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Neutron Inelastic Scattering Investigation of Water and Ionic Solutions

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Electrochemically Controlled Ion-Exchange

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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 chemically determined ion-exchange kinetics at anion- and cation-responsive electrodes were used to refine a previously developed model to represent the transport processes associated with electrochemically controlled ion-exchange. New binder systems were investigated for electrode fabrication. Electrochemical experiments were carried out: to obtain information as to the limiting currents that could be associated with this process, to evaluate new combinations of binder systems, ion-exchange resins, and carbons, and to determine the suitability of electrodes to ions other than sodium and chloride.

INTRODUCTION

For the past several years, the Rocketdyne Research Division has, under the sponsorship of the Office of Saline Water, engaged in a study of the application of electrochemical techniques to the demineralization of brackish water. Early work in this program was concerned with a mechanistic study of electrochemically induced demineralization at chemically treated carbon electrodes. The results of this study led to the development of a process called electrochemically controlled ion-exchange.

The following developments reflect the progress attained at Rocketdyne on the Office of Saline Water (OSW) electrochemical demineralization program:

1. The elucidation of the mechanism of cation-exchange (e.g., Na^+) at chemically treated carbon electrodes^{1,2}
2. The extension of the mechanism to include cation-exchange at electrodes containing commercial weak acid, ion-exchange resins^{2,3}
3. The development of anion-responsive electrodes, e.g., electrodes fabricated with commercial weak base, ion-exchange resins, that participate in anion exchange, e.g., chloride⁴
4. The laboratory demonstration of the feasibility of the electrochemically controlled ion-exchange process⁴
5. The preparation of a preliminary cost estimate for the electrochemically controlled ion-exchange process⁵

The above developments were presented to the OSW evaluation committee for Ion-Adsorption Processes⁵. The cost estimate of \$1.85 per 1000 gallons was based on actual small-scale laboratory studies. The high cost was due largely to the limited current densities at which this process could be undertaken; low current density processes require high capital costs. The evaluation committee felt⁶ that the present electrodes were seriously limiting from a kinetic point of view and that it was essential to elucidate the transport mechanism within the electrode. Accordingly, current research (OSW Contract 14-01-0001-1316) has been focused on: developing a model for transport within the electrode, developing electrodes with superior kinetics, and determining the maximum current that can be used in this process. A brief review of the mechanism of the electrochemically controlled ion-exchange process will be presented prior to a discussion of the progress made during the second year of the current program. The effort of the first year has been published as an OSW report⁷.

2. 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⁽¹⁷⁻¹⁸⁾ has proposed a semi-quantitative 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.

II. EXPERIMENTAL

The measurements were made using a beryllium filtered incident beam and a neutron time-of-flight spectrometer described previously⁽⁴⁾. General descriptions of this type of spectrometer and its applications to studies of liquids are in the literature⁽¹⁹⁾. The samples of the solutions (prepared from analytical-grade reagents and deionized water) were contained in grooves of average thickness of 0.42 mm in an aluminum plate backed by a flat piece of cadmium. A 2μ layer of an inert polymer film protected against corrosion, and the cell was shielded with cadmium to prevent scattering by the sample holder. As reported previously⁽²⁰⁾, the polymer film and the aluminum window gave negligible spectral

distortions or background contributions and the sample thickness used gave negligible spectral contributions due to multiple scattering. For the spectra taken at 274°K, the sample was cooled by circulating water from an ice-water bath, appropriately shielded to avoid the scattering of neutrons by the coolant.

The procedures used for the treatment of the data, for checking their reliability and reproducibility, and for the analysis of the quasi-elastic components have been extensively described in previous papers⁽²⁰⁾ and only a summary is given below.

The observed spectra were corrected for background, counter-efficiency, and chopper transmission. The background corrections were made by a channel-by-channel subtraction of spectra obtained for the empty sample holder. The background was predominantly a flat component upon which was superimposed a weaker, broad distribution centering at about channel 146. The latter component varied with rotor speed as expected for the "180° burst." Small, but significant, variations occurred in the background with scattering angle and cell geometry, but spectra independent of a given cell could be systematically obtained after background corrections. Typical statistical uncertainties are shown with the reported spectra and correspond to plus or minus one standard deviation as calculated from the total number of background counts-per-channel. The solid curves in the neutron spectra were averaged through the data points with regard to the statistical uncertainties. Where a singularity was marginal in intensity with regard to statistical error, it was assigned only if it was systematically reproduced at more than one scattering angle, temperature, and concentration. In addition to statistical considerations, the reproducibility and reliability of spectral features were tested by (a) comparisons of spectra remeasured with fresh solutions, (b) comparisons of spectra for different scattering angles and for different temperatures, (c) comparisons of data collected on the four independent counter banks, electronics, and memory banks of the time-of-flight analyzer, and (d) comparisons with background spectra for the empty cell to show that no spectral features arose from neutrons scattered by the sample holder or shielding.

III. RESULTS AND DISCUSSION

1) Anion Effects

The effects of strongly hydrating anions (F^- and SO_4^{-2}) have been studied to obtain further information on anion hydration and its influence on cation hydration. As discussed above, most previous work involved singly-charged anions and their relative influence (e.g., Cl^- vs. NO_3^-). During the present year, measurements on a cesium fluoride solution were compared with those obtained previously for cesium chloride and cesium bromide, and measurements on Na_2SO_4 and $MgSO_4$ solutions were compared with those for the corresponding chloride solutions. A number of the effects typically observed for anions in aqueous solutions are summarized briefly in Table III. It can be seen that the following general trends for the influence of anions should be considered.

(a) In the case of strongly hydrating cations, large -1 anions (as discussed above) play a minor role. The ion-water coordinations, the self-diffusion coefficients, and the residence times are primarily determined by the cations. However, as the anion "strength" is increased, the anion may more readily approach the primary hydration layer, disorder the orientation of the primary water molecules, and decrease their residence times. One should consider this as "indirect ion-pairing" on a "time average" as the anion need not necessarily pair directly with the cation but may only simply approach it and spend an average time in this vicinity during which time its field and coordination to the hydration waters may cause such effects. Large +1 ions which form much weaker primary water coordinations are more susceptible to direct ion-pairing; thus, for example, for the cesium ion a number of experiments have reported⁽²¹⁾ the presence of direct ion-pairing and that this increases in passing from iodide to bromide to chloride (e.g., with increasing charge-to-radius of the cation and anion).

(b) The temperature may also influence ion-pairing. Thus, as the temperature is decreased, the anions which attempt to approach the cation on a time-average are forced further away as the primary hydration layer becomes more stable⁽⁹⁾.

(c) Any degree of direct ion-pairing may effectively dehydrate the cation and strongly reduce the residence times and strength of bonding of any remnant primary waters⁽²²⁾.

(d) Where strongly coordinated cation-water complexes exist, such that diffusive motions involve both the transfer of the individual water molecules and the diffusion of hydrated ions together with the hydration layers, with increasing basicity anions may, in general, restrict the diffusive motions associated with the hydration complexes⁽⁸⁾. This behavior and its relationship to glass formation will be discussed in more detail below.

(e) In the formulation of his theory for the interactions of two salts in ternary solutions, Samoilov⁽¹⁷⁻¹⁸⁾ (as detailed below) has argued that with increasing hydration strength the anions tend to "salt-in" or stabilize water molecules around the cations. Samoilov's theory does not take into account direct ion-pairing and, thus, the water molecules that are being stabilized may well be those in second and higher hydration layers. Samoilov argues that the stabilization results from the strengthening of the potential between the primary cation-water coordinations together with a dipole field interaction whereby the hydrated anion interacts with the electric moments of the water molecules in the primary hydration layers of the cations, and serves to stabilize them against reorientations.

(f) In the presence of a strongly hydrating anion, i.e., F^- or SO_4^{2-} , and a weakly hydrating cation, it must also be questioned which ion, if any, dominates in determining the ordering of the water molecules. Thus, in an approximate sense, the strongly hydrating anions may orient water molecules around them, and then, in turn, the hydrated anions may pack around the weaker cations. A similar question for the inverse case has been raised by Brady⁽²³⁾ who questions whether the chloride hydration is indeed a true one in lithium chloride solutions. Rather, he suggests that the lithium ions may strongly coordinate water molecules toward them, and then these hydrated complexes in turn pack around the chloride ions.

The results of our investigations to date may be summarized as follows:

A. CsF Solutions. Previously⁽⁶⁾ it has been shown that both cesium chloride and cesium bromide act as "negative hydrators," increasing the self-diffusion coefficient and decreasing the residence times for water molecules relative to pure water. In addition, it was noted that while the cesium ion serves to disrupt the water structure and decrease the activation energy, defined primary ion-water coordinations exist with the Cs^+ ion. Thus, the NIS inelastic spectra for both concentrated CsBr and CsCl solutions showed similar frequencies characteristic of the primary cesium ion-water coordinations. However, the larger Br^- ion (relative to the Cl^-) disrupted the water structure and allowed the Cs^+ ion to more fully hydrate at a lower concentration. At higher concentrations the values of the self-diffusion coefficients and residence times for both of these salts tended to "saturate" due to the effects of increased ion-pairing and approached nearly equal values for the two salts (being approximately independent of anion and being primarily dependent on the cesium ion-water coordinations).

In contrast, the spectrum for CsF shows marked variations from the above two salts. In Figure 1, the spectra for a 4.6 m solution of CsF are compared with spectra for $\text{KF}\cdot 2\text{H}_2\text{O}$ and for a 4.6 m solution of KF . In Figure 2, the curve of Γ vs. K^2 , obtained from the analysis of the quasi-elastic component, is also shown. Previously^(4,6) it was shown that with increasing concentration the inelastic frequencies for a KF solution departed from those of water and closely approached those of $\text{KF}\cdot 2\text{H}_2\text{O}$, indicating the formation of local ion-water primary complexes similar to those in the solid salt. In Figure 1, it is seen that the inelastic frequencies for the CsF show no similarities within resolution to those observed previously for CsBr and CsCl , but rather correspond strongly to those observed for the KF solutions and for $\text{KF}\cdot 2\text{H}_2\text{O}$. Thus, in the presence of larger, singly-charged cations, the F^- anion appears to dominate and to determine the coordinations of the primary water and the relative influence of the cations appears secondary, at best. In keeping with this behavior it is seen that CsF has decreased the self-diffusion coefficient and increased the residence time relative

to water, thus acting as a positive hydrator, while CsBr and CsCl, as noted previously, acted as strong "negative hydrators."

Danford et al⁽²⁴⁾ have recently argued from x-ray diffraction results on NH_4F solutions that the ammonium ion is able to incorporate into and stabilize the water structure, while the small fluoride ion is unable to sterically disrupt the water structure and goes into an interstitial position. Further, Brady⁽²⁵⁾ has argued that the K^+ ion (being about the same size as a water molecule and having a low charge) is unable to strongly disrupt water structure and may actually incorporate into it. However, unlike the ammonium fluoride case, it is clear that KF can break down existing water structures and form strong ion-water complexes. In the case of ammonium fluoride, it appears that the ammonium ion substituting into the water structure has stabilized it sufficiently to prevent the field of the fluoride ion from disrupting it. However, for KF the K^+ cation would not promote such a stabilization and the field of the fluoride ion would be sufficient to further disrupt the water structure. In a CsF solution, the large Cs^+ ion would even more readily disrupt and break the water structure than the K^+ cation, allowing the fluoride ion to hydrate more readily. While the curve of Γ vs. K^2 for CsF lies well below those for CsBr, CsCl and water, it does not appear to be as strong a positive hydrator as KF due in part to the influence of the cations. X-ray diffraction data⁽²⁶⁾ have shown that in $\text{KF} \cdot 2\text{H}_2\text{O}$ each potassium has six close neighbors, two of which are fluorides -- the fluorides being hydrogen-bonded to waters in the primary coordination spheres of the cation. However, Lawrence and Kruh⁽²¹⁾ have argued that in cesium salts ion-pairing occurs, and that the degree of ion-pairing should increase with decreasing size of the anion. Thus, while fluoride-water coordinations may be as strong as those of cesium fluoride and potassium fluoride, ion-pairing may have reduced their relative number in the former solution, and thus effectively increased the self-diffusion coefficient and decreased the residence time, τ_0 , for water molecules relative to potassium fluoride.

B. MgSO₄ and Na₂SO₄ Solutions. As previously reported⁽⁴⁾, the spectra of solutions containing small and/or highly-charged ions show well-defined primary ion-water frequencies similar to those observed in the corresponding solid state hydrates. It was shown that for solutions of lanthanum and lithium salts both the primary ion-water frequencies and the curves of Γ vs. K^2 are only slightly changed when chloride ions are replaced by nitrate ions, indicating that both the ion-water coordinations and the diffusive kinetics are primarily determined by the cations. In Figures 1 and 2, the spectra and the curves of Γ vs. K^2 are compared for a 2.2 m solution of MgSO₄ and a 4.6 m MgCl₂ solution. The Γ vs. K^2 for the more dilute 2.2 m solution of MgSO₄ lies slightly below that for a 4.6 m solution of MgCl₂. Thus, the sulfate ion has further decreased the self-diffusion coefficient and increased the residence time in the magnesium sulfate solution (relative to the magnesium chloride), and hence effectively increased the "positive hydration." However, for both the magnesium sulfate solution and its corresponding solid salt hydrate, the frequencies in the region of librational modes of H₂O molecules coordinated to the cation are similar to those observed in magnesium chloride, indicating that a degree of similarity in the primary cation-water coordinations persists. However, at lower frequencies where the hydrogen bond stretching modes are typically observed, spectral differences occur. These results can be readily understood by consideration of the reported structures and local orderings obtained from x-ray diffraction for a large number of magnesium salt hydrates. For many magnesium salt hydrates (MgCl₂·6H₂O, MgBr₂·6H₂O, Mg(ClO₄)₂·6H₂O, MgS₂O₃·6H₂O)⁽²⁶⁾ the magnesium ion is always surrounded octahedrally by six water molecules with cation-water distances typically ranging between 2 and 2.2 Å. However, for Mg₃(PO₄)₂·8H₂O where the magnesium is again surrounded octahedrally by oxygens, the coordinations consist of some waters and some oxygens from the phosphate groups. Thus, it would appear that the similarity in the inelastic frequencies observed for the magnesium chloride and the magnesium sulfate solutions may primarily reflect a

tendency of the magnesium ion to be octahedrally coordinated to $6\text{H}_2\text{O}$ molecules in the primary layer. Further, the reported⁽²⁶⁾ crystal structure for magnesium sulfate heptahydrate shows that the magnesium ion is again octahedrally coordinated. The extra H_2O molecule is not coordinated to a metal atom, but instead occupies a hole in a structure of primary hydration octahedra and SO_4 tetrahedra. In magnesium sulfate tetrahydrate the magnesium atoms are again octahedrally coordinated with oxygens; however, four of these oxygens belong to water molecules and two to sulfate groups. Thus, in a 2.2 m solution of magnesium sulfate (where there are approximately 24 water molecules per ion pair) six of the water molecules could be expected to octahedrally surround the magnesium cation; the remaining water molecules in principle could be distributed between sulfate groups and the second hydration layer of the magnesium ion. However, the fact that the Γ vs. K^2 curve for the 2.2 m solution of magnesium sulfate lies lower than that for an equivalent concentration of magnesium chloride indicates that the sulfate ion serves to decrease the self-diffusion coefficient and increase the residence time of such H_2O 's in the high hydration layers of the cation. Thus, the sulfate groups do not serve solely to bridge $\text{Mg}(\text{H}_2\text{O})_6^{+2}$ octahedra, but affect quite a number of H_2O molecules without contributing significantly to the spectral features of specific anionic coordinations.

Further evidence is obtained from the spectrum of a Na_2SO_4 solution. The inelastic frequencies in the spectrum of a Na_2SO_4 solution are very similar to those of a NaCl solution (Fig. 3). It must be pointed out that ordinarily the Na^+ ion is generally considered to be a weak structure-making cation. However, it has been reported that in $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ the sodium atoms have six water neighbors with a slightly distorted octahedral coordination, indicating that the cation has a uniquely coordinated hydration sheath. In addition, the Γ vs. K^2 curve for a 1 m Na_2SO_4 solution lies well below that of a 4.6 m NaCl solution, again showing that the $\text{SO}_4^{=}$ serves to decrease the self-diffusion coefficient and increase the residence time of the H_2O 's. These results support the argument that the $\text{SO}_4^{=}$ ion enhances the hydration of the cations. Thus,

neglecting the absence of direct ion-pairing, Samoilov^(17,18) has pointed out that the hydration of the cation is increased by the anions due to the decrease in disorientated water molecules about the cation. This hydrating effect increases with increasing charge of the anion. However, this effect also depends upon the hydrating strength of the cation⁽²⁷⁾. For a highly charged cation the tendency for direct ion-pairing with an anion would reduce the cation hydration. Thus, at high enough temperatures, NMR measurements of solutions of rare earth sulfates⁽²²⁾ showed that the cations pair with the $\text{SO}_4^{=}$ ion. X-ray diffraction measurements on $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ⁽²⁶⁾ also show that in contrast to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the $\text{SO}_4^{=}$ ion closely surrounds the La^{+3} ion and keeps the H_2O 's away. This interpretation agrees well with the NIS observations on the effects of the $\text{SO}_4^{=}$ ion, and may probably predict the effect of the $\text{SO}_4^{=}$ in rare-earth sulfate solutions which we have not measured.

2) Diffusive Motions of Hydrated Ions and Their Relationship to Glass Formation

A. The Dependence of the "Quasi-elastic" Component on the Nature of the Diffusion Processes.

As discussed previously in detail, at lower temperatures (typically below 25°C) the angular dependences and temperature dependences of widths, gamma, and areas of the observed quasi-elastic maxima are in accord with a simple delayed diffusion behavior⁽²⁸⁾. However, a jump-diffusion model, in general, constitutes only an approximation as it does not go to the short time or limit properly, as required for any complete correlation function. However, at lower temperatures significant contributions from such free-particle motions would not occur until very short times (corresponding to high K^2 values) are reached, and hence, if the delay times, τ_0 , are long, a simple delayed diffusion constitutes an adequate approximation. For this model the width and the area and their dependences on K^2 are as follows:

$$\Gamma = \frac{\hbar}{\tau_0} \left[1 - \frac{e^{-1/6} \langle \mu^2 \rangle K^2}{1 + K^2 \tau_0 D} \right] \quad \ln A = C - \frac{K^2 \langle \mu^2 \rangle}{6}$$

H₂O vibrates for period (τ_0) and diffuses for time (τ_1) such that ($\tau_0 \gg \tau_1$) over length $\langle l^2 \rangle$. Then:

$$D = \frac{1}{6} \frac{\langle l^2 \rangle + \langle \mu^2 \rangle}{\tau_0 + \tau_1} \longrightarrow \frac{1}{6} \frac{\langle l^2 \rangle}{\tau_0}$$

The dependence of the width Γ on K^2 is shown schematically below:

It should be noted that the curve of Γ vs. K^2 initially rises linearly with the slope given by $\hbar D$ as expected for long interaction times where the diffusive kinetics should be characteristic of classical diffusion. At shorter times (i.e., larger values of K^2), the curve approaches asymptotically the value of $\hbar/\tau_0$. In reality, however, at some higher value of K^2 , the curve must rise again in accord with a "free particle" behavior for which the simple jump diffusion model, shown above, does not account. However, as can be seen by reference to the data of Fig. 4, and, in particular, to the curve of Γ vs. K^2 for 3.5 m LaCl₃ and 5.7 m MgCl₂ solutions, a good approximation of this jump diffusion behavior within the observed range of K^2 is achieved at lower temperatures.

More generally, in order to calculate a broadening for the quasi-elastic maxima that would arise where contributions both from motions of hydrated cations and from the exchange of primary waters could occur, it is useful to consider a model derived by K. E. Larsson and L. Bergstedt⁽²⁹⁾. It assumes that a protonic group may vibrate on a center of mass of a larger molecule for a time τ_0 and then jump a characteristic distance l in a time τ_1 . In correspondence, the center of mass of a larger molecule carrying the protonic group may vibrate for a time τ_0' time, and then undergo diffusion characterized by a self-diffusion coefficient, D , for a time τ_1' . The most general expression obtained is complex. However, certain simplifying assumptions can be made which are in keeping with what might be expected for ionic solutions containing strongly hydrated cations at high concentrations. If it is assumed that the times τ_0 and τ_1' are much larger than the characteristic period time τ_0' , then the expression for Γ vs. K^2 is again a Lorentzian and the value of the width for small and large K^2 values is given below:

If $\tau_1', \tau_0 \gg \tau_0'$,

$$\text{Then, for } K^2 \text{ Small } \Gamma \approx \hbar \left[D + \frac{\langle l^2 \rangle}{2\tau_0} + \frac{\langle r_1^2 \rangle}{6} \left(\frac{1}{\tau_0} + \frac{2}{\tau_1'} \right) \right] K^2$$

$$\text{Then, for } K^2 \text{ Large } \Gamma \approx \hbar \left[DK^2 + \frac{1}{\tau_0} + \frac{1}{\tau_1'} \right]$$

As for the simple jump diffusion model, Γ is again linear in K^2 for small values. However, the slope now involves both the self-diffusion coefficient, D , for the center of mass, and the effective self-diffusion coefficient $\ell^2/2\tau_0$ for the protonic group, as well as a third factor depending upon the amplitude. However, in contrast to the simple jump diffusion model, at large values of K^2 , a constant value is not approached. Rather, a different curve again rises linearly but with a different slope which is simply $\hbar D$. In the above model it has been assumed that τ_0 and τ_1' time are of the same order of magnitude. This might be a realistic approximation if the residence times for the H_2O molecules were sufficiently short so that they occurred within the neutron interaction time, but yet were sufficiently long so that the waters of hydration could diffuse part of the time with the cations. As shown in Figure 5, evidence of such a double slope behavior is observed for 10 m solutions of $LiCl$ and $LiNO_3$ and may reflect motions of H_2O molecules in the second hydration layer, which could exchange within the neutron interaction period but also more with the cation part of the time.

Further, if it is assumed that the limit is approached whereby

$$D \gg \left[\frac{\langle l^2 \rangle}{2\tau_0} + \frac{\langle r_1'^2 \rangle}{6} \left(\frac{1}{\tau_0} + \frac{2}{\tau_1'} \right) \right]$$

and

$$DK^2 \gg \left(\frac{1}{\tau_0} + \frac{1}{\tau_1'} \right),$$

then

$$\Gamma \longrightarrow \hbar DK^2 \text{ and is linear in } K^2 \text{ over the entire range.}$$

Indeed, as shown in Figure 4, such a simple straight-line behavior involving a low value of D is observed for 15 m $LiCl$ and for concentrated $CrCl_3$ and $Cr(NO_3)_3$ solutions. Here the observed quasi-elastic maxima and its broadening is then primarily characteristic of motions of the hydrated cation as a whole. The residence times for the exchange of primary waters of hydration is longer than the neutron interaction time of 10^{-11} - 10^{-13} (see Table IV) and the time τ_1' that the center of mass is unbonded

is long compared to any period τ_0' that it is bonded, and also long compared to neutron interaction time. Under such conditions, the broadened quasi-elastic maxima would be dominated primarily by the diffusive motions of the hydrated ions and would rise nearly linearly with the slope proportional to D.

The question arises as to the type of motions that the centers of mass undergo and how they depend functionally on the motions of the hydrated ions, as described in terms of Langevin's equation^(30,19):

$$1) \quad M\ddot{\mathbf{r}} + M\xi\dot{\mathbf{r}} = \mathbf{F}(\tau) \quad \text{where } \mathbf{F}(\tau) \text{ is a rapidly varying Stochastic Force} \quad (1)$$

$$2) \quad \text{where } D = \frac{kT}{M\xi} \quad (2)$$

ξ is the friction coefficient and $1/\xi$ is, in essence, to be considered as a short delay time before diffusion sets in. As pointed out by Larsson⁽³¹⁾, it is a measure of the collision time itself. In addition, the above relation for the self-diffusion coefficient predicts that it should be inversely proportional to the mass. A comparison of the curves of Γ vs. K^2 for 15 m LiCl and 4.23 m CrCl₃ solutions shows that although the CrCl₃ is more dilute, the Γ vs. K^2 is also linear and indeed has a smaller slope, corresponding to a smaller value of the self-diffusion coefficient. Just such a behavior would be expected in view of the heavier mass of the chromium hydration complex relative to the primary lithium hydration complex. If the assumption is made that all the water molecules present are moving with the cations, then the ratio of the masses of the hydration complexes ($M_{\text{Cr}}/M_{\text{Li}}$) obtained would be equal to 3.62 and the observed ratio of the D's (Li/Cr) is equal to 4.28. Hence, to the first approximation, the majority of the change in the self-diffusion coefficient in going from the lithium to the chromium solution can be accounted for in terms of just the expected change in the mass of the hydrated cations, in accord with Eq. 2 above. Values for $1/\xi$ of 6.26×10^{-15} and 5.31×10^{-15} sec. respectively are obtained for the lithium and chromium solutions.

As shown by Larsson, one can define an interaction time $\tau_{\text{obs}}^2 = M/K^2kT$. If the neutron is to observe a classical diffusion

behavior it is then required that $(l/\xi)/(\tau_{\text{obs}})$ is much less than unity. Using the above values for l/ξ , the masses, the temperatures, and the largest available values of K^2 , it is indeed seen that this ratio would be less than unity throughout our entire observation range of K^2 and, thus, a classical diffusion behavior as observed could logically and consistently be expected. Further, a value of the self-diffusion coefficient has been reported⁽³²⁾ for the motion of the $\text{Cd}(\text{H}_2\text{O})_4^{+2}$ complex in melts of salt hydrates. If, using the reported value of D and the mass of this complex, a value of l/ξ is calculated, it is of the order of magnitude of the characteristic times observed in the present neutron experiments, as reported in Table IV. NMR investigations⁽³³⁾ have reported a possible reorientation involving the hydrated lithium ion in aqueous solutions. A correlation time of the order of 10^{-11} has been reported from the NMR data and can be compared to the present data. The NMR correlation time, τ_c , is given by

$$\tau_c = \frac{\eta_0 V_m}{kT} \quad (3)$$

where V_m is the volume of the hydrated ion and η is the viscosity. Then, from the formula⁽¹⁹⁾

$$\eta = \frac{kT}{2R_g D} \quad (4)$$

and the Stokes-Einstein relationship in Eq. (2) above, the following relation is obtained between the correlation function and the friction coefficient:

$$\tau_c = \frac{M^* V_m \xi}{2R_g kT} \quad (5)$$

If the values of ξ , the friction coefficient from the neutron spectra (as given above), are used together with reasonable values of the masses and the radii of the hydration complexes, a value of τ_c typically equal to 10^{-10} secs. is obtained for the lithium hydration complex. The order

of magnitude is in reasonable agreement with reported values from the NMR experiments.

As noted above, in contrast to the behavior observed for the simple jump diffusion cases, the more basic anions (i.e., NO_3^- relative to Cl^-) serve to decrease the observed self-diffusion coefficient associated with the hydration complex. It would appear that the more basic anion may be effectively increasing the friction coefficient, ξ , a picture which would be in accord with suggestions (discussed below) by Angell and Sare⁽⁸⁾ that anions may bridge the hydrated cations and further restrict their motions. While such a picture must be considered as tentative at present, Zitseva and Fisher⁽³⁴⁾ have proposed a hydrodynamic theory for the motion of ions in solution taking into account the effect of ion hydration. They derive a complex expression for the product of the mass and friction coefficient, as appears in the Stokes-Einstein relationship for the self-diffusion coefficient, which depends upon the coefficients of both the shear and volume viscosities as well as the potential describing the cation-water forces holding the hydration shells. Both the "effective mass" and the friction coefficient depend upon these primary cation-water interactions, since both the time average number of waters moving with the cation and the strength of the interactions between the hydration sphere and the anions would be strongly determined by the primary water-ion interactions. Thus, these authors argue that as such interactions become weaker and H_2O molecules may exchange more rapidly between the hydration layers and the solvent, both the effective mass and ξ must decrease.

B. Discussion of Results and Their Relationship to Glass Formation

In the above formulation, it has been assumed that scattering law was in accord with a correlation function obtained by the classical formulation of the Langevin equation. Further, the curves of Γ vs. K^2 were interpreted to be in accord with the long time limit

$$\frac{\tau_{\text{obs}}}{\tau_B} \gg 1,$$

in accord with a classical diffusive behavior with

$$D = \frac{kT}{M\xi} = \frac{kT}{M} \tau_B \quad (6)$$

However, in the quantum mechanical case, recoil effects may also contribute to the observed width for certain values of K^2 . It is therefore necessary to consider the relative contributions of both the intensity and width of each component in order to convincingly assign the Γ vs. K^2 curves to classical diffusion. Vineyard⁽³⁰⁾ has shown that there exists a critical value of

$$K = K_c = \left(\frac{kT}{MD^2} \right)^{1/2} \quad (7)$$

such that:

a) when $K \ll K_c$, the contribution from the recoil term is low and broad, while the diffusive motion gives a high and relatively narrow contribution whose width goes as $\hbar DK^2$

b) when $K \gg K_c$, the reverse of (a) is true, with the recoil term giving the predominant contribution, and with an energy shift

$$\omega_0 = \frac{\hbar^2 K^2}{2M} \quad (8)$$

In both (a) and (b) the slope is linear in K^2 , and therefore, for small slopes on Γ vs. K^2 curves, it can be dangerous to assume that an observed linear behavior of Γ vs. K^2 necessarily implies a simple diffusive behavior. If K is taken as K_c such that the recoil effects have significant intensity, then the energy shift:

$$\omega_0 = \frac{\hbar^2}{2M} \frac{kT}{MD^2}; \quad \text{or,} \quad \frac{\omega_0}{kT} = \left(\frac{\hbar}{\tau_B} \right)^2 \frac{1}{(kT)^2} \quad (9)$$

where $\tau = 1/\xi$; the corresponding width, Γ' , is of the order of magnitude of ω_0 . Under such conditions, if quantum effects are not to contribute, then

$$\frac{\Gamma_{\text{obs}}}{kT} \gg \frac{\Gamma'}{kT}, \text{ which may not be true for small values of } M, \text{ of } D, \text{ or of } \tau_B.$$

In the present experiment the range of K^2 was such that $0 \leq K^2 \leq 5 \text{ (\AA}^{-2}\text{)}$. The smallest value of M involved was $\sim 80 \text{ A.M.U.}$ (for 15 m LiCl) and the values of D involved were of the order of $10^{-5} \text{ cm}^2/\text{sec}$. Hence, in the range of the present experiment $K^2 \ll K_c^2$ and recoil effects should be negligible. In like manner, $\Gamma \approx 8 \times 10^{+2} \text{ mev}$, hence, $\Gamma_{\text{obs}} \ll \Gamma'$, and any contribution of the recoil effects would give rise to a broad contribution relative to Γ_{obs} .

It has been suggested that the diffusive motions of hydrated cations and their restriction with decreasing temperature and with increasing anion basicity may be intimately related to the formation of glasses. To investigate this problem, concentrated solutions of lithium chloride, lithium nitrate, chromium chloride, chromium nitrate and lanthanum nitrate have been investigated. The concentrations and salts were selected for the forthcoming reasons. For most of these salts, solubility allowed concentrations to be reached such that the majority of the water molecules present would be expected to be strongly coordinated in the primary hydration layers of the cations. In such primary layers, the exchange times for the water molecules undergoing individual jumps would be expected (see, for example, Table IV) to exceed neutron interaction time ($10^{-11}, 10^{-13} \text{ sec.}$). Such motions would not be expected to contribute to the neutron spectra, which would then be characteristic of motions involving hydration complexes if they occurred many times during the interaction time. Evidence has been cited in the literature (Table IV) to indicate that diffusive motions of cations together with their waters of hydration may also contribute to the overall diffusive kinetics as well as the jump diffusion of individual water molecules. In addition, at these concentrations, solutions of these salts could be held in a supercooled condition so that spectral measurements could be made both upon the supercooled liquid above the glass transition temperature and below the glass transition temperature.

Both the nitrate and chloride solutions were run since, as noted above, the variation between a chloride and a nitrate ion makes only a small change in the parameters characteristic of the jump diffusion of individual water molecules. In contrast, Angell et al.⁽⁸⁾ have shown that the more basic nitrate ion can increase the glass transition strongly relative to chloride at a given concentration and for a given cation. Therefore, it was desirable to determine if a corresponding anionic effect could be obtained for the diffusive motions of hydration complexes such that the nitrate ion would restrict their diffusive mobility strongly relative to the chloride anion.

In Fig. 5, the curves of Γ vs. K^2 for 4.3 m $\text{La}(\text{NO}_3)_3$, 4.3 m LaCl_3 , 4.23 m CrCl_3 , and 15.02 m LiCl solutions at 1°C are compared with that for water. In addition, quasi-elastic components observed for the supercooled solutions and the glasses of CrCl_3 and $\text{La}(\text{NO}_3)_3$ are shown, and compared both with the incident energy distribution and with this distribution broadened by the Lorentzian functions with different Γ values. The following features and trends should be noted:

- 1) The curves of Γ vs. K^2 at 1°C for these solutions lie below that for water (a "positive hydration behavior"). Thus, the formation of ion-water hydration complexes (whose characteristic frequencies appear in the inelastic region) decreases the self-diffusion coefficients and increases the residence times relative to water.

- 2) At 1°C, the curves of Γ vs. K^2 for $\text{La}(\text{NO}_3)_3$ and LaCl_3 solutions rise linearly at the origin, and then approach a nearly constant value at the larger values of K^2 , in good accord with a delayed-diffusion model (see Sec. 2A), and show only secondary variations when Cl^- anions are replaced by NO_3^- anions. The weak dependence on anion is contrary to that observed for the glass transitions, which are significantly higher for nitrate solutions than for chloride solutions. This suggested that, in solutions of strongly hydrating cations, the strong anion dependences of the glass transitions might result from other than their influence upon the ordering of H_2O molecules about the cations or upon

the activated jumps of individual H_2O molecules. The possibility exists that the anions may mainly restrict motions involving the entire hydrated cations⁽⁸⁾, and thus influence the ordering of their environment. Such motions could well contribute negligibly to the NIS spectra at 1°C and at concentrations of typically 15 H_2O 's per ion pair, where activated jumps of individual H_2O molecules predominate.

3) In contrast to the results for lanthanum salts, at 1°C , Γ is observed to depend nearly linearly on K^2 (over the observed range) for the 4.23 m CrCl_3 solution and for the concentrated (15.02 m) LiCl solution. Such a linear dependence is more in keeping with a classical diffusion behavior, for which $\Gamma = \frac{1}{3}DK^2$. However, from the slopes at the origins of the Γ vs. K^2 curves, it is seen that the self-diffusion coefficients, D , decrease in the progression $\text{H}_2\text{O} > 3.5 \text{ m } \text{La}(\text{NO}_3)_3 \approx 3.5 \text{ m } \text{LaCl}_3 > 15.02 \text{ m } \text{LiCl} > 4.23 \text{ m } \text{CrCl}_3$. The nearly linear dependences of the Γ vs. K^2 curves and the low values of the diffusion coefficients for the concentrated LiCl and CrCl_3 solutions may be explained (Section 2A) if it is assumed that the contribution to the quasi-elastic components primarily arises from diffusive motions which involve motions of the entire cation hydration complex, rather than jump reorientations of individual H_2O molecules. Thus, it has been reported⁽³⁵⁾ that, for Cr^{+3} and other strongly hydrating cations, the average exchange times for individual H_2O molecules from the hydration sheath can exceed 10^{-4} sec., and, hence, would not contribute significantly to the quasi-elastic component (as discussed above). In addition, at a concentration of 15.02 m for LiCl , most of the H_2O molecules should be in the primary layers of the cations. The diffusion coefficient for the strongly hydrating Cr^{+3} cation would then be less than that expected for the lighter lithium ion and its smaller primary hydration layer. Also, the results of Angell and Sare⁽⁸⁾ show that the T_g for a 4.23 m CrCl_3 solution lies well above that for a 15.02 m LiCl solution, in keeping with a hypothesis that a higher value of T_g could result from a lower degree of mobility for a hydrated cation.

4) At temperatures below 1°C , the "quasi-elastic" components for both the supercooled liquids above T_g and the glasses of CrCl_3 and $\text{La}(\text{NO}_3)_3$ (Fig. 5) show no significant broadening within resolution and statistical uncertainties when compared with the incident energy distribution and the Lorentzian broadened distributions. This does not necessarily imply that relaxational motions have ceased. Rather, it implies that such relaxational processes are occurring sufficiently slowly and that their characteristic times now exceed the largest neutron interaction time, and here they no longer contribute to the NIS spectra. As detailed in the literature⁽³¹⁾, a neutron interaction time may be defined by $t_{\text{int}} = \frac{1}{Kv_0}$, where v_0 is the neutron velocity relative to a scattering center. t_{int} may be varied with K (and, hence, with scattering angle). Motions with characteristic times or periods longer than about 10^{-10} sec. (longer than t_{int}) would not yield experimentally distinguishable broadenings of the incident energy distribution. Thus, for example, in cooling the 3.5 m $\text{La}(\text{NO}_3)_3$ from 1°C to just above its glass transition temperature, the relaxational time increases from 6.4×10^{-12} sec. to an expected value in excess of about 10^{-10} sec.

5) At a concentration of 4.6 m, the curve of Γ vs. K^2 for lithium nitrate lies above that for lithium chloride, indicating a stronger negative hydration effect for the nitrate ion. In contrast, for the 10 m solutions, corresponding to 5.5 water molecules per ion-pair, the diffusive kinetics may involve motions of the primary hydration complex. Thus, the curve of Γ vs. K^2 for LiNO_3 is observed to lie below that of LiCl , which may indicate that the nitrate ion, acting as a "bridging" anion, is more effective in restricting diffusive motions involving hydrated cations than the chloride ion.

The time-of-flight spectra for neutrons scattered from solutions of CrCl_3 and $\text{La}(\text{NO}_3)_3$, at temperatures above and below their glass transitions, are shown in Figs. 6 and 7 and compared with those of the corresponding solid salt hydrates and of hexagonal ice. The corresponding frequency distributions shown in Fig. 8 were calculated assuming the cubic one-phonon cross section^(36,37) and a Debye-Waller factor of unity⁽⁴⁾. The following features and trends were observed:

1) A strong correspondence in spectral features and frequencies (below 900 cm^{-1}) exists between the supercooled solutions above T_g and the solid glasses.

2) The observed frequencies (which differ from those of water and ice) are associated with the characteristic modes of cation-water hydration complexes, and good correspondence is observed with reported infrared and Raman frequencies. Thus, for CrCl_3 , certain of these frequencies have been assigned to the librational modes of H_2O molecules and to the metal-oxygen stretching modes characteristic of the $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ complex. The Cr^{+3} -water coordinations may involve a degree of covalent bonding⁽³⁸⁾. Similar evidence has also been cited for the existence of octahedral ion-water complexes in solutions of rare earth halides⁽³⁹⁾. In previous NIS investigations⁽⁴⁾, similar frequencies, characteristic of strongly coordinated, primary cation-water complexes, were observed for solutions containing La^{+3} , Mg^{+2} , and Li^{+1} cations. Such frequencies (as well as the diffusive kinetics and parameters) were found to be only weakly affected by -1 anions and to be primarily determined by the cation-water coordinations.

3) The spectra of the solutions at 1°C and of the solid crystalline hydrates also show inelastic maxima at frequencies similar to those observed for the glasses and for the supercooled liquids. However, in the solutions at 1°C , these maxima are broadened by the increased diffusional and relaxational rates. In the spectrum of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, these maxima appear nearly as sharp as in the spectra of the glass and the supercooled liquid. However, for $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, despite the absence of any relaxational broadening, these frequencies appear broader than for either the glass or the supercooled liquid. It, therefore, appears possible that in $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ coupling of the "hydrated ions" to the lattice has split their characteristic frequencies into unresolved components, making them appear broadened. For $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, the influences of such couplings of complex vibrations to the lattice would be relatively less pronounced due to the stronger, and partially covalent, primary cation-water coordinations.

In summary, these results suggest a degree of similarity in the coordinations and local ordering of hydrated cations between the glasses and the corresponding supercooled, concentrated, viscous liquids. Such cation-water complexes may, in part, be responsible for inhibiting the formation of hexagonal ice, and, at lower temperatures and concentrations, for the formation of "salt-rich" and "water-rich" regions of the type postulated by Angell and Sare⁽⁸⁾. On the basis of the above results, the strong dependence of T_g on anions cannot be associated with the significant alterations in the cation-water coordinations in these complexes by anions. Rather, in keeping with the argument of Angell and Sare⁽⁸⁾, anions may bind to the protons of H_2O molecules already strongly oriented about cations, and thus affect the orderings and diffusive motions of hydrated cations. The more basic an anion, the more it could produce a cooperative restriction of the diffusive motions of the hydrated cations, and the higher the T_g would be.

3) Ternary Solutions

Most of the existing experimental information on ternary solutions has resulted from determinations of thermodynamic properties as a function of the anions and cations present, of their concentration, and of the temperature (for a summary of previous work see Table II). In addition, measurements of heats of mixing have been used more recently to infer changes that may occur in the solution structure and in the hydration of the ions present upon mixing. It is, of course, important to understand the structural features of such ternary solutions in terms of their thermodynamics, as any detailed structural model proposed must also account for such thermodynamics and the changes that occur upon mixing. However, interpretations of changes in such thermodynamic quantities at a molecular level can be complicated as they represent a summation over changes in the hydration of all ions present, in ion-pair interactions, and in the solvent structure. It has been extensively argued⁽¹¹⁻¹⁶⁾ that changes in the heat of mixing, in the heat of solution, and in the enthalpy appear to correlate strongly with the division of the ions involved into "structure-making" and "structure-breaking" categories, implying that upon

mixing significant changes occur in the region of primary hydration spheres of the ions and in their hydration due to ion-ion interactions present in solutions. Nevertheless, at present, both experimental measurements and theories treating the changes that occur in ternary solutions upon mixing at a molecular level are scarce. Thus, as shown in Table I, only a few measurements of the self-diffusion coefficients and of NMR correlation times and their changes upon mixing, relative to simple additivity, have been reported for a limited number of cases. A number of more recent theories allude to the types of interactions that must be present in such ternary solutions, but as yet the development of these theories is such that they are most difficult to compare directly with changes in the hydrations of ions and the associated diffusive mobility of the water molecules that would be observed at a molecular level. Thus, Friedman⁽⁴⁰⁾ has described the interactions between two ions in a pure solvent in terms of an electrostatic term, a repulsive core potential, a term representing a known dielectric effect in the region of the ions and a term representing the contribution of overlapping cospheres. Samoilov and coworkers^(17,18) have also developed a semi-qualitative theory which seems capable of correlating certain observed trends that occur upon mixing with concentration, with temperature, and with the strength of ion hydration. In principle, this theory appears to predict the changes in the bonding of primary water molecules and in the rates at which they can exchange which should be directly observable and comparable by neutron scattering measurements. In general, Samoilov considers that upon mixing, the ion interactions have two effects:

- (a) a perturbation of the potential describing the interaction or bonding between a given ion and its nearest neighbors waters, and
- (b) the effect of the average field associated with the cations and anions of one component salt interacting with the dipoles of water molecules in the primary layers of the ions of the second component salt (a treatment similar to Gurney's interaction in the cosphere⁽⁴¹⁾).

In regard to (a), no detailed assumptions are made directly concerning the shape or depth of the potential. Rather, the ions of the salting-out agent are considered to perturb or change the escape or "transfer probability" for water molecules closest to the ions of the salted-out material. In regard to (b), the change in the interaction energy is regarded solely to occur between the effective field arising from the ion of one component and the dipoles of the water molecules outside the primary layer of the second component. It is troublesome that Samoilov has chosen to only use changes in the number of water molecules in the primary hydration layer to treat the transition probability to higher layers, where then a dipole field interaction can occur. He has not included any energetic changes that might be associated with the change in transition rate in the primary layer itself. However, in comparing his theory with many experimental results (see, for instance, Table V), trends are observed which appear in accord with those obtained by experiments and, at least, such trends are useful in an experimental sense for comparison with other results.

In general, cation-cation interactions appear to have a "dehydrating" or "salting-out" effect, while Samoilov^(17,18) notes that anions tend to have a "hydrating" or "salting-in" effect and stabilize water molecules in the primary hydration layers of cations. Further, the solvent structure, especially in dilute solutions, can play a role⁽⁴²⁾. The more strongly the solvent structure is disordered, the more strongly an increase in hydration of the cations present is favored. Thus, a number of competing effects occur and the question for any ternary solution then remains as to which dominate and account for the thermodynamic changes upon mixing. In this regard, the recent studies of Wood et al⁽¹¹⁻¹⁶⁾ have shown that the heats of mixing correlate strongly with the "structure-making" and "structure-breaking" characteristic of the cations present. When salts of a common anion with either two "structure-breaking" or two "structure-making" cations are mixed, the heat of mixing is positive (an endothermic reaction). In contrast, when a "structure-making" and a "structure-breaking" salt with a common anion are mixed, the opposite behavior is observed. In the former case, it is often argued⁽⁴³⁾ that both "structure-making" cations suffer a partial dehydration, while in the latter case, a transference of water is observed from the weaker "structure-breaking" ion to the hydration layers of the stronger

"structure-making" ions. However, it has also been proposed on the basis of NMR^(44,45) that in the latter case, as the "structure-making" ion hydrates more strongly upon mixing, anions are forced away from it toward the "structure-breaking" cation. This, in turn, stabilizes the primary water molecules about this ion, giving rise to an overall net decrease in the heat of mixing.

In like manner, the dependence upon temperature may be complex. Thus, Samoilov's argument that upon increasing the temperature the average anion-cation distances increase, becoming more comparable to cation-cation distances, favors a dehydration of the ions. However, the solvent structure may become weakened with increasing temperature more rapidly than the primary hydration structures, which would favor an increase in the hydration of ions -- an opposite effect to that above. Finally, as the primary cation-water hydration complexes become disordered with increasing temperature, ion-pairing may be increasingly favored for certain salts which would in turn increase further the dehydration of cations.

In the initial studies of ternary solutions started during the past year, the neutron inelastic and quasi-elastic spectra of several ternary solutions for which one component was sodium chloride have been measured in order to study the changes in the hydration of the cations and in the associated diffusive kinetics of water molecules that occur upon mixing. For this purpose, the inelastic spectra for each ternary solution are compared with the corresponding inelastic spectra both for each of the individual components and for a composite spectrum based upon simple additivity. From the quasi-elastic component, the Lorentzian width, Γ , as a function of the momentum transfer, i.e., K^2 , have been obtained and are plotted. These have been compared to composite curves obtained from the individual component solutions under the assumption that the activation energy of the jumps of the individual water molecules in the ternary solutions have not changed but remain a simple average for those of its individual components. The results of these measurements are shown in Figs. 9 through 14, and the observed trends and their interpretation will be considered below in comparison with

measured changes in the correlation times of ions in ternary solutions by NMR^(27,44) and in self-diffusion coefficients and viscosity of solutions⁽⁴³⁾. The results and trends of the changes observed in the NIS spectra can be summarized as follows:

(a) 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⁽¹¹⁻¹⁶⁾ 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.

(b) In the inelastic spectra of the component solutions (as previously reported) frequencies occur characteristic of primary cation-water coordinations, the intensities and sharpnesses of such frequencies, in general, increase with the increase in strength of such coordinations and with the fraction of the total water present in the primary hydration layers. As a result, in a composite spectra formed by the addition of a spectrum for a weak hydrator like NaCl with one for a stronger hydrator (e.g., MgCl, MgSO₄ or LiCl), the frequencies with the more strongly hydrated cation-water coordinations often appear to predominate. However, as seen in Figs. 9 and 10, when sodium chloride is mixed with magnesium chloride or lithium chloride in aqueous ternary solutions such frequencies appear broadened and reduced in intensity relative to the composite. This could result from an increased anharmonicity, an increased disorder characteristic of the primary water complexes, and a decreased relaxational time for such water molecules. In contrast, when cesium chloride is mixed with sodium chloride in a ternary solution, the frequencies characteristic of the cation-water coordinations for the single cesium solution appear strongly enhanced in the ternary solution relative to the spectrum of the corresponding composite. Indeed, the spectrum for the

CsCl-NaCl solution shows a similarity to that for CsCl at higher temperatures (e.g., 50° or 75°) and differs grossly from that of the composite solution and of CsCl at 1°. As discussed in the introduction, for single cesium-chloride salt solutions, the ion-water frequencies were observed to sharpen and intensify with increasing temperature as the solvent structure was weakened more rapidly than cation-water coordination (see, for example, Table II). Thus, in the presence of sodium chloride it appears that the hydration of the cesium ion has been enhanced relative to a single salt solution of cesium chloride at this temperature. In such cases, where the anion is common, these inelastic results are in accord with the findings of Wood⁽¹¹⁻¹⁶⁾ and the trends in the thermodynamic data of the type shown in Table V. Thus, for two structure-making ions (e.g., Na-Li or Na-Mg) a dehydration occurs, cation-water frequencies broaden, and the heat of mixing would be expected to be endothermic. In contrast, upon mixing two cations of different classes (e.g., Cs⁺ - a structure-breaking cation and Na⁺ - a weak structure-making cation) a net hydration occurs, cation-water frequencies are enhanced, and the reaction would be expected to be exothermic.

The effect of anions is illustrated by a comparison to the above spectra with those for dilute NaCl-Na₂SO₄ and MgSO₄-NaCl ternary solutions. In both of these solutions, frequencies characteristic of cation-water coordinations do not appear as strongly broadened upon mixing as in the ternary chloride solutions, and thus the frequencies of Mg-H₂O coordinations appear sharpened in the MgSO₄-NaCl solution relative to those observed in the MgCl₂-NaCl solutions. Indeed, they show a strong correspondence to those observed for solid MgSO₄·7H₂O in the region of metal-water hydration stretching and bending modes. In like manner, the frequencies of Na-H₂O water coordinations appear significantly sharpened both relative to the composite and to NaCl single salt solutions.

Such a behavior would be in accord with the trend by Samoilov^(17,18), that strong anions are able to strengthen the hydration of cations. Thus, it appears that relative to the hydration effect

observed upon mixing for the $\text{MgCl}_2\text{-NaCl}$ solution the dehydration may have been inhibited by the SO_4^{2-} anions.

(c) The above trends in the inelastic spectra are supported by the observations of the diffusively broadened quasi-elastic maxima. The curves of Γ vs. K^2 for the ternary solutions at 1°C are compared with those of the individual components and with those obtained for a mixed solution under the assumption that the activation energy is a simple average of the activation energy of the individual components and that the average activation energy for each component has not changed upon mixing. As previously noted, for such solutions at 1°C , the shape of the quasi-inelastic maxima and the dependences of the area and width upon angle and temperature are in accord with a simple delayed diffusion model. Hence, as described previously, values of self-diffusion coefficients and residence times may be obtained. It is seen that for the combinations LiCl-NaCl and MgCl-NaCl where, as argued above, a net dehydration has occurred and the heat of mixing would be endothermic. An increase in the values of the self-diffusion coefficient is observed upon mixing. In contrast, for the CsCl-NaCl solutions where a net hydration has occurred and the heat of mixing would be expected to be exothermic, a decrease in the self-diffusion coefficients and an increase in the residence times has occurred relative to the curves calculated on the assumption of simple additivity. It should be emphasized that similar results have been reported⁽⁴³⁾ (see Table V) for the ratios of the self-diffusion coefficients to the viscosities. For two structure-breaking or two structure-making salts the values of D/η increase. In contrast, upon mixing a structure-breaking and a structure-making salt (e.g., CsCl-NaCl), they decrease. Thus, the present evidence argues strongly that upon a net dehydration the frequencies characteristic of the ion-water complexes of both components broaden and the average mobility of the water molecules increases. In contrast, upon mixing a structure-breaking and structure-making salt the hydration of the weaker component (e.g., the structure-breaking ion) is enhanced and the net mobility of water molecules is decreased. Further, in the sulfate solutions relative to the chloride solutions, the addition of the sulfate ion, as discussed above, appears to inhibit the dehydration effect -- actually decreasing the

self-diffusion coefficient and increasing the residence time strongly upon mixing. Thus, again this trend strongly supports that noted in thermochemical data that the sulfate ion has a salting-in effect.

It is of interest to compare the results⁽⁴⁴⁾ in (a), (b), and (c) above with those obtained from NMR for the correlation or "residence time" of a sodium ion in a series of ternary solutions containing sodium chloride as one component. At a given concentration it has been reported that the residence times of the sodium ions lie in the following progressions with the second component salts: $\tau(\text{CaCl}_2) > \tau(\text{LiNO}_3) \sim \tau(\text{LiCl}) > \tau(\text{NaCl}) > \tau(\text{KCl}) > \tau(\text{CsCl})$. Thus, these results show that salts such as CaCl_2 , LiNO_3 and LiCl , which when mixed with NaCl would enhance the hydration of Na^+ , serve to increase the correlation or residence time for the sodium ion, while those which would be expected to produce a net hydration effect (KCl and CsCl) decrease the residence time for the sodium ion relative to sodium chloride. While at first this progression would seem to contradict the results in (b) and (c) above, the authors of the NMR paper argue that indeed this is not the case when both solvent structure and the role of the anions is considered. Thus, upon mixing a strong hydrating ion and a weaker hydrating ion, three structures, in principle, can co-exist in the solution -- the hydration structure of ion (A), the weaker hydration structure of ion (B) and a remnant solvent structure.

Thus, for example, upon mixing MgCl_2 and NaCl the solvent becomes disrupted, and while the residence times of water molecules in the primary layer of the strongly hydrating magnesium ion may decrease relative to a pure MgCl_2 solution, they have not decreased as rapidly as the residence times of water molecules distant from the magnesium ion which are now also disrupted by the sodium. As a result, even though the residence times are shorter for the primary waters about magnesium, there is effectively a greater number of waters which may coordinate in its hydration sphere and, in turn, this may force the Cl^- anions from the vicinity of the magnesium ion toward the sodium. As the average Na-Cl distance is decreased in such a manner, the anion-water interactions in the outer spheres of the sodium ion may tend to stabilize and increase the residence times of the H_2O 's coordinated to the sodium. As the majority

of the water molecules are still about the more strongly hydrating ion and as their residence times have decreased relative to a single solution of magnesium chloride, the self-diffusion coefficient representing the average water molecule would increase and the cation-water frequencies for the primary waters about magnesium would tend to become broader and less intense, as observed. However, for the smaller number of water molecules in sodium, the average residence time could have increased due to the stabilization by the anion. Thus, the result is determined by the relative number and strength of the H_2O coordinations between the component cations.

In like manner, when sodium is mixed with cesium as in sodium NaCl-CsCl solutions, the sodium now is the stronger hydrator. Upon mixing, the mean residence time of the primary waters about sodium would be decreased relative to a pure sodium chloride solution but not as rapidly as the large decrease in the average τ for the solvent under the influence of the strong structure-breaking cesium ions. Thus, the tendency would be to increase the time-average number of water molecules about the sodium ion. However, as the anions are forced away from the sodium so that the average Cs-Cl distance decreases, the hydration of the weakly coordinated water molecules to the large cesium ion might be enhanced so that, on the average, the self-diffusion coefficient would be decreased in the solution relative to an additive mixture. In correspondence, the frequencies of the sodium chloride would tend to broaden relative to a NaCl solution, and the frequencies characteristic of the more strongly hydrated cesium would be enhanced. In addition, the hydration of cesium would be favored, as the sodium hydration complex would also, to some extent, have tended to disrupt the distant solvent in a manner analogous to temperature so that the cesium ion no longer had to compete with a solvent structure for waters of hydration and a full hydration could more readily occur.

It should also be pointed out that certain of these trends are consistent with the arguments of Samoilov^(17,46). He notes that in

ternary solutions, the reduction in the residence time for the average water molecule about a strongly hydrating cation increases with its strength of hydration under the influence of a weaker cation. Thus, under the influence of sodium chloride, a stronger decrease in the residence time of the primary water molecules about magnesium would be expected than that for lithium. Further, the decreases in τ for Mg^{+2} and Li^{+} would be greater than the decrease in the residence times for H_2O 's about sodium under the influence of an even weaker ion like the cesium.

While certain of the above trends and their interpretations must still be considered as tentative, additional measurements to be made during the coming year should aid in their confirmation and the extension of this picture. However, these initial results do serve to show that in any theory of mixing of ternary solutions, significant changes in the hydration spheres of the cations present and in the stabilization of such hydrations by anions can strongly determine both the thermodynamics and the diffusive mobilities for the net ternary solutions. They also serve to caution against looking upon sea water and natural saline waters in terms of a simple additive mixture of their individual components. In this regard, a very preliminary but interesting result is that seen when the neutron spectrum for a sample of Copenhagen standard sea water is compared with a spectrum for pure water and with a spectrum for sodium chloride equivalent in concentration to that for sodium chloride in the sea water. While no detailed explanation will be attempted here on the basis of these preliminary data, it is nevertheless apparent that the inelastic spectra of frequencies observed for the sea water are significantly different from both those of the pure water and of the sodium chloride solution. This may indicate that while salts other than the sodium chloride are present in much smaller concentrations in the sea water, they are yet able to produce significant changes in the mixed solution structure.

TABLE I

Technique	Comments and Conclusions	References
Dielectric properties of aqueous ionic solutions	<p>a) Primary water molecules act through both lone electron pairs interacting with the cations as well as through hydrogen bond linkage with other H_2O's and anions.</p> <p>b) The secondary hydration sphere possesses less order than the primary shell and contributes to disordering of the solvent.</p> <p>c) There are two competing effects: the two dissimilar structures of the hydration complexes and the solvent, and the polarization of H_2O's by the ions.</p> <p>d) As strong interactions and mixing occur, any individual relaxation times that would be associated with different hydration shells are probably smeared into a broad distribution with a most probable value.</p>	F.E. Harris and C.T. O'Konski, J. Phys. Chem. <u>61</u> , 310 (1957).
Mobility of H_2O molecules in aqueous solutions of NaCl and KI	Ions strongly alter the bonding of the neighboring H_2O 's, but may also affect the ordering of the more distant solvent due to polarization of H_2O 's.	A. Matyash, A.I. Torryanik, and V.I. Yashkichev, Zhur.Struk. Khimii <u>5</u> , 777 (1964).
Review article	Polarization of the primary waters of hydration can occur as the result of the fields of small and/or highly charged cations. Such polarization may then have the effect of reducing an entropy loss beyond the primary layer and into the region where the structure has been disrupted. Such an effect would be more pronounced for strongly hydrated ions like Be^{+2} , Mg^{+2} , and Li^+ . Evidence is noted that for Li^+ , an orientation of water molecules may occur, even beyond the second hydration layer.	J.L. Kavanov, "Water and Solute-Water Interactions," Holden-Day, Inc. San Francisco, 1964, pp. 57-62.
Quadrupole relaxation measurements of electrolyte solutions	<p>The hydration complexes of the type $\text{Me}(\text{H}_2\text{O})_6$ may produce effects of two opposing types:</p> <p>a) Due to the structural differences of the hydration complex and the solvent, the solvent structure is disrupted for a region about it.</p> <p>b) Polarization of the waters by the cation tends to cooperatively strengthen bonds for a distance from the complex.</p>	M. Valiyev and M.M. Zripov, Zhur.Struk. Khimii <u>8</u> , 494 (1967).

TABLE I (continued)

Technique	Comments and Conclusions	References
Infrared spectroscopy	As the cation-primary water interactions become stronger and more covalent, the polarization of water molecules and the strength of hydrogen bonding increase.	G. Zundel and A. Morr, Zeit.Phys.Chemie <u>54</u> , 4 (1967).
Measurements of heats of solution and of transfer of free energy (E.M.F.)	The structural influence of strongly hydrating, alkaline earth cations has been attributed to their long-range interactions with the bulk solvent.	J. Greyson and H. Snell, J.Phys.Chem. <u>78</u> , 3208 (1969).
NMR studies on aqueous solutions of 1-1 electrolytes	Even for cations of high charge density, the effective field beyond the primary layer is too weak to significantly orient H_2O 's or to disrupt hydrogen bond coordinations. However, the component of the field along the bond direction can serve to augment the strength of the hydrogen bonding. Li^+ may orient waters outside the primary hydration layer.	J.C. Hindman, J.Chem. Phys. <u>36</u> , 1000 (1962).
Dielectric properties of aqueous electrolyte solutions	With increasing charge of the cation, it can increasingly restrict the rotational freedom of H_2O beyond the primary layer, and the number of broken bonds and irrotational H_2O 's increase.	J.B.Hasted and G.W. Roderick, J.Chem.Phys. <u>29</u> , 17 (1958).
Spectrophotometric measurements on solutions	Li^+ , Mg^{+2} and La^{+3} can polarize large numbers of water molecules.	O.D.Bonner and G.B. Woolsey, J.Phys.Chem. <u>72</u> , 899 (1968).
Raman spectroscopy of aqueous solutions of alkali metal nitrates	In dilute solutions (typically 1.5 M) the $\nu_3(E')$ mode of the nitrate ion broadens due to the cation-induced polarity of the solvation sheath about the NO_3^- ion.	D.E.Irish and A.R. Davis, Can.J.Chem. <u>46</u> , 943 (1968).
A qualitative theory on the effects of ions on the ordering of water molecules in aqueous solutions	A decrease in the number of bonds relative to water occurs in solutions due to the geometric difference in the structures of the hydration complexes and the solvent. In contrast, this is counteracted by an ordering effect which is due to the polarization of water molecules that is transmitted large distances from the ion.	V.I. Tikhomirov, Zhur.Struk.Khimii <u>4</u> , 521(1963).

TABLE II

Technique	Comments and Conclusions	References
Heat capacity data have been used to study the hydration of Na^+ , Cs^+ , and I^- ions.	At lower temperatures, the ions show negative hydration; at higher temperatures, they show positive hydration. At lower temperatures, these ions disrupt the water structure in their vicinity. With increasing temperature, the water structure is disrupted more rapidly than are ion-water coordinations, and the "breaking" influence of these ions decreases.	G.A. Krestov and V.K. Abrosimov, Zhur. Struk. Khimii <u>8</u> , 822 (1967).
Apparent molar heat capacities of alkali halide solutions.	It is argued that the primary hydration layers are largely unaffected at temperatures typically below 120°C for K^+ and 100°C for Cs^+ . This, in part, may explain the decrease in negative hydration behavior of such ions with increasing temperature.	H. Rüterjans, F. Schreiner, U. Sage, and Th. Ackermann, J. Phys. Chem. <u>73</u> , 986 (1969).
Viscosity measurements	With increasing temperature, the structure-breaking effect of large, singly-charged ions decreases, and the hydration of the ions may increase.	M. Kamansky, Disc. Faraday Soc. <u>24</u> , 171 (1957).
Dielectric relaxation	The short-range order around an ion may increase with temperature as the competing order of the solvent decreases.	J.B. Hasted, D.M. Ritson, and C.H. Collie, J. Chem. Phys. <u>16</u> , 1 (1948).
NMR: T_1 measurements	At 25°C, K^+ and Cs^+ increase the rotational freedom of water molecules, while Na^+ and Li^+ decrease it relative to water. In contrast, at 90°C all of these ions decrease the rotational freedom. At room temperature, the boundary for positive and negative hydration lies between Na^+ and K^+ .	V.I. Ionov and R.K. Mazitov, Zhur. Struk. Khimii <u>2</u> , 895 (1968).
Changes in coordination numbers of ions with temperature, as estimated from thermodynamic data.	The breaking effect of ions on the solvent structure decreases with increasing temperature.	M.N. Buslaeva and O. Ya. Samoilov, Zhur. Struk. Khimii <u>4</u> , 682 (1963).
Ionic mobilities.	The boundary line between positive and negative hydration lies between Na^+ and K^+ for singly-charged ions. Any increase in temperature displaces the boundary line toward ions with larger radii. With increasing temperature, the breakdown of the mutual ordering of H_2O 's is greater than that of the ordering of H_2O 's to ions.	A.F. Borina and O. Ya. Samoilov, Zhur. Struk. Khimii <u>8</u> , 817 (1967).

TABLE II (continued)

Technique	Comments and Conclusions	References
Activation energies associated with self-diffusion coefficients	The boundary line between positive and negative hydration is found to occur between Na^+ and K^+ for singly charged cations.	A. Matyash, A.I. Toryanik, and V.I. Yashkichev, Zhur. Struk.Khimii <u>5</u> , 777 (1964).
Self-diffusion coefficients of H_2O molecules in aqueous solutions of KI, KCl, and NaCl as a function of concentration.	Relative to water, the self-diffusion coefficients of KI and KCl initially increase with concentration, then go through maxima and decrease. The H_2O 's coordinated to ions have lower mobilities than those in the region about the ions where the solvent structure has been disrupted.	V.V. Goncharov, I.I. Romanova, O. Ya. Samoilov, and V.I. Yashkichev, Zhur. Struk.Khimii <u>8</u> , 613 (1967).

TABLE III

Technique	Comments and Conclusions	References
NMR: O^{17} studies of solutions of rare earth ions	Nitrate, acetate, and sulfate anions are able to form inner sphere complexes with rare earth cations and decrease the number of H_2O 's in cation hydration spheres. The chloride ion is much less effective. The mean residence times of such anions in the vicinity of the central cation is larger than that of an H_2O .	J. Reuben and D. Fiat, J.Chem.Phys. <u>51</u> , 4909 (1969).
Raman spectroscopy on In^{+3} solutions	At room temperature, there is a tendency for NO_3^- and SO_4^{2-} ions to displace H_2O molecules from the hydration clusters of the cations. However, at lower temperatures, inner sphere anions are increasingly displaced by H_2O 's.	R.E. Hester and W.E.L. Grossman, Spectrochim. Acta <u>23A</u> , 1945 (1967).
NMR study of ^{115}In solutions	The nitrate ion may approach the cation briefly and probably disrupt the In-O covalent bonding, causing a fluctuating field gradient.	T.H.Cannon and R.E. Richards, Trans.Faraday Soc. <u>62</u> , 1378 (1966).
Calculations of interactions between neighboring ions in solution, based on activity coefficients.	It is argued that positively hydrating cations (e.g., Na^+ , Li^+) repel anions more strongly at low temperatures. The more weakly hydrating the cation, the higher the probability of ion-pairing at low temperatures.	Yu.M.Kessler, Yu.M. Povarov, and A.I. Gorbanev, Zhur.Struk. Khimii <u>3</u> , 93 (1962).
NMR	Ion-pairing occurs for RbCl and CsCl resulting in a decrease in ion hydration.	R.W.Creekmore and C.N.Reilly, J.Phys. Chem. <u>73</u> , 1563 (1969).
X-ray studies of alkali metal halide solutions	<p>a) Ion-pairing exists in cesium halide solutions and increases both with concentration and with increasing size of the halide ion. The formation of direct pairing leads to regions in the solution which are dominated primarily by solvent molecules.</p> <p>b) For lithium halides, maxima appear at positions in the radial distribution corresponding to secondary waters of hydration.</p> <p>c) As cation size increases, the more easily halide ions can compete for waters of hydration.</p>	R.M. Lawrence and R.F. Kruh, J.Chem.Phys. <u>47</u> , 4758 (1969).

TABLE III (continued)

Technique	Comments and Conclusions	References
Small angle x-ray diffraction	Even in solutions containing 40 H ₂ O's per cation, Mg ⁺² , Ca ⁺² , Ni ⁺² and Co ⁺² ions are octahedrally surrounded by 6H ₂ O's and the chloride ions are drawn in and located at opposite faces of the octahedron.	A.K. Dorosh and A.F. Skryshevskii, Zhur.Struk.Khimii <u>8</u> , 348 (1967).
Diffusion coefficients for lithium ions and water molecules, and the relative effect of Cl ⁻ and NO ₃ ⁻ anions.	The self-diffusion coefficients for Li ⁺ and H ₂ O's 2M solutions are nearly unaffected when Cl ⁻ anions are replaced by NO ₃ ⁻ anions.	G.A. Andrew, Zhur.Struk.Khimii <u>3</u> , 358 (1962).

TABLE IV

Technique	Comments and Conclusions	Reference
NMR: O^{17} in water	H_2O 's in primary hydration sphere do not exchange rapidly with bulk.	R.E. Connick and R.E. Paulson, J.Chem.Phys. <u>30</u> , 759 (1959).
NMR: O^{17} in solutions of Vd^{+2} and Cr^{+3}	A correlation time of $\tau_c = 2.5 \times 10^{-10}$ sec associated with a diffusional motion of Cr^{+3} with its second coordination sphere intact.	M.V. Alson, Y.Kanazawa and H. Taube, J.Chem.Phys. <u>51</u> , 289 (1969).
Study of exchange kinetics of water between $Cr(H_2O)_6^{+3}$ and the solvent	The effectiveness of anions in promoting the exchange of H_2O 's from the $Cr(H_2O)_6^{+3}$ complex decreases in the progression $NO_3^- > ClO_4^- > Cl^- > Br^-$. Anions can share primary H_2O 's of a cation and reduce the energy necessary to remove H_2O from the cation.	R.A. Plane and H. Taube, J.Phys.Chem. <u>59</u> , 33 (1952).
Quadrupole relaxation rates of alkali metal chlorides in aqueous solution	Dipolar correlation time of $\tau_c = 7 \times 10^{-12}$ sec tentatively associated to rotation of $Li(H_2O)_4^+$ as a unit.	D.E. O'Reilly and E.M. Peterson, J.Chem.Phys. <u>51</u> , 4906 (1969).
Review of NMR studies of hydration of ions in aqueous solution	Cr^{+3} forms covalent $Cr^{+3} - OH_2$ bonds which are 15-20% shorter than those formed by other ions.	V.A. Shcherbakov, Zhur.Struk.Khimii <u>2</u> , 484 (1961).
NMR of O^{17} spectra	Exchange times can exceed 10^{-4} sec for Al^{+3} , Ga^{+3} and Be^{+2} primary waters	J.A. Jackson, J.F. Lemons, and H. Taube, J.Chem.Phys. <u>32</u> , 553 (1960).
NMR of O^{17} spectra	$Cr(H_2O)_6^{+3}$ exists as a species in aqueous solution. The half-time for exchange of water of hydration is about 40 hours.	J.P. Hunt and H. Taube, J.Chem.Phys. <u>19</u> , 602 (1951)
NMR of O^{17}	The paramagnetic $Cr(H_2O)_6^{+3}$ ion holds back water so that exchange times exceed 10^{-4} sec.	M. Alai, Jr. and J.A. Jackson, J.Chem.Phys. <u>41</u> , 3402 (1966)
Ionic mobilities in dilute aqueous solutions and their relationship to measured self-diffusion coefficients.	It is argued that for strong positive hydrating cations that the ion may move in solution partially, together with its primary hydration shell.	V.V. Goncharov, I.I. Romanova, O.Ya. Samoilov, and V.V. Yashkichev, Zhur.Struk.Khimii <u>8</u> , 613 (1967).

TABLE IV (continued)

Technique	Comments and Conclusions	References
NMR study of O^{17} in aqueous solutions of rare earth ions	Lower limits have been calculated for rates of exchange of primary hydration for Tb^{+3} , Dy^{+3} , Ho^{+3} and Tm^{+3} . They range between $0.3-2.6 \times 10^{-7}$ sec. The exchange rate increases with cation radius. This is taken to suggest that any degree of covalent bonding between rare earth cations and primary waters is of minor importance.	J. Reuben and D. Fiat, J.Chem.Phys. <u>51</u> , 4918 (1969).
Measurement chronopotentiometric diffusion coefficients for Ag^{+1} , Tl^{+1} , and Cd^{+2} ions in molten calcium nitrate tetrahydrate	Evidence is presented for the diffusion of the mobile entity $Cd(H_2O)_4^{+2}$. The possibility that multivalent ions diffuse together with those of hydration while singly charged ions diffuse unhydrated in molten salt hydrates, is discussed. Motions of hydrated ions may represent a cooperative rearrangement mechanism of the melt structure.	C.T. Moynihan and C.A. Angell submitted for publication in J.Phys.Chem.
Measurements of the glass transition temperatures for aqueous electrolyte solutions and their dependence on cation, anion, and concentration.	Evidence is presented to indicate that the formation of glasses may, in part, involve a restriction of motions of hydrated multivalent cations upon cooling. Anions of increasing basicity may increasingly restrict the motions of the hydrated cations by binding to protons of water molecules already associated with the cation.	C.A. Angell and E.J. Sare, J.Chem.Phys. <u>52</u> , 1058 (1970).

TABLE V

Technique	Comments and Conclusion	References
Heats of solution at 25°C for chlorides of Li, Na, K, Mg, Ca, Sr and Ba in aqueous solutions of MgCl_2 and of nitrates of Na, K, Cs, Mg, Ca, Sr and Ba in aqueous solutions of $\text{Ca}(\text{NO}_3)_2$ at different concentrations of the solvent solutions	It is argued that a) The dehydration of the cation salted-out is strengthened and rehydration weakened with decreasing radius and increasing charge of the cation salted-out. b) The dehydration of the cation salted-out increases with the hydration of the salting-out cation.	T.A. Nosova and O.Ya. Samoilov Zhur.Struk.Khimii <u>5</u> , 363 (1964).
Changes in hydration of cations of salted-out and salting-out agents obtained from thermodynamic data and NMR measurements	For a weakly hydrating, salted-out cation, the stronger the salting-out cation the more its hydration is strengthened. For a strongly hydrating, salted-out cation, the reverse is true. This results because the hydration of the "salting-out" cation is increased and anions are forced close to the "salted-out" cation and thus increase its hydration. Cs^+ is salted-in increasingly by $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. Li^+ is salted-out increasingly by $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The resident time for Na, τ_{Na} , is increased by $\text{CaCl}_2 > \text{LiNO}_3 > \text{LiCl} > \text{NaCl} > \text{KCl} > \text{CsCl}$.	O.Ya. Samoilov, M.N. Buslaeva, K.T. Dudnikova and N.V. Bryushkova, Z.Struk.Khimii <u>10</u> , 580 (1969). V.I. Ionov, R.K. Mazitov and O.Ya. Samoilov, Z. Struk. Khimii <u>10</u> , 407 (1969).
Temperature dependence of heats of mixing of aqueous solutions of LiCl-KCl , LiCl-NaCl , NaCl-KCl , HCl-NaCl , $\text{LiCl}-(\text{CH}_3)_4\text{NCl}$ at 40, 60 and 80°C	a) Heats of mixing are positive for the mixture of two "structure-makers" or two "structure-breakers" (e.g., LiCl-NaCl , HCl-NaCl , $\text{KCl}-(\text{CH}_3)_4\text{NCl}$) b) Heats of mixing are negative for mixtures of a "structure-maker" and a "structure-breaker" (e.g., $\text{NaCl} + \text{KCl}$, $\text{LiCl} + \text{KCl}$, $\text{LiCl} + (\text{CH}_3)_4\text{NCl}$) c) It is argued that the changes that occur upon mixing are associated with changes in the region between the primary hydration region and the region of the disordered solvent.	H.L. Anderson and L.A. Petree, J. Phys. Chem. <u>74</u> , 1455 (1970).

TABLE V (continued)

Technique	Comments and Conclusion	References
<p>Changes upon mixing of the solution enthalpy as a function of the salting-out agent were studied for the following salting-out agents:</p> <p style="margin-left: 40px;"> $\left(\begin{array}{l} \text{LiI} \\ \text{LiBr} \\ \text{LiCl} \end{array} \right)$ salted-out ion LiCl </p> <p style="margin-left: 40px;"> $\left(\begin{array}{l} \text{NaCl} \\ \text{NaBr} \\ \text{NaI} \end{array} \right)$ NaCl </p> <p style="margin-left: 40px;"> $\left(\begin{array}{l} \text{KF} \\ \text{KCl} \\ \text{KBr} \\ \text{KI} \end{array} \right)$ KCl </p>	<p>In accord with the predictions of Samoilov's theory of "salting-out", with increasing hydration strength of the anion of the salting-out agent the dehydration of weakly hydrated cations is increased and that for strongly hydrated cations is decreased. With common cations, for weakly hydrating, salted-out cations, salting-out increases with increasing hydration strength of the anion of the salting-out agent. For the case of strongly hydrating salted-out cations, the reverse is true.</p>	<p>M.N. Buslaeva, K.T. Dudnikov and O. Ya. Samoilov, Zhur. Struk. Khimii <u>10</u>, 8 (1969)</p>
<p>The effects of heats of solution on the isotope effects in the solvent</p>	<p>The enhanced solvent structure in D₂O relative to H₂O enhances the dehydration upon mixing.</p>	<p>O. Ya. Samoilov and V. G. Tsvetkev, Zhur. Struk. Khimii <u>9</u>, 197 (1968)</p>
<p>The kinematic fluidity D/η is compared as a function of the relative volume concentration of two component salts to that expected on the basis of simple additivity</p>	<p>For two strongly hydrating cations, $D/\eta >$ additive values (e.g., LiCl + NaCl, LiCl + CaCl₂, NaCl + CaCl₂, CaCl₂ + BaCl₂) due to the net dehydration of the ions upon mixing. For mixtures of structure-making and -breaking salts, $D/\eta <$ additive value (e.g., LiCl + KCl, NaCl + KCl, KCl + NH₄Cl). This is associated with a redistribution of water from the weak to the strong cation.</p>	<p>A.B. Zdanovskii and F.I. Ivanovo, Zhur. Struk. Khimii <u>8</u>, 162 (1967). Zhur. Struk. Khimii <u>7</u>, 794 (1966).</p>

FIGURE 1

The NIS spectrum of 4.6 m CsF is compared with the spectra of 4.6 m KF and $\text{KF} \cdot 2\text{H}_2\text{O}$. The spectrum of 2.2 m MgSO_4 is also compared with the spectra of 4.6 m MgCl_2 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The spectra for the solutions were measured at 1°C , while for the solid hydrates at -25°C .

FIGURE 2

The observed values of Γ vs. K^2 at 1°C for several solutions are shown. The uncertainty in the magnitude of an individual value of Γ is typically ± 0.02 meV.

The solid lines represent theoretical curves based on the Singwi-Sjölander jump diffusion model. The dash lines for 4.23 m CrCl_3 , 15.02 m LiCl , and 10 m LiCl are best fit through the data points. The diffusive kinetics of these solutions are discussed in the text.

FIGURE 3

The spectra of neutrons scattered at an angle of 45° and 1°C are compared for 4.6 m NaCl and 1.0 m Na_2SO_4 solutions. In addition, a composite spectrum of a 4.6 m NaCl solution and a 1.0 m Na_2SO_4 solution (assuming simple additivity) is compared to a mixed solution of 4.6 m NaCl + 1.0 m Na_2SO_4 .

FIGURE 4

The Γ vs. K^2 curves for various chloride solutions are shown at several concentrations to illustrate the functional dependence of different diffusion mechanisms. The dashed line extensions were drawn to show the linear shape of the curves.

FIGURE 5

The energy distribution of the incident beam, determined by measuring the distribution of neutrons elastically scattered from vanadium, is shown in the lower left graph. This distribution broadened by Lorentzian functions with various half-widths, Γ , as discussed in the experimental section and the main text, are also shown on the same graph.

The quasi-elastic distributions for the supercooled liquid above T_g and for the glass of the 4.23 m CrCl_3 and 4.3 m $\text{La}(\text{NO}_3)_3$ solutions are shown in the upper graph. When compared to the Lorentzian broadened incident distributions, these quasi-elastic distributions have half-width Γ 's below 0.005 meV, which is close to the resolution limit.

In the lower middle graph, Γ 's are plotted as a function of K^2 for several solutions and H_2O at 1°C . The Γ 's for 15.02 m LiCl and 4.23 m CrCl_3 appear to be linear with K^2 , as expected for classical diffusion. The lower right graph contains the plots of Γ vs. K^2 for 4.6 m and 10 m solutions of LiCl and LiNO_3 . The lines were drawn by averaging through the data. For 3.5 m $\text{La}(\text{NO}_3)_3$ and LaCl_3 solutions, the lines are optimum fits to the delayed-diffusion model. The diffusive parameters obtained by the fitting are:

	$D \times 10^5 \text{ cm}^2/\text{sec}$ (From the slope of Γ vs. K^2 near the origin)	$\tau \times 10^{12} \text{ sec}$
3.5 m $\text{La}(\text{NO}_3)_3$	0.5	6.3
3.5 m LaCl_3	0.5	7.9
4.6 m LiNO_3	1.1	2.8
4.6 m LiCl	0.9	3.2

FIGURE 6

The time-of-flight spectra for a CrCl_3 solution at temperatures above and below the glass transition are compared with its solid hydrate. The vertical lines indicate similar frequencies among the spectra. The correspondence between these frequencies and the reported IR frequencies and the frequency distribution are shown in Figure 8.

FIGURE 7

The time-of-flight spectra for a $\text{La}(\text{NO}_3)_3$ solution at temperatures above and below the glass transition are compared with its solid hydrate. The vertical lines indicate the similarity in the frequencies. The corresponding frequency distributions for the glasses and supercooled solutions are shown in Figure 8.

INTENSITY IN ARBITRARY UNITS

FIGURE 8

The one-phonon frequency distributions calculated from the time-of-flight spectra of CrCl_3 and $\text{La}(\text{NO}_3)_3$ solutions above and below their glass transitions are compared. The spectra shown for CrCl_3 were measured at 173°K (glass) and 188°K (liquid), and the spectra for $\text{La}(\text{NO}_3)_3$ were measured at 183°K (glass) and 227°K (liquid). In order to reduce the size of the graph, the intensity of the right half of each spectrum has been reduced by the factor indicated on the graph. Frequencies enclosed by brackets are reported IR frequencies of the corresponding hydrates. The frequency with the asterisk was calculated from the reported value of the $\text{La}-(\text{OD}_2)$ "rocking" vibration.

A noticeable change in intensity is observed for $\text{La}(\text{NO}_3)_3$ in passing from the glass to the liquid in the region around 160 cm^{-1} where anion-water frequencies occur. This change may be due to the broadening of the liquid spectrum as compared to that of the glass. This change is less noticeable for the CrCl_3 however. In general, the spectra of the glasses exhibit better resolution. Note, for example, the splitting of the frequency which occurs at 554 cm^{-1} in liquid $\text{La}(\text{NO}_3)_3$ into two components (440 cm^{-1} and 600 cm^{-1}) in the spectra of the glass. This and other small shifts cannot be excluded because of experimental resolution and the uncertainty in assigning frequencies.

FIGURE 9

The spectra of neutrons scattered at an angle of 45° are compared for a 1.0 m MgCl_2 solution, a 5.7 m MgCl_2 solution, a composite mixture of a 1.0 m MgCl_2 solution and a 4.6 m NaCl solution (assuming simple additivity), a mixture of 1.0 m MgCl_2 and 4.6 m NaCl solutions, and a 4.6 m NaCl solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid and dashed lines. A solid line indicates the persistence of such frequencies between two consecutive spectra; a dashed line indicates frequencies that appear in a given spectrum, but are lost or absent in a second spectrum.

FIGURE 10

The spectra of neutrons scattered at an angle of 45° are compared for a 3.0 m LiCl solution, for a 4.6 m LiCl solution, for a composite spectra of a 4.6 m LiCl solution with a 4.6 m NaCl solution (assuming simple additivity), for the mixture of a 4.6 m LiCl solution with a 4.6 m NaCl solution, and for a 4.6 m NaCl solution. The sample temperatures were 1°C .

FIGURE 11

The time-of-flight spectra, measured at 1°C , are compared for a 4.6 m NaCl solution, a 4.6 m CsCl solution, a composite spectrum of a 4.6 m NaCl solution and a 4.6 m CsCl solution, and a mixture of 4.6 m NaCl and 4.6 m CsCl solutions. They are also compared with a composite spectrum of 4.6 m NaCl and 4.6 m CsCl solutions measured at 75°C .

FIGURE 12

The spectra of neutrons scattered at an angle of 45° are compared for a 4.6 m NaCl solution, a 2.2 m MgSO_4 solution, a composite spectrum of a 4.6 m NaCl solution and a 2.2 m MgSO_4 solution (assuming simple additivity), and a mixture of 4.6 m NaCl and 2.2 m MgSO_4 solutions. The sample temperatures were 1°C . The solid lines indicate the persistence of vibrational frequencies between two consecutive spectra.

CRE-SCHEMATIC

DEMINERALIZATION

(T) Na^+ ENTERS, Cl^- AND OH^- LEAVES

REGENERATION

(T) Na^+ AND H^+ LEAVES, Cl^- ENTERS

Figure 14. Representation of a Cation-Responsive Electrode

Because the model considers the electrode as a cation-ion-exchange membrane, the maximum demineralization current density will be either limited by external solution transport or the production of base at the electrode-solution interface due to high potentials. Recent results have shown that the current density is limited by solution transport in our cell. The model also predicts that demineralization will tend to be more efficient than regeneration, since the cation-membrane can transport H^+ into the solution. This has been found experimentally.

CONTINUOUS-SERVICE TESTS

The continuous-service tests were initiated towards the end of this program so that the extent of experimentation was limited. The tests were undertaken to evaluate the best anion-responsive electrodes found to date. Demineralization was carried out for 15-minute periods at 10 milliamperes, while regeneration was undertaken for half-hour periods at 6 milliamperes.

Two anion-responsive electrodes were evaluated, namely, GN-1 and GN-2. Electrode GN-1 showed a decrease in electrochemical performance as a result of the test. There was no difference in the electrochemical behavior of electrode GN-2 before and after the test. Thus, for electrode GN-2 there was no change in potential during demineralization or regeneration during the time of the test (Fig. 8 and 9). Under conditions simulating the continuous-service tests, there was no difference in the behavior of electrode GN-2 and the two control electrodes (Table 27). In the conventional electrochemical evaluations before and after the test, there was no difference in the characteristics of electrode GN-2; the results obtained with this electrode were similar to those obtained with the control electrodes (Tables 25 and 26). It cannot be ascertained whether the deterioration in the properties of electrode GN-1 were caused by the problems encountered on the fifteenth day of the test (flow stoppage). Particulate matter was observed in cell 1 which contained this electrode.

The potentials observed during the continuous-service tests were low in comparison to previous experience with Kraton electrodes (Fig. 8 and 9).

Under conditions of 100-percent efficiency, the electrodes would have been spent 960 times and regenerated 960 times during the period of the continuous tests. Though it is likely that efficiencies were more of the order of 50 percent, it is significant that the ion-exchange resin (IRA-68) was not degraded as a result of the tests. While it is true that this does not represent significant long-term testing, it is noteworthy that, under the conditions of these experiments (demineralization at 10 milliamperes, regeneration at 6 milliamperes, solutions not deaerated) the ion-exchange resin maintained its integrity (Table 24).

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INVENTIONS AND PATENTS

No inventions have been made as a result of work performed on this contract during the period 20 November 1968 through 20 January 1970.