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Study of Aqueous Electrolyte Solutions by Raman and n.m.r. Spectroscopy

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The $\nu_s(SO_4^{2-})$ and $\nu_s(NO_3^-)$ vibrations, as observed in the Raman spectrum, were studied for several alcali- and earth-alcali sulfates and nitrates in water solution. For the sulfate solutions also the high frequency Raman band of water was observed. The p.m.r. solvent shift for these solutions and for solutions of $CdCl_2$, $MgCl_2$, $ZnCl_2$, $CdBr_2$ were also investigated. A discussion is presented of possible correlations between the Raman spectral parameters, the ionic contributions to the p.m.r. shifts and the structure of electrolyte solutions.

Introduction

Several investigators[1,2,3] have forwarded evidence that the symmetrical valence vibration ν_s of oxyanions XO_n^{m-} depends on the nature of the coordination around the cations and on the ionic environment as a whole. In this report new Raman data on nitrate and sulfate solutions in water are discussed and an attempt is made to correlate them to some parallel proton magnetic resonance data.

In a previous report[4] the changes in the relative scattering yield (S/S_o) for the high frequency Raman band of water in electrolyte solutions as a function of the Raman frequency were treated in terms of a solution structure where cations and anions are separated by at least one water molecule. In the present investigation the study of the high frequency Raman band of water for sulfate solutions is shown to confirm the earlier conclusions derived for halide solutions.

Experimental Section

2.1. *Raman spectral data.* The Raman spectrometer used in this work and the techniques for preparing the solutions and recording the spectra are the same as those published earlier.[5] For every recording the experimental conditions such as scan velocity, slit width and time constant were in agreement with those mentionned by Brandmüller and Moser.[6]

Intensity measurements on the $\nu_s(SO_4^{2-})$ (980 cm^{-1}) band were taken with 16 cm^{-1} slit width, those for $\nu_s(NO_3^-)$ (1049 cm^{-1}) with 10.7 cm^{-1}. For the frequency and band width measurements of the nitrate solutions slits of resp. 8.6 cm^{-1} and 5.4 cm^{-1} were used. The scattering yields were calculated using the formula

$$\frac{S}{S_o} = \frac{S(XO_n^{m-})}{S(N)} =$$

$$\frac{Ia(XO_n^{m-})}{Ia(N)} \cdot \frac{Ro(XO_n^{m-})}{Ro(N)} \cdot \frac{x(N)}{x(XO_n^{m-})}$$

(XO_n^{m-}) and (N) are the molecular concentrations of the anion, resp. the reference solution. All the other symbols have their usual meaning.[4,5,6] Ammonium sulfate, resp. nitrate were selected as reference electrolytes because it is generally agreed that the NH_4^+ ions fit without distortion in the tetrahedral water structure.[1] Concentrations for the reference solutions are 1.992 *M* $(NH_4)_2SO_4$ and 10.26 *M* NH_4NO_3. For these solutions the intensity is arbitrarily taken equal to unity. Because very narrow slits could be practiced and the band width of the peaks observed changes very little, the peak height is used as a measure of Ia instead of the band area. The results of the intensity measurements are listed in Table I for the highest concentrations investigated. In Table II are given the measured band widths at half height for the nitrate solutions.

Table I. Scattering yield data for the $\nu_s(SO_4^{2-})$ (980 cm^{-1}) and $\nu_s(NO_3^-)$ (1049 cm^{-1}) Raman lines in electrolyte solutions

Electrolyte	max. mol. conc.	S/S_o
$(NH_4)_2SO_4$	2.999	1.00
Li_2SO_4	1.989	0.82
Na_2SO_4	2.032	0.92
$BeSO_4$	1.898	0.57
$MgSO_4$	2.005	0.84
$CdSO_4$	2.626	0.83
$ZnSO_4$	2.631	0.85
NH_4NO_3	10.26	1
$LiNO_3$	7.988	0.75
$NaNO_3$	6.700	0.89
KNO_3	2.838	0.94
$Mg(NO_3)_2 \cdot 6H_2O$	3.592	0.84
$Cd(NO_3)_2 \cdot 4H_2O$	3.584	0.77

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[1] P. M. Vollmar, *J. Chem. Phys.*, 39, 2236 (1963).

[2] I. Steger and S. Pauly, *Naturwissenschaften*, 6, 154 (1966).

[3] H. Brindzinger and R. E. Hester, *Inorg. Chem.*, 5, 980 (1966).

[4] H. A. Lauwers, G. P. Van der Kelen, *Inorg. Chim. Acta*, 2 281 (1968).

[5] H. A. Lauwers, G. P. Van der Kelen, *Bull. Soc. Chim. Belges*, 72, 477 (1963).

[6] J. Brandmüller and H. Moser, Einführung in die Ramanspektroskopie pag. 203, Dr. Dietrich Steinkopff Verlag, Darmstadt 1962.

Table II. Frequency and band width data for nitrate solutions

Electrolyte	Max. mol. conc.	$S_1 = S_2 = 8.6$ cm^{-1} $\nu_s(NO_3^-)$	$\Delta\nu_{1/2}$	$S_1 = S_2 = 5.4$ cm^{-1} $\nu_s(NO_3^-)$	$\Delta\nu_{1/2}$
NH_4NO_3	10.26	1046.0 cm^{-1}	11.4 cm^{-1}	1047.4 cm^{-1}	11.8 cm^{-1}
$LiNO_3$	7.988	1046.6 cm^{-1}	16.7 cm^{-1}	1047.2 cm^{-1}	15.5 cm^{-1}
$NaNO_3$	6.700	1050.5 cm^{-1}	14.8 cm^{-1}	1052.9 cm^{-1}	12.9 cm^{-1}
KNO_3	2.838	1046.6 cm^{-1}	10.6 cm^{-1}	1047.6 cm^{-1}	8.8 cm^{-1}
$Mg(NO_3)_2 . 6H_2O$	3.592	1049.4 cm^{-1}	14.9 cm^{-1}	1050.6 cm^{-1}	14.7 cm^{-1}
$Cd(NO_3)_2 . 4H_2O$	3.584	1046.9 cm^{-1}	17.2 cm^{-1}	1046.5 cm^{-1}	15.2 cm^{-1}

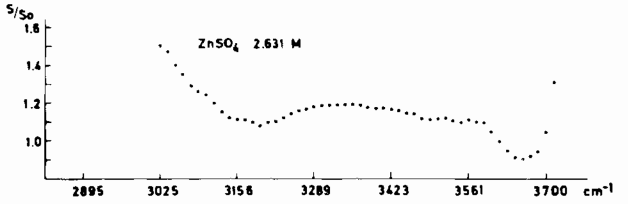

Figure 1.

The method to evaluate the relative scattering yield (S/S_o) of the high frequency Raman band of water, as a function of the Raman frequency has been described earlier.[4,5] In Figure 1 a plot of S/S_o versus ν similar to those published for the aqueous halide solutions[4] is shown for a $ZnSO_4$ solution. Several differences between both types of curves are worth mentioning. First, instead of a sharp maximum at about 3400 cm^{-1} sulfate solutions produce a rather flat curve over the region 3200 to 3500 cm^{-1} and the S/S_o value is only slightly higher than unity. Second, at about 3650 cm^{-1} there is observed a dip in the curve, where S/S_o values are less than unity (*e.g.* 0.9). A similar dip was also noted[6] only for $MgCl_2$ solutions but there the S/S_o minimum value for that frequency region was still equal to 1; for the other halide solutions the S/S_o versus ν curve decreases monotonously in this frequency region. The parameters of this dip $(S/S_o)_d$ and ν_d are listed in Table III for the highest concentrated sulfate solutions only.

Table III. Data on the high frequency Raman band of water in sulfate solutions

Electrolyte	Max. mole conc.	$(S/S_o)_{min}$	$(S/S_o)_d$	(ν_d) cm^{-1}
$ZnSO_4$	2.631	1.10	0.90	3658
$MgSO_4$	2.005	1.09	0.78	3658
$CdSO_4$	2.626	1.12	0.83	3644
Li_2SO_4	1.989	0.90	0.90	3658
$BeSO_4$	1.898	0.95	0.90	3658
Na_2SO_4	2.032	0.78	1.00	3644

2.2. *Proton magnetic resonance data.* The experimental conditions for these measurements and the apparatus used have been described in a previous paper.[7] The frequency difference between the resonance signal of water protons in the solutions investigated and the signal of water protons in the reference solution were however measured by the superposition method. A correction for the diamagnetic volume susceptibility of the solution was applied as suggested by Hindman.[8] The data are given in Table IV. By $\frac{\delta^c}{C}$ is meant the corrected shift devided by the molar concentration of the solution. Extrapolation of $\frac{\delta^c}{C}$ values to infinite dilution yields the $\delta_{C=0}$ values.[8] These values are mentionned in Table V. The division of salt effects $\delta_{C=0}$ on the proton resonance of water into individual ionic effects was accomplished also using Hindman's procedure. First $\delta^\circ_{NO_3^-}$ and $\delta^\circ_{SO_4^{2-}}$ the specific chemical shifts of these anions at infinite dilution were calculated from the experimental chemical shift measured on their ammonium salt solution. With these values the experimental data of the other solutions (Table V) yielded the $\delta^\circ_{M^{n+}}$ values, *i.e.* the specific shifts at infinite dilution caused by the cation. These values are listed in columns 6 and 7 of Table VI. It is of importance to stress that the basic assumption underlying this procedure is the absence of specific ion-ion interactions. This means that any possibility of ion pairing is excluded *a priori.*

Moreover, some $\delta_{C=0}$ values were also obtained for halide solutions of Cd^{2+}, Mg^{2+} and Zn^{2+}. These values are also listed in Table V.

Discussion

3.1. *Raman spectral data on* $\nu_s(XO_n^{m-})$. The frequency shifts observed for $\nu_s(NO_3^-)$ in this investigation are of the same order of magnitude and in the same direction as these observed by Vollmar.[1] The frequencies measured in solution are, however, always considerably lower than these observed for the anhydrous crystals.[9] For the sulfate solutions the frequency shifts are even smaller and the band withs are nearly constant. For the nitrate solutions, however, the band width at half height is seen to be concentration dependent and cation sensitive. Vollmar has interpreted these changes as a function of the hydration radius of the cations. This seems to be fairly well confirmed by the sequency found from the data of this investigation:

$$Cd^{2+} \propto Mg^{2+} > Li^+ > Na^+ > K^+ > NH_4^+$$

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[7] H. A. Lauwers, G. P. Van der Kelen, *Bull. Soc. Chim. Belges,* *75,* 238 (1966).

[8] J. C. Hindman, *J. Chem. Phys.,* 36, 1000 (1962).

[9] I. R. Rao, *Proc. Roy. Soc.* (London), *A* 144, 159 (1934).

Table IV. P.m.r. data concerning several electrolyte solutions

Electrolyte	Mol. conc.	$-\frac{\delta^c}{C} \times 10^8$	Electrolyte	Mol. conc.	$-\frac{\delta^c}{C} \times 10^8$
$(NH_4)_2SO_4$	0.984	18.8	$Mg(NO_3)_2 \cdot 6H_2O$	3.592	−7.7
$(NH_4)_2SO_4$	1.615	18.5	$Mg(NO_3)_2 \cdot 6H_2O$	2.210	−6.7
$(NH_4)_2SO_4$	1.992	19.9	$Cd(NO_3)_2 \cdot 4H_2O$	3.584	−7.8
$(NH_4)_2SO_4$	2.999	19.1	$Cd(NO_3)_2 \cdot 4H_2O$	1.984	−8.3
$ZnSO_4$	1.031	24.4	$MgSO_4$	1.227	17.9
$ZnSO_4$	1.471	23.6	$MgSO_4$	1.875	17.0
$ZnSO_4$	2.150	22.0	$MgSO_4$	2.005	18.9
$ZnSO_4$	2.169	22.9	$BeSO_4$	1.107	4.1
$ZnSO_4$	2.631	21.4	$BeSO_4$	1.553	4.0
$CdSO_4$	1.168	23.2	$BeSO_4$	1.898	4.0
$CdSO_4$	2.110	21.2	$CdCl_2$	1.083	7.4
$CdSO_4$	2.626	20.1	$CdCl_2$	1.661	6.3
Li_2SO_4	0.990	6.3	$CdCl_2$	2.014	5.5
Li_2SO_4	1.355	7.5	$CdCl_2$	2.076	4.9
Li_2SO_4	1.718	6.6	$CdCl_2$	2.609	5.1
Li_2SO_4	1.989	6.3	$MgCl_2$	1.181	11.7
NH_4NO_3	10.26	−7.2	$MgCl_2$	2.362	11.2
NH_4NO_3	5.43	−5.6	$MgCl_2$	3.001	10.4
$NaNO_3$	6.700	6.6	$MgCl_2$	4.618	9.9
$NaNO_3$	5.234	7.2	$ZnCl_2$	0.989	13.0
$NaNO_3$	3.345	8.3	$ZnCl_2$	2.072	8.2
$LiNO_3$	7.988	2.6	$ZnCl_2$	2.989	6.5
$LiNO_3$	3.856	3.2	$ZnCl_2$	3.955	5.9
KNO_3	2.838	8.7	$ZnCl_2$	4.885	5.0
KNO_3	1.568	8.9			

Table V. Extrapolated p.m.r. salt effects

			$\delta_{c=0} \times 10^8$		
Li_2SO_4	− 6.8	NH_4NO_3	3.9	$CdBr_2$	−3.4
$MgSO_4$	−18.0	$NaNO_3$	−10.2	$CdCl_2$	−9.5
$(NH_4)_2SO_4$	−18.8	$LiNO_3$	−3.9	$ZnCl_2$	−10.0
$CdSO_4$	−25.5	KNO_3	−9.1	$MgCl_2$	−12.3
$ZnSO_4$	−26.5	$Mg(NO_3)_2$	5.1		
$BeSO_4$	−40.5	$Cd(NO_3)_2$	8.9		

Table VI. Comparison of various physical data on electrolyte solutions

Ion	Δ_M* (13)	$M^{n+}...OH_2$ (Å)	$S/S_o(NO_3^-)$	$S/S_o(SO_4^{2-})$	$+\delta^o{}_M{}^{n+}(NO_3^-)$	$+\delta^o{}_M{}^{n+}(SO_4^{2-})$	pK_A (12)	$\frac{Ze}{a}$
NH_4^+		—	1.00	0.98	0	0	9.25	
Na^+		2.42 (15)	0.91	0.92	−14.1	—	14.7	0.413
K^+		2.94 (15)	0.93	—	−13.6	—	—	0.340
Li^+		2.15 (15)	0.74	0.85	−7.8	+6.0	14.1	0.465
Cd^{2+}	6.5	2.34 (16)	0.79	0.83	+1.1	−6.7	8.5	0.855
Mg^{2+}	6.0	2.04 (15)	0.85	0.85	−2.8	+0.8	11.41	0.980
Be^{2+}	12.0	1.2 (15)		0.57		−21.7	—	1.665
Zn^{2+}	13.0	2.2 (15)		0.88		−7.7	9.6	0.909

* Measurements on nitrate solutions

The most sensitive parameter seems to be the relative scattering yield S/S_o of the $\nu_s(XO_n{}^{m-})$ frequency band and the data of Tables I and II show a close parallelism for the influence of the cation on this parameter in both series of systems. The sequency thus suggested also duplicates fairly well the sequency derived above from band width measurements. The same interaction mechanism can therefore be supposed to be active in both the sulfate and the nitrate solutions.

Chantry and Plane[10] have shown that the polarizability tensor α(X–O) is higher for the NO_3^- ion than for the SO_4^- ion. The decrease of the relative scattering yield observed for nitrate solutions is also stronger than for sulfate solutions. The polarization of the covalent N–O, resp. S–O bands by the nearest cation obviously is the reason of the decreased scattering yields. Direct interaction, in the sense of ion pair formation, is however, not very plausible. First of all the frequencies are too much different from these for the crystals and secondly the relative frequency changes with increasing concentration are too small. Moreover in the crystal spectra, with direct coordination, the large frequency differences correlate clearly with the polarizing strength of the cation.[3,11] In water solution, however, the

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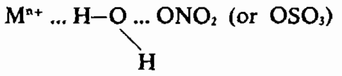
[10] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, *32*, 319 (1960).

$\nu_s(NO_3^-)$ frequency shows very little difference on changing the cation. The low frequencies observed are rather to be taken as evidence for the continuing existence of considerable hydrogen bonding to the oxy anions ,and the small frequency changes as a function of concentration could also be caused wholly or in part by a decrease of the X–O force constant.

The most plausible explanation should then be based on an interaction model where the anion is polarized by the cation from which it is separated by one water molecule



$$M^{n+} \ldots H\text{–}\underset{\diagdown\; H}{O} \ldots ONO_2 \text{ (or } OSO_3)$$

This is also the system agreed on by Chantry and Plane[11] and also by Lee and Wilmshurst.[12]

3.2. *Raman spectral data on the OH Raman band.* According to the observations of Walrafen[17,18] on the behaviour of the liberational frequency bands ν_{h2} of water, the sulfate ion should effect little influence on the surrounding water. The reason for this observation is believed to be that the SO_4^{2-}...H–O bonds should be very similar to the surrounding O...H–O hydrogen bonds. With reference to the structural model pointed out in the previous section in which the cation can be considered to be the center of the complex structure, one could agree that, if the cation does not influence the sulfate ion, *via* the sandwiched water molecule the high frequency Raman band of water should be nearly insensitive to the nature of the cation and to the solution. The changes in the S/S_o curve as shown in the figure are believed to show that both these parameters influence the relative scattering yield. In this respect the most important feature is the observation of a nearly flat region in this curve (3200-3600 cm^{-1}) where S/S_o is about equal to unity for every sulfate solution studied. These observations are therefore believed to confirm our previous conclusion that the oxyanions are influenced by the cations, *via* the first hydration layer of the latter. The decrease of S/S_o for $\nu_s(XO_n^{m-})$ is then corresponding to a decrease of the covalency contribution in H_2O–H_2O interaction.

Let us now consider again the specific cation effects reported previously.[4] It was found that the cations were to be devided into two groups: first: Na^+, K^+ and Ba^{2+} and second Li^+, Be^{2+}, Cd^{2+} and Mg^{2+}. The former of these are reputed to be structure-breakers, *i.e.* they cause the number of hydrogen bonds in their surrounding to decrease. Moreover there is always the electrostatic interaction between a cation and the water dipole decreasing the electron density in the OH bond and also decreasing the degree of covalency contribution to the bond strength of the hydrogen bonds between the first and the second hydration layer. In many cases there is also the sterical hindrance of the ion-aquocomplex that results in a decrease of the number of hydrogen bonds between those two layers. The decreased electron density in the OH bond of the coordinated water molecule can result in a decreased scattering yield of the OH-Ramanband. This mechanism could explain the observations concerning $(S/S_o)_{min}$ values for solutions of Na^+, K^+ and Ba^{2+} halides, reported in our first report;[4] Li^+, Be^{2+}, Cl^{2+} and Mg^{2+} on the other hand are thought to be structure-forming ions.[19] With these ions there results apart from their polarizing influence, an additional cation-water interaction, which may eventually increase the degree of covalency contribution to the bond strength of the hydrogen bonds between the first and the second hydration layer.

The fact that for halide solutions of Li^+, Be^{2+}, Mg^{2+} and Cd^{2+} the $(S/S_o)_{min}$ values stay about equal to unity,[4] in contrast with solutions of Na^+, K^+ and Ba^{2+} should then be ascribed to a compensation of both effects discussed above, resulting in only minor changes of the electron density in the OH-bond. The $(S/S_o)_{min}$ values of the sulfate solutions also agree with this interpretation (Table III).

It can be shown that the minimum in the S/S_o versus ν curve at 3650 cm^{-1} can also be explained on the basis of the interaction model sketched above. It was seen that the intensity of $\nu_s(SO_4^{2-})$ decreases when the immediate neighbouring OH group is strongly polarized. This results in a weaker interaction of this group with the surrounding water molecules. These molecules become less prone to form hydrogen bonds to their neighbours. Walrafen has shown that the intensity of the ν_{h2} band, due to the stretching vibration of a hydrogen bond, decreases with increasing electrolyte concentration. If we rely on the assignment of Senior and Thompson[20] [although this assignment was later on questioned again[21]] the 3615 cm^{-1} band can be considered as a combination band: $\nu_1+\nu_{h2}$, (3450+175 cm^{-1}), whose intensity is enhanced by a Fermi resonance with ν_1. This argument rests mainly on the assumption that the band observed in the Raman spectrum at 3450 cm^{-1} is ascribed to the ν_1 fundamental, whereas in the IR spectrum the band at 3450 cm^{-1} should be due to the ν_3 fundamental. Decreasing the ν_{h2} intensity would naturally thus be followed by a decreased intensity for the combination tone at 3615 cm^{-1}. This reasoning lends support also from our observations on the (S/S_o) versus ν curves for $MgCl_2$ and some other solutions, published in our first report,[4] where also a sharp dip in this curve is observed in the same frequency region. That a similar dip is not observed in most solutions of alkali halides (see Figure 1 ref. 4) is probably due to the very efficient anion effect that causes an explosive increase of the central (3450 cm^{-1}) band. This band then overlaps efficiently far beyond the 3600

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[11] R. E. Hester and R. A. Plane, *J. Chem. Phys.*, *45*, 4588 1966).
[12] H. Lee and I. K. Wilmshurst, *Australian J. Chem.*, *17*, 943 (1964).
[13] V. M. Vodovenko and V. A. Shcherbakov, *J. Struct. Chem.*, *1*, 25 (1960).
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[17] G. E. Walrafen, *J. Chem. Phys.*, *44*, 1546 (1966).
[18] G. E. Walrafen, *J. Chem. Phys.*, *40*, 3249 (1964).
[19] J. L. Kavanau « Water and solute-water interactions ». Holdenday Inc., San Francisco (1964).
[20] W. A. Senior and W. K. Thompson, *Nature*, *205*, 170 (1965).
[21] W. K. Thompson, W. A. Senior, B. A. Pethica, *Nature*, *211*, 1086 (1966).

cm^{-1} region and thus masks any changes in the intensity of the combination tone. Moreover, in the halide solutions the scattering yield of the 3615 cm^{-1} band could have been increased substantially due to Fermi resonance with the 3450 cm^{-1} ν_1 band. This band is indeed much stronger in the halide solutions, and the increased Fermi-resonance contribution at 3615 cm^{-1} might easily mask any decrease in this region due to the other mechanism.

3.3. *P.m.r. data.* To relate the data $\delta^\circ_{M^{n+}}$ of Table VI to the changes that occur in solution by dissolving electrolytes a theory has been forwarded by Hindman.[8] According to this theory the observed specific shift is the sum of four terms

$$\delta^\circ = \delta_{bb} + \delta_{st} + \delta_p + \delta_{non}$$

which are each related to some action of the dissolved ions on the solvent water: (bb) bond breaking (refers to structure breaking by ions), (st) structural (refers to structural increase by ions), (p) polarization, (non) non electrostatic interaction.

Obviously it is impossible to make a clear-cut decision about the contribution of each of these terms to the δ° value, when p.m.r. data alone are considered. It was therefore our purpose to see wether the Raman data and the p.m.r. data could lead to similar conclusions.

Several authors have tried to correlate various physical parameters with the degree of covalency of the $M^{n+}...OH_2$ bond, for instance the M–O distance in crystalilne hydrates, the p_{KA} value of the cations, the molar relaxation shift ΔM[13] and the charge of the cation divided by the radius of the cation.[14] The new data presented in this work: ((S/S_0) values and δ° values for nitrate and sulfate solutions) seem to correlate fairly well with the last mentioned parameter as can be seen from Table VI.

If, however, our p.m.r. data for the $MgCl_2$ solutions are used to calculated a value for $\delta^\circ_{Cl^-}$, using the $\delta^\circ_{Mg^{2+}}$ values gained from measurements on nitrate and sulfate solutions, a value of 6.05 is obtained as compared with Hindman's value of 2.6 for NH_4Cl solution. In NH_4Cl solutions we can agree that an unperturbed value for $\delta^\circ_{Cl^-}$ is measured. If the same kind of calculation is done for the $ZnCl_2$ and $CdCl_2$ data still other values of $\delta^\circ_{Cl^-}$ are obtained. The obvious conclusion then seems that, unlike the assumption underlying the theory about specific p.m.r. shifts for electrolyte solutions, cations and anions do interact with each other in solution, at least to such a degree as to change the magnetic environment of the solvent protons.

The electrolytes $ZnCl_2$, $HgCl_2$, $CdCl_2$ and $CdBr_2$ are also these that yielded rather different Raman results[4] as compared to the alcali halides in aqueous solution. It seems therefore that at this moment a straightforward interpretation of all these results is rather difficult and that more experimental material should be gained.