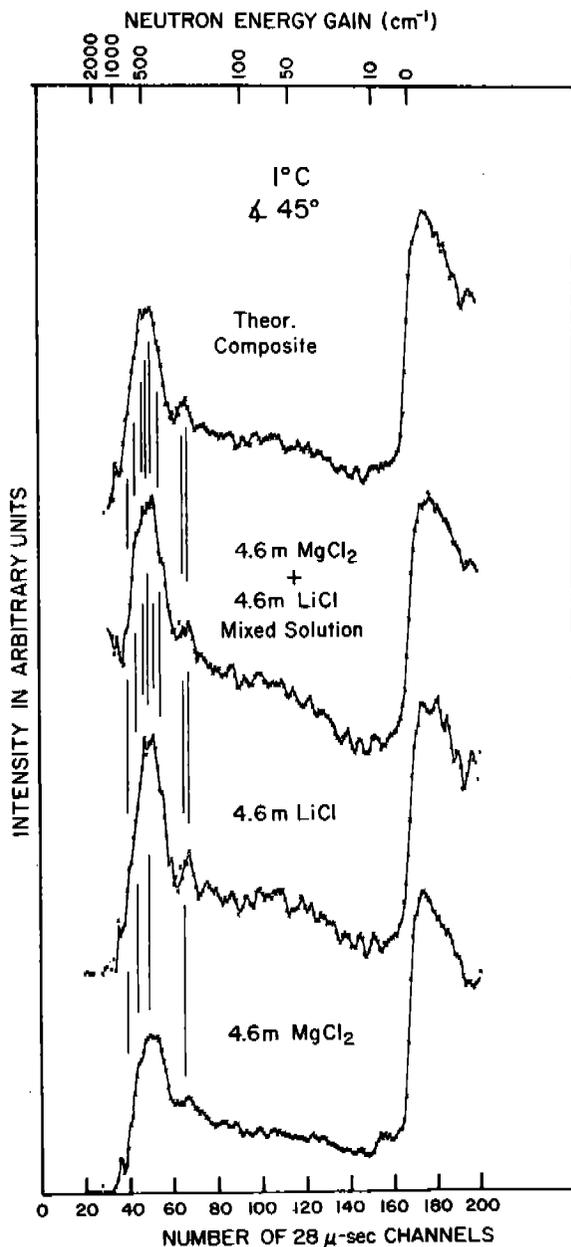


FIGURE 10

The observed dependence of the half-width at half-maxima (Γ) of the Lorentzian broadened, quasi-elastic maxima on K^2 are shown for ternary mixture of a 4.6 m $MgCl_2$ solution with a 4.6 m $LiCl$ solution. In addition, the curve is compared with its individual components and with that for a calculated composite. The curve of Γ vs. K^2 for the composite was calculated on the simplified assumption that the activation energy in a mixed solution of two salts would be the simple average of their individual solutions.

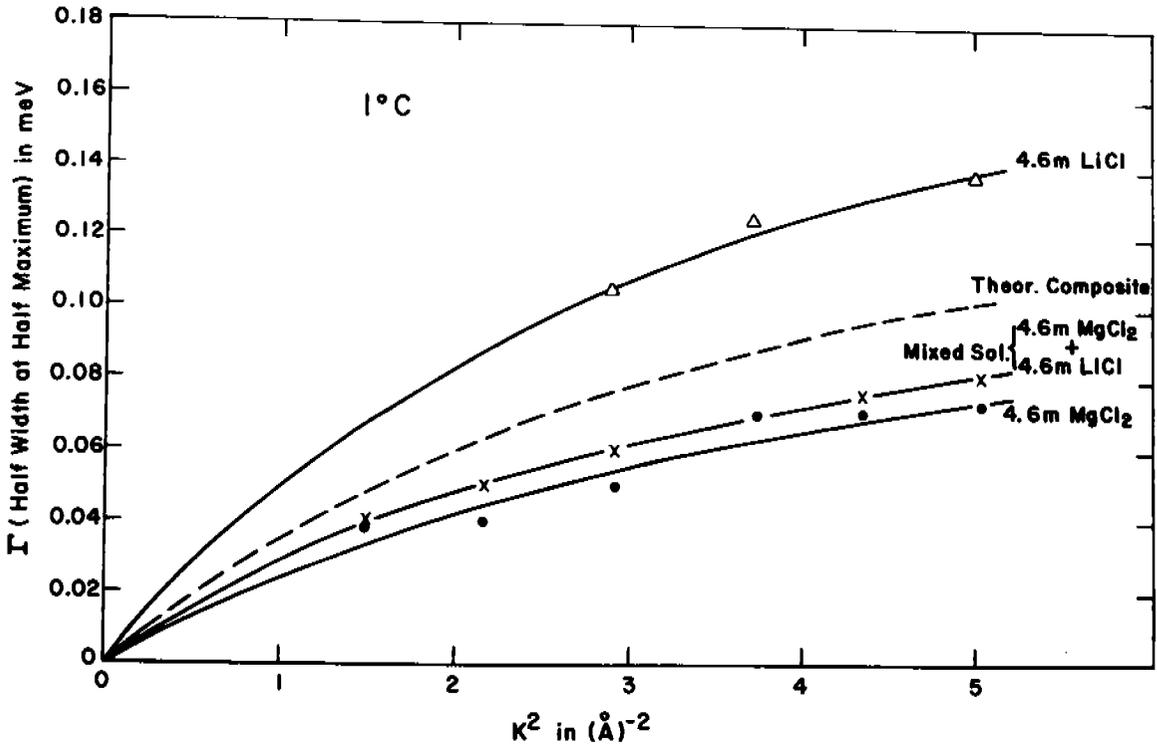


FIGURE 11

The spectrum of neutrons scattered inelastically from a ternary solution of 4.6 m CsCl + 4.6 m MgCl₂ is shown and compared with the inelastic spectrum that would be expected on the basis of simple additivity.

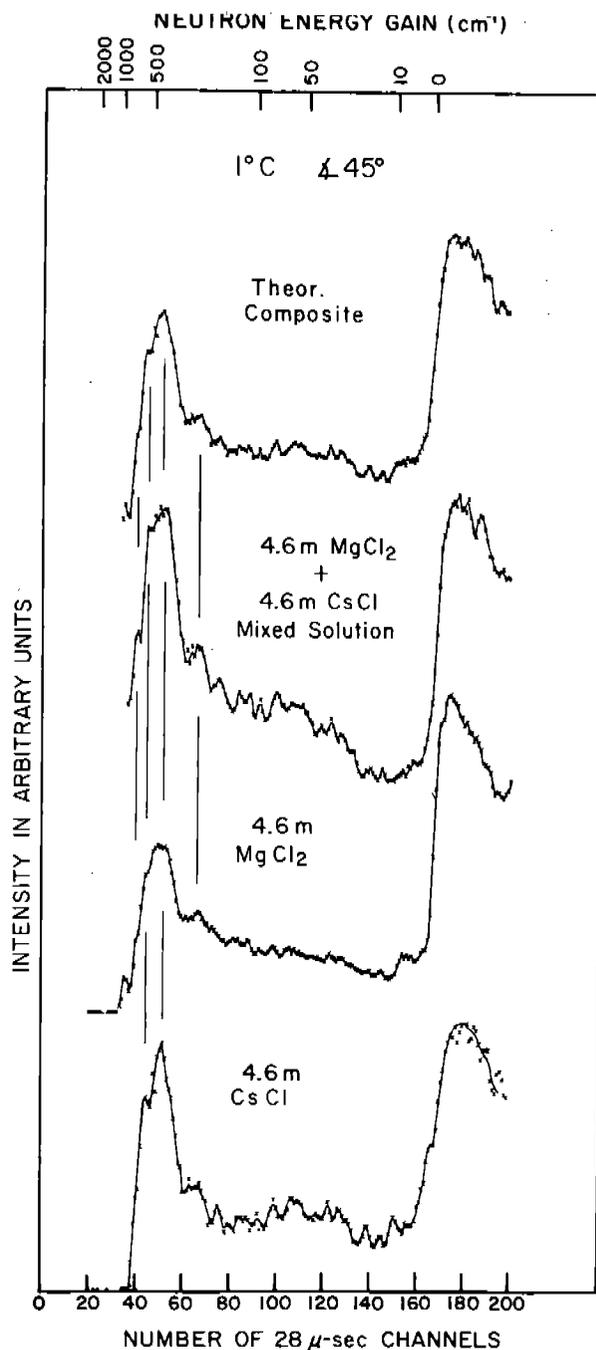


FIGURE 12

The curve of Γ vs. K^2 for a ternary solution of 4.6 m CsCl + 4.6 m MgCl₂ is shown and compared with a similar curve based on the assumption of simple additivity.

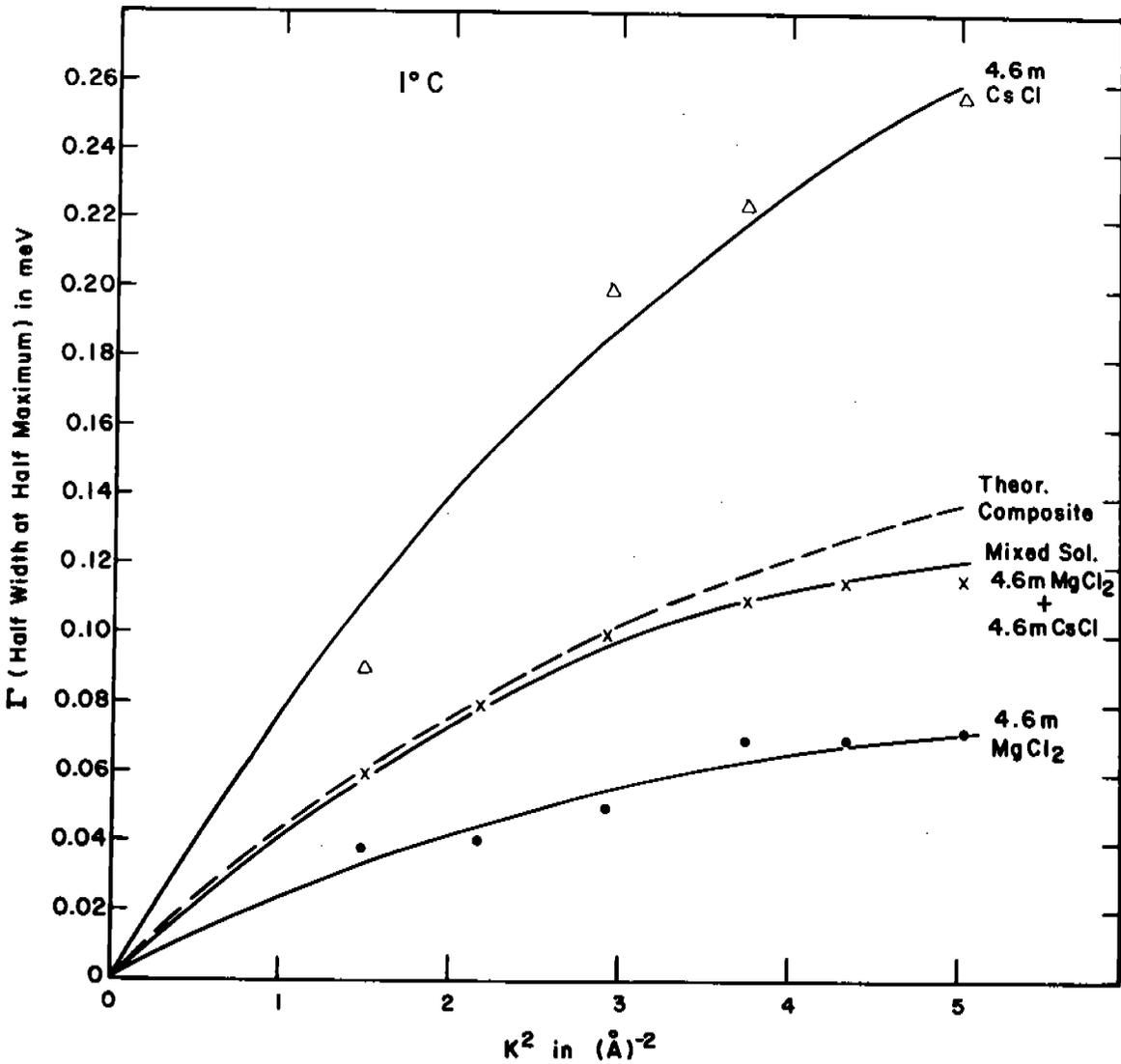


FIGURE 13

The spectra of neutrons scattered at an angle of 45° are compared for a 1.0 m MgCl_2 solution, a composite spectra of a 1.0 m MgCl_2 solution, and a 2.3 m MgSO_4 solution (assuming simple additivity), a mixture of 1.0 m MgCl_2 and 2.3 m MgSO_4 solutions, and a 2.3 m MgSO_4 solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid lines.

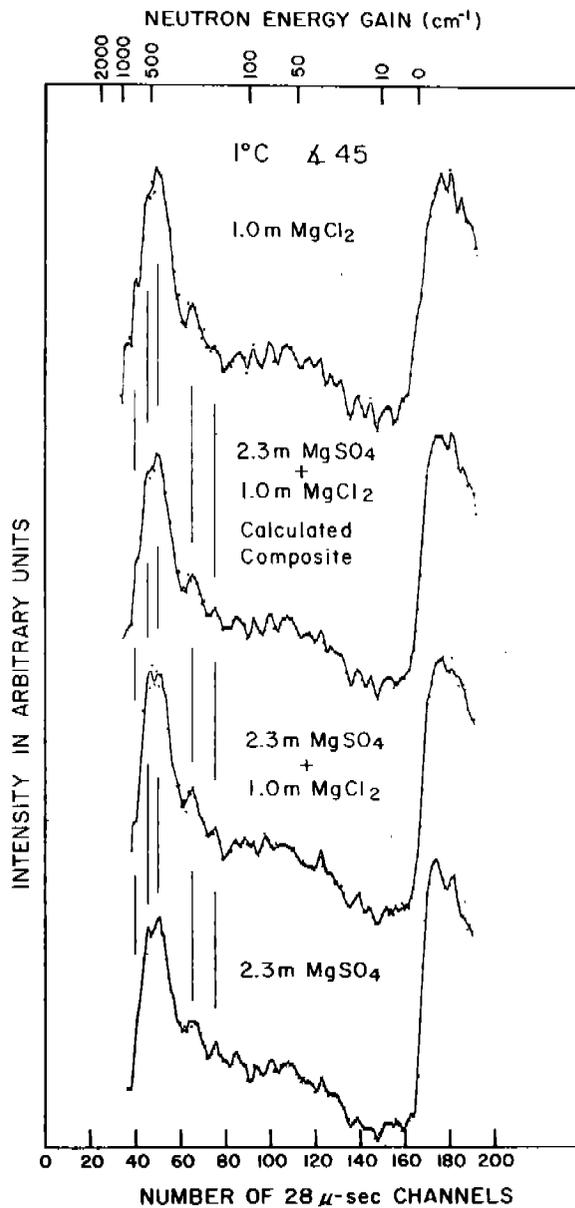


FIGURE 14

The observed dependence of the half-width at half-maxima (Γ) of the Lorentzian broadened, quasi-elastic maxima on K^2 are shown for ternary mixture of a 1.0 m $MgCl_2$ solution with a 2.3 m $MgSO_4$ solution. In addition, the curve is compared with its individual components and with that for a calculated composite. As discussed in the text, the curve of Γ vs. K^2 for the composite was calculated on the over-simplified assumption that the activation energy in a mixed solution of two salts would be the simple average of their individual solutions.

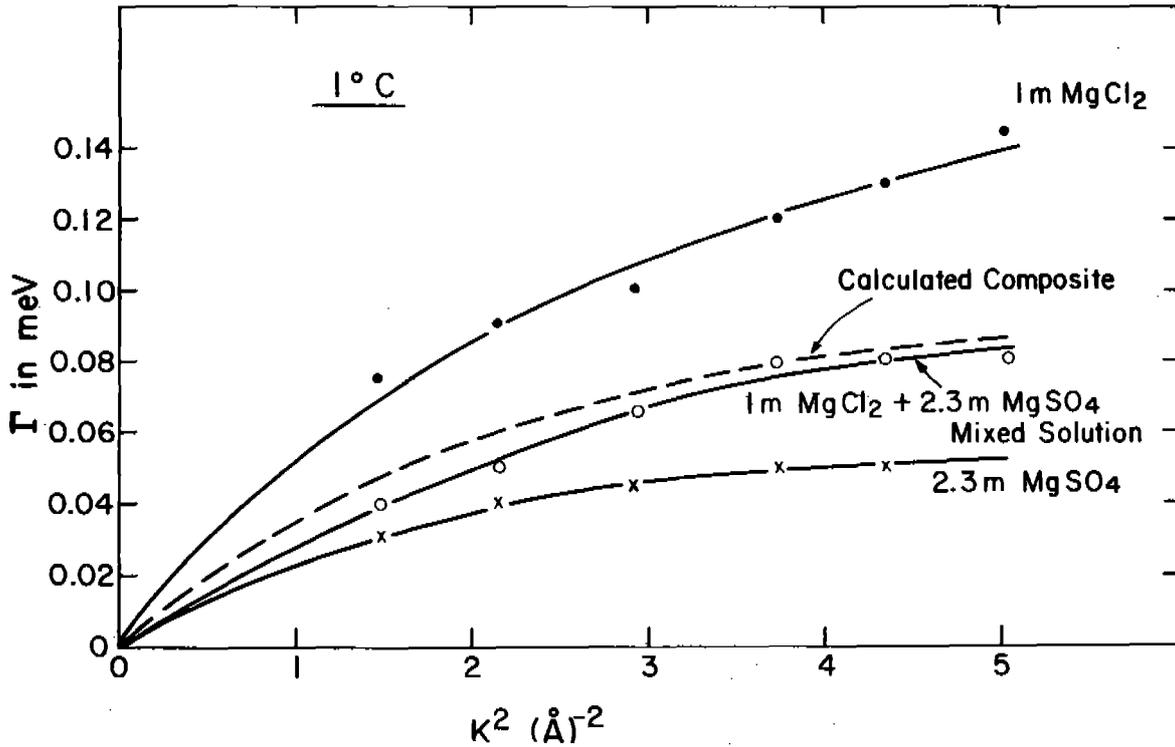


FIGURE 15

The spectra of neutrons scattered at an angle of 45° are compared for a 4.6 m KI solution, a composite spectra of a 4.6 m KI solution, and a 3.2 m KCl solution (assuming simple additivity), a mixture of 4.6 m KI and 3.2 m KCl solutions, and a 3.2 m KCl solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid lines.

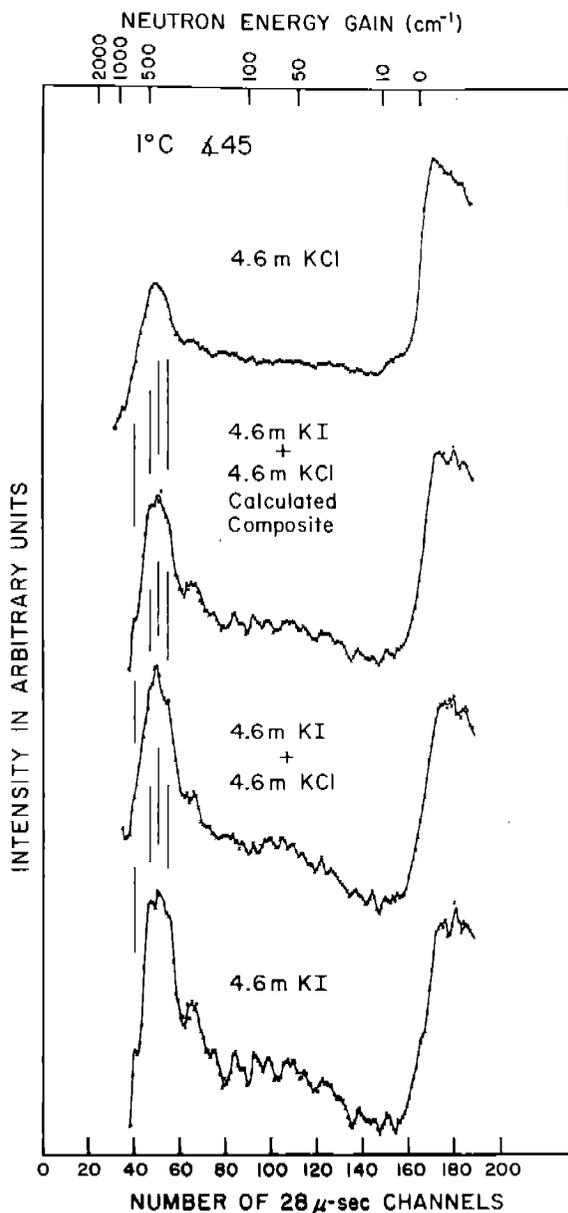


FIGURE 16

The observed dependence of the half-width at half-maxima (Γ) of the Lorentzian broadened, quasi-elastic maxima on K^2 are shown for ternary mixture of 4.6 m KI solution with a 3.2 m KCl solution. In addition, the curve is compared with its individual components and with that for a calculated composite.

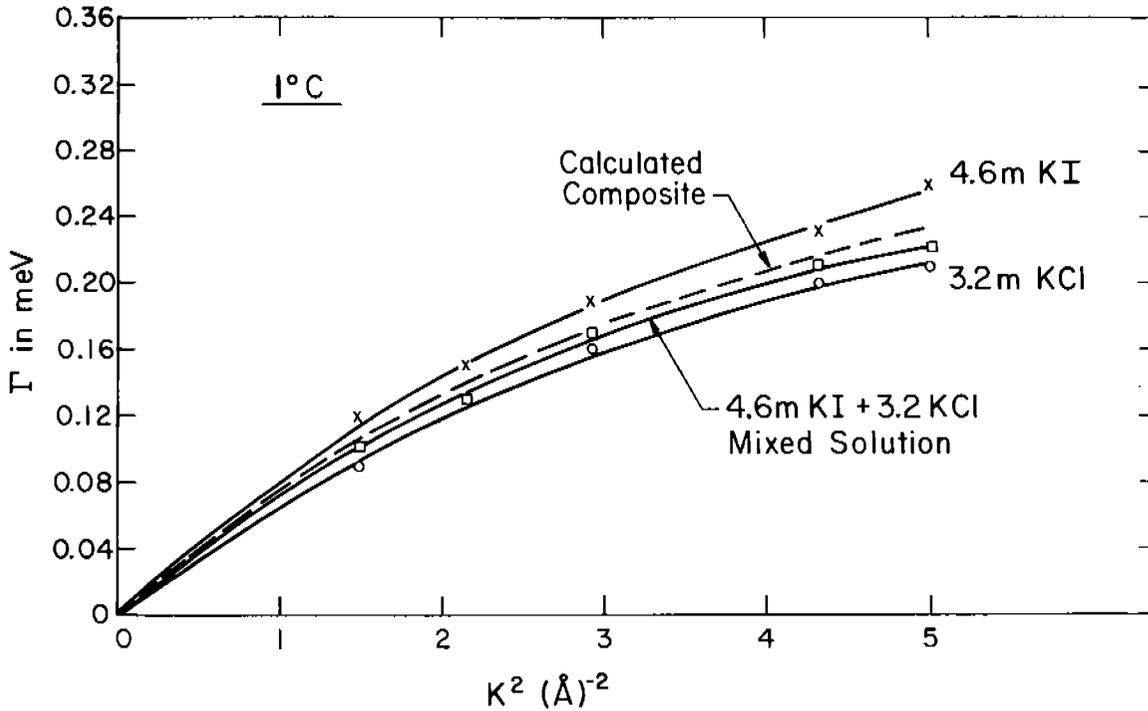


FIGURE 17

The spectra of neutrons scattered at an angle of 45° are compared for a 4.6 m LiI solution, a composite spectra of a 4.6 m LiI solution, and a 4.6 m LiCl solution (assuming simple additivity), a mixture of 4.6 m LiI and 4.6 m LiCl solutions, and a 4.6 m LiCl solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid lines.

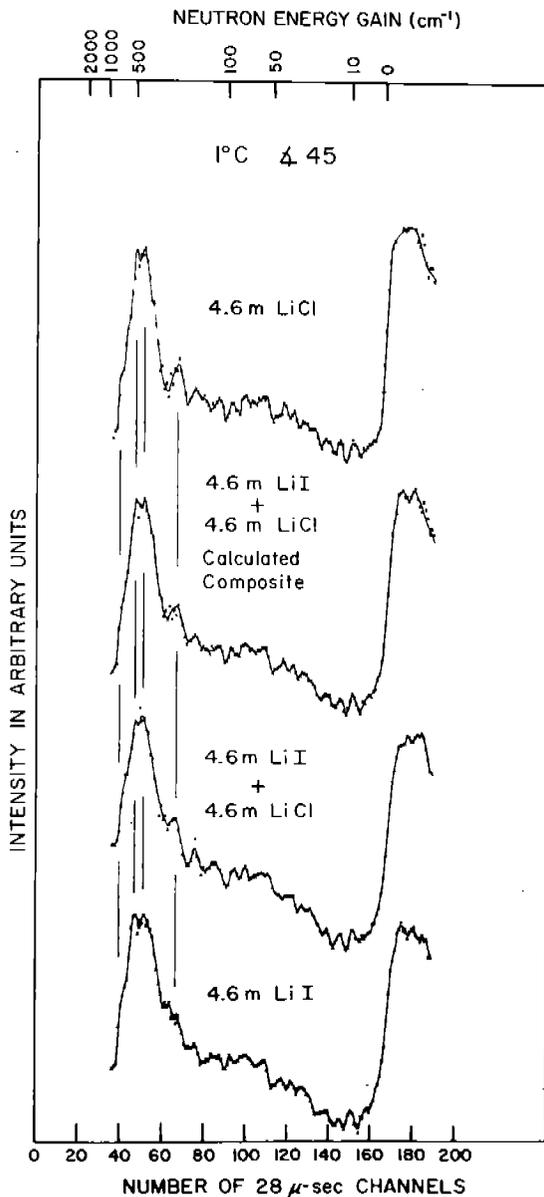
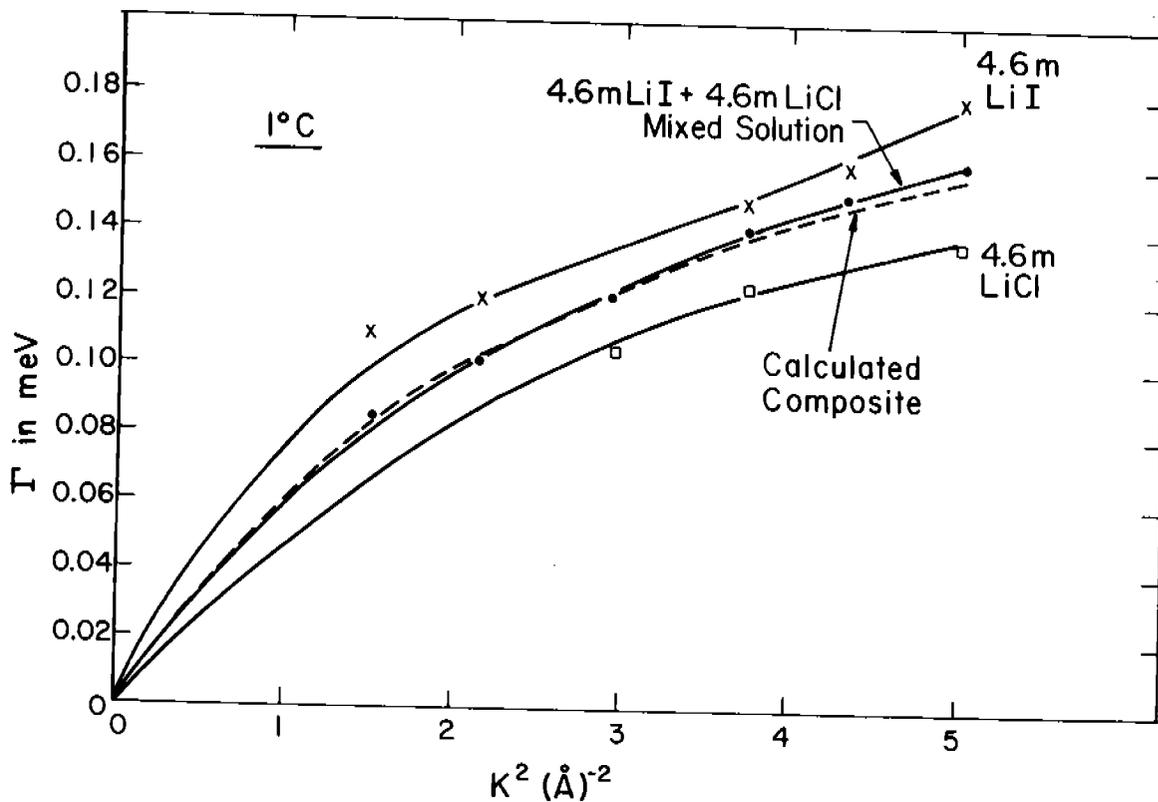


FIGURE 18

The observed dependence of the half-width at half-maxima (Γ) of the Lorentzian broadened, quasi-elastic maxima on K^2 are shown for ternary mixture of 4.6 m LiI solution with a 4.6 m LiCl solution. In addition, the curve is compared with its individual components and with that for a calculated composite.



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