Proton Magnetic Resonance Study of the Water Lattice

Distortions in Aqueous Alkali Halide Solutions

M. S. BERGQVIST and E. FORSLIND

Division of Physical Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

Dedicated to Professor *Ole Lamm* on his 60th birthday

The concentration dependence of PMR chemical shifts in aqueous solutions of all alkali halides, except the insoluble lithium fluoride, has been investigated at 40 Mc/sec, making use of an external reference substance and adding a macroscopic susceptibility correction.

An attempt has been made to resolve the molal shift into ionic contributions, assuming a law of approximate additivities shown to be successful, except in the cases of the lithium and the fluoride ions, which do not fit the simple linear relationship valid for the remaining alkali halides. The reasons for the deviation are discussed.

A comparison of PMR data with dielectric data of electrolytic solutions is made.

Already in 1954 Shoolery and Alder [1] investigated the influence of a dissolved diamagnetic salt on water using NMR techniques. By measuring the water proton resonance shifts in concentrated aqueous solutions of electrolytes, they were able to establish a relative scale of specific contributions made by ions to the total measured chemical shift, which, however, lacked corrections for magnetic susceptibility. The data of Shoolery and Alder have been included in Table 1 for a comparison with the results of the present investigation.

In the same year Gutowsky and Fujiwara [2] published a study of the PMR shifts in aqueous ammonium salt solutions.

A method for the interpretation of PMR shifts for acids and bases was first suggested by Gutowsky and Saika [3] who applied it to HNO_3, $HClO_4$, H_2SO_4 and NaOH in aqueous solution. Hood *et al.* [4-9] extended the method to the calculation of acid constants for $HClO_4$, HNO_3, H_2SO_4, HIO_3, CF_3COOH and C_3F_7COOH. Their procedure necessitated some assumptions concerning certain states of acid-water complexes which, however, seem to be supported by Raman spectroscopy investigations [10]. Happe *et al.*[11] made a study of the system HNO_3—H_2O.

A thorough study of the chemical shifts in diamagnetic salt solutions was published by Hertz and Spalthoff[12] in 1959. Concentration and temperature effects were investigated. Previously internal standards in water solutions had been avoided due to the influence of most solutes on water proton resonances. Hertz and Spalthoff showed the possibility of using t-butanol or, in a few cases, some tetraalkylammonium salts as internal standards and thus avoided the problem of susceptibility corrections. Hertz and Spalthoff maintained that the shift due to a constant concentration of the reference compound was constant in the whole electrolyte concentration range. This appeared to be a reasonable assumption in view of the fact that none of their results seemed to contradict it. A comparison between their values and the results of the present investigation is made in Table 1.

Recently Hindman[13] developed a model for correlating "effective hydration numbers" of 1—1-electrolytes with measured PMR shifts in water solutions. Hindman made use of c-pentane as an external reference.

In 1959 Axtmann[14] found a linear correlation between the molar proton chemical shifts for hydrated polyvalent cations and pK_a, where K_a is the first protolysis constant for the complex hydrate ion. Later, Axtmann et al.[15] found evidence for a strong coupling between aluminium ions and hydrate water in nitric acid solutions.

Connick and Poulson[16] measured the broadening of ^{17}O resonance signals in water caused by the paramagnetic ions Mn^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+}, Cr^{3+} and Ni^{2+}.

Chemical shifts and relaxation effects in ^{17}O-resonances caused by gadolinium(III)-ions in aqueous solution were studied by Shulman and Wyluda[17].

Gutowsky and McGarvey[18] found large chemical shifts and concentration effects in a study of ^{205}Tl magnetic resonances in thallium(I) and thallium(III) solutions. To explain the shifts they assumed delayed collisions between positive and negative ions, i.e. a kind of ion pair formation which caused electronic excitation leading to a second order paramagnetic term (according to Ramsey[19]) and negative shifts *. Freeman et al.[20—22] observed a strong action of counter-ions upon the chemical shifts of thallium(I) in aqueous solutions.

Another type of presumed electronic process in water solution was studied by McConnell and Weaver[23]. By measuring the widths of the ^{63}Cu resonance line in acid solutions containing cuprous and cupric chloride they computed the bimolecular rate constant for the reaction $Cu^{2+} + Cu^{+} \rightarrow Cu^{+} + Cu^{2+}$.

^{35}Cl resonance was used by Wertz[24,25] and Chesnut[26] to study the exchange between water in bulk and hydrate water of some paramagnetic ions.

Wertz studied ^{24}Na magnetic resonance effects in water solutions of metabolites[27,28] and of inorganic and organic salts[29,30].

Connick and Poulsen[31] studied ^{27}Al and ^{19}F resonances in water solutions of NaF and $Al(NO_3)_3$ and could calculate the stability constants for AlF^{2+} and AlF^{+}. The same authors[32] also studied ion-pair effects in water solutions of NaF and KF. The sodium and potassium ions seemed to behave in entirely

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* In this work a shift of a certain specimen is termed positive when the resonant field of the specimen is larger than that of a reference compound. This is also the case when reference is made to other authors who may have used the reverse definition in their original papers.

different manners when acting as counterions to the fluoride ion. The authors inferred that NaF formed ion pairs even at very low concentrations. For KF the phenomenon seemed to appear only at higher concentrations (> 5 M).

Carrington et al.[33],[34] performed ^{19}F magnetic resonance measurements for their study of ion-solvent and ion-ion interactions. They also measured the magnetic resonance of [133]Cs and could observe effects indicating ion pair formation.

The magnetic resonance of [127]I in aqueous solutions of alkali iodide was studied by Itoh and Yamagata [35].

[79]Br, [81]Br and [127]I magnetic resonances were utilized by Hertz [36],[37] in a study of concentration dependent line broadening effects in aqueous solutions of alkali and earth alkali halides.

Although the investigations quoted above shed some light on the various problems of electrolytic solutions, the situation is still far from clear. The aim of the present investigation is to contribute some additional information about the behaviour of the water proton in moderately concentrated aqueous solutions of alkali halides by means of PMR techniques.

In the experimental study, the water proton shifts have been measured using benzene as an external reference. The complex chemical situation introduced by an internal reference standard can be avoided by making use of the best available susceptibility [38],[39] and density [40] data and applying susceptibility corrections according to the classical formula [41].

EXPERIMENTAL

The proton resonance measurements were made with a Varian Associates V-4300B spectrometer, operating at a fixed frequency of 40 Mc/sec. Field stability was achieved by a Varian V-K3506 Super Stabilizer. Precision coaxial glass tubing [42] was used with benzene reference in the annular space and electrolyte solution in the inner tube. The resonance line shifts were determined by means of conventional side-band techniques, using a Hewlett-Packard 200 CD Audio Oscillator. In order to attain an exact adjustment of the benzene side-band signal to the resonance line the oscillator frequency was varied around the coincidence positions during at least 50 or 100 sweep periods before the final reading was made. Three or four such readings were made for each specimen. An average was then taken over the obtained readings not exceeding the range 0.3 c/sec. Measurements which occasionally exceeded this range, due to accidental instability of the spectrograph or inhomogeneity of the magnet field, were discarded and repeated after the necessary adjustments were made. Room temperature was held at $22 \pm 1°C$. The purest chemicals available were used. Thus LiCl, LiBr, NaF, NaCl, NaBr, NaI, KF.H_2O, KCl, KBr, KI and CsCl were of reagent grade quality, while the salts LiI·$2H_2O$, RbF, RbCl, RbBr, RbI, CsF, CsBr and CsI contained a few per cent impurities, these being other alkali halides. Emission spectroscopy was used to test the presence of iron group metals and showed no trace of paramagnetic ions. The preparation of solutions of different electrolyte concentrations were carried out by simple weighing and dilution procedures for the non-hygroscopic salts. The concentrations of the hygroscopic salts were determined by conventional chemical analysis.

In an investigation of this kind, requiring measurements of so small shifts as $0.1 - 10$ c/sec, a very important point is the removal of irrelevant paramagnetic impurities. From that point of view dissolved paramagnetic oxygen called for a special investigation, because of the susceptibility effects on liquids due to dissolved oxygen found by Eggleston [43]. A comparison was therefore made between water specimens which had been (1) degassed by boiling in vacuum, (2) saturated with air, (3) degassed by bubbling through nitrogen and (4) degassed by Freon 12.

Ten frequency readings were made for each specimen. Statistical analysis of the results indicated that the averages drawn from the samples 2, 3 and 4 were identical with the average of specimen 1 — the level of significance being fixed at 99.5 %. It was accordingly concluded that ordinary distilled water could be used for the preparation of the solutions.

This result was expected, since a simple calculation leads to the conclusion that the susceptibility difference between chemically pure water and water saturated with oxygen would produce a proton resonance shift not exceeding 3×10^{-4} ppm.

The observation made by Solomon [44], that the spin-lattice relaxation time increased with the deoxygenation of water, is not at variance with the present conclusion, since the corresponding effects on the line width are unobservable.

For each salt, measurements of 8 — 16 solutions of different concentrations were made in the range 0 — 3 m (molal).

EXPERIMENTAL RESULTS

When evaluating the observed proton resonance shifts of the solutions, it is necessary to correct for certain macroscopic susceptibility effects when an external reference substance is used *. In the present case pure water was taken to relate the measurements performed on the various solutions.

The chemical shift Δ, corrected for the macroscopic susceptibility effect g, is defined by

$$\Delta = [(H-H_w)/H_w - g] \times 10^8 \tag{1}$$

where $g = (2\pi/3)\ (k-k_w) = (2\pi/3)\ [\varkappa_w\ (d-d_w) - (\varkappa_w - \varkappa_s) \cdot c \cdot M \times 10^{-3}] \tag{2}$

where H = water proton resonant field of the solution
   k = volume susceptibility (c.g.s. units)
   $\varkappa$ = specific   »   (c.g.s. units)
   d = density g/ml
   c = molarity
   M = mole weight of salt.

The index w refers to pure water and s to the crystalline salt.

The molal shift δ for an 1—1 electrolyte, wholly dissociated, is defined as

$$\delta = m^{-1}\Delta \tag{3}$$

where m = molality.

A satisfactory approximation to the linearity assumed in eqn. (3) could actually be observed in the concentration range 0—2 m, permitting δ to be calculated from the Δ/m plot. The results of the measurements are summarized in Fig. 1.

The molal chemical shifts are given in Table 1. To illustrate the necessity for the susceptibility corrections (g) to the molal shifts they are included in Table 1, together with the estimated error of g evaluated from literature data.

This uncertainty, Δg, has been calculated according to the expression

$$\Delta g = (2\pi/3)\ [(\varkappa_w \Delta d)^2 + (c_1 \times 10^{-3}\ \Delta \varkappa_s)^2]^{1/2} \tag{4}$$

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* A detailed investigation into the problem of the macroscopic susceptibility correction will be published elsewhere.
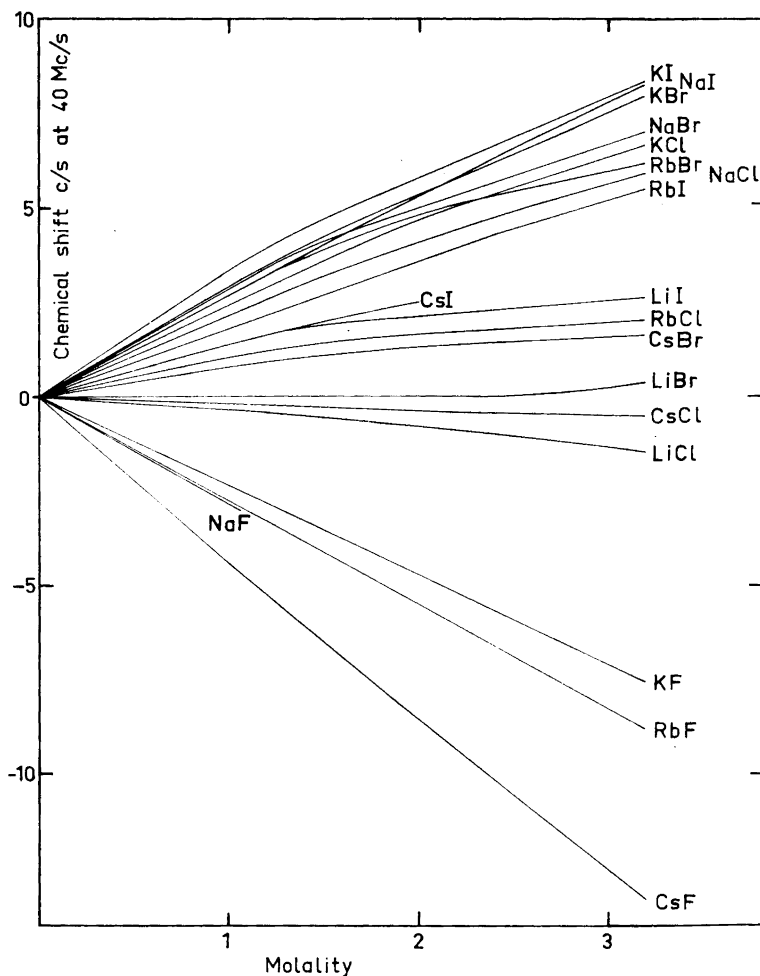
Fig. 1. The concentration dependence of the shift; no susceptibility correction is performed.

where Δd = uncertainty of the density of an 1-molal solution

$\Delta \chi_s$ =   »   »   »   molecular susceptibility of the salt, indicated in literature [38]

c_1 = molarity number, corresponding to molality m = 1.

ANALYSIS OF EXPERIMENTAL DATA

In the analysis of the properties of ions in aqueous solutions, the partitioning of a specific effect among the contributing types of ions presents a main problem. The question arises in studies of ionic entropies [45], dielectric data [46,47],

Table 1.

Salt	$(-g \pm \Delta g) \times 10^8$ [a]	$\delta \pm \varepsilon$ [b]	δ_{calc} [c]	$\delta_{H \& S}$ [d]	$\delta_{S \& A}$ [e]	δ_{Hn} [f]
LiCl	2.40 ± 0.06	1.7 ± 0.3		2.2 + 0.5	−0.8	1.0
LiBr	3.12 ± 0.05	3.1 ± 0.3			1.2	3.8
LiI	5.34 ± 0.18	8.8 ± 0.3				
NaF	3.48 ± 0.07	−3.6 ± 0.3		−2.5 ± 1		−1.8
NaCl	3.50 ± 0.05	8.6 ± 0.3	9.4	8.8 ± 0.5	5.8	7.3
NaBr	4.70 ± 0.06	11.9 ± 0.3	11.9	11.3 ± 0.5		10.0
NaI	6.41 ± 0.07	13.2 ± 0.3	14.4	15.0 ± 0.5	9.2	11.6
KF	3.58 ± 0.12	−2.2 ± 0.3		−2.5 ± 0.5	−4.9	−2.8
KCl	3.76 ± 0.06	9.9 ± 0.3	10.3	8.8 ± 0.5		7.1
KBr	4.93 ± 0.06	12.3 ± 0.3	11.4	11.3 ± 0.5		
KI	6.60 ± 0.17	15.0 ± 0.3	14.8	15.0 ± 0.5	10.6	
RbF	4.47 ± 0.14	−2.4 ± 0.3				
RbCl	4.80 ± 0.17	7.5 ± 0.3	8.2			6.1
RbBr	5.50 ± 0.18	12.3 ± 0.3	9.4			
RbI	7.02 ± 0.22	11.5 ± 0.3	(16.0) [g] 12.8	15.0 ± 0.5		
CsF	5.68 ± 0.16	−5.3 ± 0.3				
CsCl	6.38 ± 0.17	5.9 ± 0.3	(7.6) [g] 5.9			5.0
CsBr	6.60 ± 0.21	8.6 ± 0.3	7.0			
CsI	9.15 ± 0.25	9.5 ± 0.4	(14.9) [g] 10.4	14.6 ± 0.5		
NaClO₄	1.28 ± 0.11	13.2 ± 0.3				

a) Susceptibility correction and its uncertainty for 1-molal solutions.

b) ε is the estimated uncertainty in δ, $\varepsilon = [0.25^2 + (\Delta g)^2]^{1/2}$. The value 0.25 is the standard deviation of the shift due to errors in the frequency readings.

c) δ_{calc} is the molal shift calculated from estimated values of π and σ.

d) Molal shifts, determined by Hertz and Spalthoff [12], using internal standard.

e) Molar shifts, determined by Shoolery and Alder [1], without susc. correction.

f) Molal shifts, determined by Hindman [13], using external standard. A susceptibility correction has been included.

g) The values in parenthesis are molal shifts measured in this work with internal standard.

viscosity B-factors [48] etc. and plays a prominent role in the study of NMR molal shifts. Often rather arbitrary methods are chosen. In spite of the fact that Shoolery and Alder [1] neglected the susceptibility corrections, they were led to the assumption of an approximate additivity law for molal ionic shifts. This is perhaps not so surprising in view of the fact that molecular susceptibilities of salts are very nearly additive properties [49–52]. (Density effects, however, destroy the additivity of molal volume susceptibilities of electrolytic solutions to a certain degree, a fact, which can be seen in the calculations of g in Table 1).

In evaluating the experimental data, we have made use of the following conceptions regarding the structure and general behaviour of water and aqueous solutions.

Liquid water is treated as an essentially crystalline system, closely related to a slightly expanded, idealized ice lattice (Fig. 2), containing defects in thermal equilibrium with the lattice (theoretical papers [53–56], neutron diffraction studies [57–60], X-ray work [61], self-diffusion work with isotopic tracers [62].) The structure is very open and the interstitial space between the groups of molecules in tetrahedral coordination is sufficiently large to accomodate free, non-associated molecules without greatly disarranging the structural order.
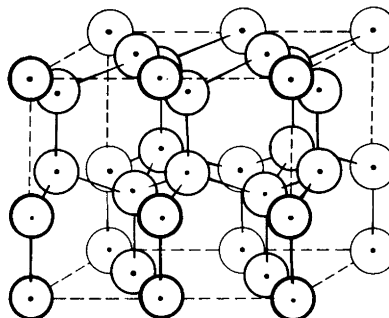
Fig. 2. Oxygen positions in the ideal ice lattice. Hydrogen bonds are indicated by full lines.

We may derive the properties of liquid water from the structure of the idealized ice lattice, if we remember that the molecules perform thermal vibrations around their positions of equilibrium, the intermolecular movements being both dilational and deformational. With rising temperature, the amplitudes of the deformational vibrations will gain in importance and eventually become large enough to break some hydrogen bonds, permitting the freed molecules to enter the interstitial spaces in the lattice. The arising lattice defects consist each of one vacant lattice point and one interstitial, non-associated molecule. This type of lattice imperfection is usually called a Frenkel defect. Each component of the defect is free to diffuse in the lattice, and some of the vacant lattice points may eventually reach a boundary of the molecular system, where they may be annihilated, causing a reduction of the total volume and leaving behind lone, interstitial molecules, so-called Schottky defects, which increase the density in bulk.

The density increase, associated with the appearance of Schottky defects at the ice/water transition will, in fact, continue until the thermal amplitudes have become sufficiently attenuated by the interstitial molecules to prevent the formation of new defects. At this stage, we say that the system has attained thermal equilibrium. Disregarding a slight thermal expansion of the lattice, the structure of the liquid phase is then essentially the same as that of the solid, the only difference being a higher bulk density due to the new Schottky defects, and an increased amount of complete Frenkel defects. Still, in liquid water at 0°C, only 9 % of the lattice points are vacant, while the number of interstitial molecules amounts to some 16 % of the total number of molecules in the system [55,56]. It is obvious that the rheological properties of the system will depend on the association of point defects to form dislocations which, under the influence of a shearing stress, will move against a rather small energy barrier to produce the relative lattice displacements constituting the flow process. Excess of interstitial matter will raise the barrier and counteract the flow.

Making use of the preceding conceptions, we may now visualize the internal boundary conditions of the water lattice to be affected by the introduction of foreign matter in the lattice interstices and vacancies in a similar manner, as occurs in solid solution.

Dissolved electrolytes are accordingly expected to produce lattice distortions due to steric effects, which depend on the size and shape of the ions. It is evident, that only those ions which possess a smallest radius larger than the radius of the interstitial space, are able to distort the lattice for purely geometrical reasons. Chemical bonding between the solute and the water lattice may, on the other hand, be expected to occur both in interstitial and lattice positions, giving rise to additional lattice distortions associated with the changes in the ionic and molecular charge distributions which are due to the bonding effects [63],[64]. As may be inferred from the theoretical calculations for pure water, corroborated by experimental data [65],[55] for water as well as for aqueous solutions, the number of free, *i.e.* interstitial water molecules is, in general, very small and, moreover, rather insensitive to changes in solute concentration. The implication of this observation is that nuclear spin relaxation mechanisms depending on the free rotation of water molecules or their translational motion in lattice interstitial channels, contribute very little indeed, to the total relaxation of the proton spin system.

In our model the reorientations of the overall molecular dipoles responsible for the high dielectric constant of water and ice, take place almost exclusively by way of simultaneous shifts of the proton positions as implied by Pauling's [54] structural model for ice. The individual proton shift occurs as a sort of chain reaction without disruption of hydrogen bonds. Increasing lattice distortion and coupling to solute molecules will, however, reduce the probability for unrestricted simultaneous proton displacements due to an increased number of barriers against the rehybridizations necessary for proton exchange between hydrogen bonded water molecules. The outcome is a reduction of the dielectric constant with increasing solute concentration. The effect may give the impression of being due to a restriction imposed on free molecular rotation. The free rotation, supposed to occur, is, however, expected to increase with weakening hydrogen bonds, which has sometimes given rise to an apparent contradiction. The simultaneous shortening of the dielectric and the proton magnetic relaxation times is, of course, due to the weakening of hydrogen bonds.

We moreover conclude from our model that the hydration process, *i.e.* the coupling between the solute and the solvent does not, as a rule, give rise to the formation of a distinct coordination sphere of water molecules surrounding an ion or an ionized atomic group, disrupted from the remainder of the lattice, and moving as an entity in the solvent. The dissolved ion or atom is instead regarded as integrated in the water lattice by ordinary chemical bonds of variable duration and strength, depending on the type of instantaneous coupling and the thermal excitation of the lattice. Under such conditions, it is obviously desirable to regard the relaxation processes as depending on the whole water lattice, the rotational energy of the observed nuclei being dissipated by a number of different, cooperating mechanisms, which for a proper treatment have to be described in terms of the lattice dynamics.

The present investigation is not concerned with this aspect of the problem, the solution of which, in our opinion, should only be attempted when more information about the structural properties of the water lattice has been obtained. In conformity with these ideas, we have, in the meantime, been looking for a correlation between the observed proton magnetic resonance shift of

aqueous solutions of the alkali salts and some ionic properties expected to influence the structural behaviour of the water.

Taking the proton resonance shift as a measure of the mean hydrogen bond energy changes, we have used the ionic volume and polarizability to characterize the solute. In order to find a quantitative expression for the relative polarizabilities of the ions and, at the same time, accounting for the characteristic ionic charge distributions, we have chosen to make a theoretical calculation of the atomic dipoles associated with a given ionic hybrid orbital state.

To this end we postulate that the molal shift δ, for an $1-1$ electrolyte with the cation i and anion j, is composed according to the matrix equation

$$\begin{vmatrix} \sigma_{ii} & \sigma_{ij} & \pi_{ii} & \pi_{ij} \\ \sigma_{ji} & \sigma_{jj} & \pi_{ji} & \pi_{jj} \end{vmatrix} \begin{vmatrix} s_i \\ s_j \\ p_i \\ p_j \end{vmatrix} = \begin{vmatrix} \delta_{ij} \\ \delta_{ji} \end{vmatrix} \tag{5a}$$

$$\delta_{ij} + \delta_{ji} = \delta \tag{5b}$$

δ_{ij} is the water proton shift produced by the cation i when the anion j is present, δ_{ji} is the water proton shift produced by the anion j when the cation i is present. s and p stand for the hydrogen bond breaking (steric effect) and polarization effects respectively. σ and π are the proportionality factors. Then the sum of the terms containing ii and jj factors expresses the simple additivity law for ionic molal shifts, while the cross terms with ij or ji indices stand for ion-counterion effects, *i.e.* non-additivity and concentration dependence.

The parameter s. This parameter is chosen to represent the steric effect on the water lattice of the dissolved ions. It should accordingly be associated with the breaking of hydrogen bonds due to lattice distortion. The larger the volume of a dissolved ion, the stronger the steric disturbance on the water structure and the more extensive the zone around the ion in which hydrogen bonds are being disturbed or broken. Therefore the steric effect factor is put equal to the ionic volume, *i.e.*

$$s = (4\pi/3)r^3 \tag{6}$$

where r is expressed in Ångström units.

The choice of a suitable value for r can be discussed from many points of view [66]. The simplest way and the one chosen in this work is to make use of Pauling's [67] crystallographic radii. Objections can be raised to this choice since the difference between ionic environments in crystals and water solutions can be expected to influence the radii. Several authors have, however, shown that there is a simple relation between the crystallographic radii and the radii in aqueous solutions. U.V. absorption measurements of anions in solution led Stein and Treinin [68] to a calculated, constant ratio

$$f = r_{soln.}/r_{cryst.} = 1.30 \pm 0.03$$

for the halide ions. Mukerjee [69] in a study of partial molal volumes of ions in aqueous solutions recently redetermined this ratio obtaining the value $f = 1.21$.

Even if the correct ionic volumes are not expressed by the crystallographic radii, the deviation will be included in the nearly constant factor f. In the present case f enters the σ-factors.

The calculated s-values are shown in Table 2.

The polarization effect p. The electronic state of halides in solution and the ion/solvent coupling has long been studied by U.V. absorption methods [68,70-73].

Also in a recent investigation of aqueous alkali halide solutions, Walrafen [74] found peaks in Raman spectra which could be explained only by assuming hydrogen bonds of the type O—H...X⁻. It then seems natural to develop our model in the following way. When an ion is inserted into a water lattice it will leave its ground state $(ns)^2(np)^6$ due to the interaction with the surrounding water molecules. An atomic dipole μ, created by the orbital component np which is an unpaired electron left in the ground state, henceforth denoted by the index o, and the excited electron, henceforth denoted by the index m, can be written

$$\mu_{om} = e \cdot R_{om} \tag{7}$$

where e is the charge of the electron and R_{om} represents the radius vector to the centroid of the hybrid, according to

$$R_{om} = \int \bar{r}[\sqrt{\lambda_{om}}\varphi_o + \sqrt{1-\lambda_{om}}\varphi_m]^2 d\tau = 2\sqrt{\lambda_{om}(1-\lambda_{om})}\int \bar{r}\varphi_o\varphi_m d\tau \tag{8}$$

Here φ_o and φ_m are taken as normalized Slater-functions for the orbitals o and m. λ_{om} is the mixing coefficient expressing the fractional amount of o-character (ground state) in the normalized hybrid. $\bar{r}$ is the radius vector and $d\tau$ is the volume element.

Assuming preferential forms of hybridization and constant mixing coefficients for both cations and anions, we postulate the orbital m as the lowest available s-orbital above the np state, *i.e.* a $(n + 1)$s state. (The lithium ion having no p electrons constitutes an exception. In this case we have made use of a hybrid of the orbitals 2s and 2p).

We are accordingly allowed to write the atomic dipole moment for a cation i and an anion j as:

$$\mu_i = 2e\sqrt{\lambda_i(1-\lambda_i)} \cdot \int \bar{r}\varphi_i(np)\varphi_i((n + 1)s)d\tau \tag{9a}$$

resp.

$$\mu_j = 2e\sqrt{\lambda_j(1-\lambda_j)} \cdot \int \bar{r}\varphi_j(np)\varphi_j((n + 1)s)d\tau \tag{9b}$$

The moment integrals, given in Table 2, are now identified with p_i and p_j, *i.e.*

$$p_i = \int \bar{r}\varphi_i(np)\varphi_i((n + 1)s)d\tau \tag{10a}$$

and

$$p_j = \int \bar{r}\varphi_j(np)\varphi_j((n + 1)s)d\tau \tag{10b}$$

and the π-factors will include the mixing coefficient square root factors.

The complete assembly of nineteen salts gives 19 equations of the type (5) but involves in all 36 unknown σ- and π-factors. Thus, some simplifications

must be made, and this is possible in more than one way. A reasonable assumption seems to be

$$\pi_{ii} = \pi_+ = \pi \tag{11}$$

implying that the polarization proportionality factors are the same for all the cations. Similarly we may write

$$\pi_{jj} = \pi_- = \alpha\pi \tag{12}$$

implying a common polarization mechanism for the anions. In order to simplify the calculations the parameter α has been introduced, to express the ratio between π_- and π_+. Similar considerations of the steric effects lead to the assumption

$$\sigma_{ii} = \sigma_{jj} = \sigma \tag{13}$$

expressing a linear relationship between the disturbance and the ionic volumes, the proportionally factor σ being common for both cations and anions.

Further, neglecting the non-additive contributions to the shift, we obtain

$$\pi_{ij} = \pi_{ji} = 0 = \sigma_{ij} = \sigma_{ji} \tag{14}$$

Although the eqns. (11)—(14) are all rather crude approximations their justification may be inferred from the success of the procedure in its practical application.

Writing

$$p_i + \alpha p_j = P_{ij} \tag{15}$$

and

$$s_i + s_j = S_{ij} \tag{16}$$

we obtain for each salt, when omitting indices, the equation

$$\pi P + \sigma S = \delta \tag{17}$$

Writing this equation in the form

$$\pi(P/\delta) + \sigma(S/\delta) = 1 \tag{17a}$$

it is at once realized that if π and δ are real constants their values could be derived from the reciprocal axis intercepts of Fig. 3. In eqn. (17), however, another unknown constant is involved, namely $\alpha = \pi_-/\pi_+$, defined in eqns. (11) and (12). This constant may be chosen to optimize the adaptation to a linear relationship between P/δ and S/δ in eqn. (17a). This is achieved by letting α take the values 0, 0.1, 0.2 . . . 1.0. The regression line parameters and the statistical correlation coefficient r for each α-value are then calculated. The latter, expressing the closeness of fit to a straight line, has its maximum for $\alpha = 0.2$ (see Fig. 4). Inserting this α-value in eqn. (17a) leads to the result shown in Fig. 3. All the points except those due to the lithium and fluoride salts lie close to the straight line which is the average of the two possible regression lines.
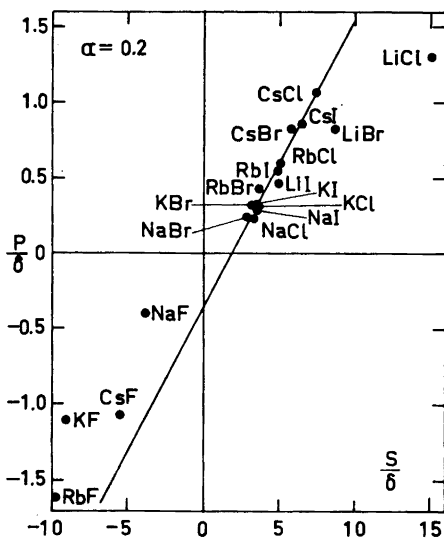
Fig. 3. The function $\pi(P/\delta) + \sigma(S/\delta) = 1$. The straight line is an average of the two regression lines, estimated from all the salts excepting the Li-salts and the fluorides.
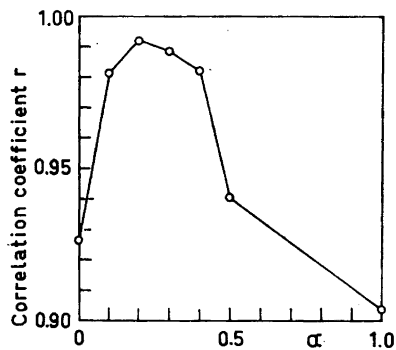

Fig. 4. Correlation coefficient as a function of the parameter α.

Hence the calculation of the constants α, π and σ does not include salts which contain lithium or fluorine. From Fig. 3 we obtain

$$\pi = -2.969 \ (\text{a.u.})^{-1}$$
$$\sigma = 0.5603 \ \text{Å}^{-3}$$

The ionic molal shifts may now be computed from the equations

$$\delta_i = \pi p_i + \sigma s_i \tag{18}$$

$$\delta_j = \alpha \pi p_j + \sigma s_j \tag{19}$$

valid for cations and anions respectively. The molal shifts of Li^+ and F^-, however, have been computed according to the explanation given in Table 2. The results are summarized in Table 2 and shown in Fig. 5.

We find that for Cl^-, Br^- and I^- the shifts are essentially determined by the steric effects whereas the steric and polarization effects for Na^+ and K^+ almost cancel. The shifts of Rb^+ and Cs^+ indicate a stabilizing effect on the water lattice but are far from the extreme value of Li^+. The F^- shift value lies markedly lower than those of the other halides.

It appears that the coupling mechanisms for Li^+ and F^- deviate from those of the remaining salts. Since stable covalent bonds can, in general, only be formed when the main contribution to the bonding energy depends on stable electronic configurations, Li^+ obviously represents an exception with only

two 1s electrons in the ground state. Similarly, F^- is exceptional due to the extreme electronegativity of the fluorine atom and the correspondingly high polarizing ability in combination with an ionic volume/interstitial volume ratio close to unity. The assumption of an approximately constant ratio π_-/π_+ employed in the derivation of the eqn. (17a) obviously cannot be maintained in these two cases.

Table 2.

Ion	Dipole forming orbitals		p(a.u.)	s(Å³)	σs	$-\pi_+ p$	$-\pi_- p$	$\delta_{\text{ion(calc)}}$
Li+	2s	2p	1.090	0.94	—	—		— 7.8 [a]
Na+	2p	3s	0.899	3.68	2.06	2.67		— 0.62
K+	3p	4s	1.934	9.88	5.53	5.74		— 0.21
Rb+	4p	5s	3.354	13.70	7.68	9.96		— 2.28
Cs+	5p	6s	5.150	19.03	10.66	15.29		— 4.63
F-	2p	3s	2.611	10.10	—		—	— 1.5 [a]
Cl-	3p	4s	5.626	24.67	13.82		3.34	10.48
Br-	4p	5s	9.742	31.09	17.42		5.78	11.64
I-	5p	6s	14.96	42.69	23.92		8.88	15.04

a For Li+ we estimate from LiCl $\delta_{\text{Li}+} = 1.7 - 10.5 = -8.8$, from LiBr $\delta_{\text{Li}+} = -8.5$ etc. The average value is -7.8. The corresponding calculation is made for F⁻.

COMPARISON WITH OTHER INVESTIGATIONS

The agreement of our data with those of Hertz and Spalthoff[12] is rather satisfactory, except in one or two cases which are discussed below. The shift value of 1 m solutions generally coincide within the limits of error for the two methods. However, Hertz and Spalthoff find that the concentration dependence first deviates from the linear form in 3 m solutions, whereas we are able to prove the existence of non-linear forms of the chemical shift $\varDelta$ (including the susceptibility correction) already in the concentration range 1—2 m. These findings cannot be ascribed to the use of susceptibility corrections since these are very linear up to high concentrations, a fact which has been shown previously [49-52] and also in control measurements initiated by us. To explain the difference we could assume that the error margins are larger than stated — which is not probable — or that the use of t-butanol or similar compounds as internal standards will complicate the chemical situation to produce anomalies due to some kind of "complexing". In the latter case the lines, which are in reality curved, appear straight owing to the presence of the large organic molecule.

In two special cases, namely RbI and CsI, a definite anomalous effect has been proved. We found a striking difference between our results and those of Hertz and Spalthoff, as can be seen from Table 1. To check the deviation we tested Hertz and Spalthoff's method using 0.3 m t-butanol as internal standard and found $\delta = 16.0$ and 14.9 for RbI and CsI, respectively. The correctness of Hertz and Spalthoff's values was thus confirmed but it is also clear that a fundamental difference exists between the two methods used in this case. To be still more certain, we compared results for CsCl (not measured by Hertz and Spalthoff) and found $\delta_{\text{int}} - \delta_{\text{ext}} = 7.5 - 5.9$. This result led us to

the conclusion that the combined action of the cations in question and t-butanol upon the water molecules give rise to upfield shifts which actually deviate from the law of additivity.

In order to investigate these observations in detail, it is desirable to perform measurements on solutions with constant electrolyte concentration but varying concentrations of the internal standard compound. Extrapolation of the shift may then be made to zero concentration of the reference compound.*

When Hertz and Spalthoff defined their reference point for the ionic chemical shifts, they refrained from a discussion of the detailed interactions between the ions and the solvent water owing to the complexity of the question. They preferred instead to make the molal shifts of the potassium and chloride ions equal, *i.e.* $\delta_{K^+} = \delta_{Cl^-} = 4.4$, a choice based upon the known similarities in the conductivities, transport numbers, hydration numbers and ionic sizes of the two species.

Recently Fabricand and Goldberg [75] published some PMR measurements for certain aqueous alkali halide solutions. Our experimental uncorrected values of molal shifts are in excellent agreement with theirs which were also obtained using an external reference method. There are, however, certain points in their treatment which we believe require some comments. (1) Instead of discussing their results on the basis of experimentally found susceptibilities, they have preferred the use of theoretically calculated ionic susceptibilities [76] which unfortunately show considerable deviations from the experimental values. (2) By an error of calculation they seem to have obtained corrections which are about two times too large. We regard our results as satisfactorily verified by their unambiguous agreement with those obtained by the independent method of Hertz and Spalthoff and also with those recently obtained by Hindman [13]. (3) After arbitrarily putting $\delta_{Cl^-} = 0$, to establish their shift scale, they stated that the shift difference between K^+ and F^-, $\delta_{F^-} - \delta_{K^+} = 2.8$, depends on the difference in the polarization contributions for these ions, the volumes being very nearly equal. Had they instead defined their zero point as $\delta_{Br^-} = 0$ the "difference in the polarization terms" would equal 4.0. Failure to introduce a physically or chemically satisfactory definition of the reference point make comparisons of this kind between positive and negative ions rather illusory. (4) Fabricand and Goldberg maintain that the ionic effects on the proton resonance shifts do not extend beyond the nearest-neighbour water molecules, a statement which they based upon certain breaks in the shift-concentration curves for six of the fourteen salts. Unfortunately the other eight salts did not show this behaviour.

The molal shifts of 1—1 electrolytes, measured by Hindman [13] do not differ appreciably from our results and those of Hertz and Spalthoff, though in general they tend to be slightly lower. Hindman also observed the anomalous behaviour of the lithium ion which he explained as a "structure-making effect". His point of reference was established by putting the molal shift of the ammonium ion equal to zero, justifying this choice by reference to the small effects produced on various properties of water by ammonium chloride in solution.

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* Measurements performed after the completion of this investigation have confirmed the existence of a general internal standard effect on the water lattice and the proton resonance shift, elucidating the extrapolation conditions in the case of t-butanol.

COMPARISON BETWEEN THE EFFECTS OF ENHANCED TEMPERATURE AND DISSOLVED ELECTROLYTES ON THE HYDROGEN BOND STRENGTH IN WATER

Shoolery and Alder [1] made an early estimate of the steric effect on the total shift of an electrolyte. Making use of "the liquid association shift" determined by Schneider et al.[77] and applying the method of least squares we have tried to estimate the temperature dependence of "the liquid association shift", δ_{LAS}. This is the difference between the real shift of a certain compound in the liquid state and the shift value which is calculated for the liquid state. The latter shift value is derived from experimental data for the shift of the compound in the gaseous state and from the volume susceptibility of the liquid state, as expressed by the equation

$$\delta_{LAS} = \delta_{liq} - (\delta_{liq})_{calc} = \delta_{liq} - \delta_{gas} - (2\pi/3) \cdot k \times 10^8 \qquad (20)$$

resulting in

$$\delta_{LAS} = 1.153 \ t - 458 \qquad (21)$$

for water, where t is °C. From eqn. (21) we obtain the value 115.3 for the shift between two water specimens at 100°C and 0°C, respectively.

From a knowledge of the difference in the number of broken hydrogen bonds for the two water specimens, the shifts per mole of broken hydrogen bonds in 1000 g water can be estimated. Several authors have computed the number of broken hydrogen bonds in water as a function of temperature. Thus Haggis et al.[65] found that the difference in the percentage of hydrogen bonds broken between 100°C and 0°C was 11.2. The corresponding number found by Forslind [55] was 8.6.

If an average of 10 % is assumed we obtain a "steric" shift of

$$\frac{115.3}{0.1} \cdot \frac{18}{1000} = 21$$

when two moles of hydrogen bonds are broken in 1000 g water. Assuming further that (a) one water of hydration molecule implies two broken hydrogen bonds and that (b) an arbitrary alkali halide has an apparent hydration number of 6 for the cation and anion together, then it should be possible to calculate the ionic sum of the polarization contributions, δ_{pol}, according to

$$\delta_{pol} = \delta_{salt} - 6 \times 21 \qquad (21)$$

It is quite evident that this model leads to results which are difficult to accept since the probability that the two opposite effects (hydrogen bond stabilization resp. disrupture) should cancel for all the alkali halides is extremely small. This line of approach further gives rise to values of the steric effect which seem to be at variance with those of the present model. We therefore conclude that hydrogen bond rupture resulting from a rise of temperature bears very little resemblance to water lattice deformations caused by dissolved ions (cf. Kujumzelis [78]).

COMPARISON OF PMR DATA WITH DIELECTRIC DATA FOR ELECTROLYTIC SOLUTIONS

The dielectric methods for the study of ionic properties in electrolytic solutions were mainly developed by Hasted *et al.*[46,47,65] who interpreted the decrease of dielectric relaxation time $(\delta\lambda_s)$ in increasingly concentrated solutions of strong, inorganic electrolytes as due to disrupture of hydrogen bonds. The dielectric constant depression $(\delta\varepsilon)$ was regarded as being due to restriction of the water dipole rotation produced by the ions — the stronger the dipole coupling, the more effective the restriction of rotation (*cf.* the introductory notes on p. 2076). In this work we regard the PMR shift as resulting from both the effects of hydrogen bond rupture and polarization, also reflected in the two dielectric parameters. In Fig. 5 a remarkable parallelism is exhibited by (*a*) the molar dielectric relaxation depression $\delta\lambda_s$, (*b*) the molar dielectric constant depression $\delta\varepsilon$ and (*c*) the molal NMR shift δ of the alkali metal ions and halide ions. However, whilst we have an absolute scale for δ, according to the theoretical considerations used in this paper we have had to define arbitrary reference points for $\delta\lambda_s$ and $\delta\varepsilon$ by a procedure which is explained in Fig. 5. In all three diagrams of Fig. 5, the halide ions, without exception form a homologous series with the iodide ion exerting the largest effects and the fluoride ion the least. For the cations, the analogy is not quite so evident. Firstly, no dielectric studies known by us include measurements on cesium salts. Secondly, the uncertainty of $\delta\varepsilon$ does not allow any definite quantitative conclusions to be drawn concerning the ordering (analogous to the lyotropic series) of the cations. However, the anomalous behaviour of the lithium ion in the cation series is confirmed by the $\delta\lambda_s$ curve. Whilst Hasted correlated the dielectric constant decrease to "irrotationally bound water" and thus to
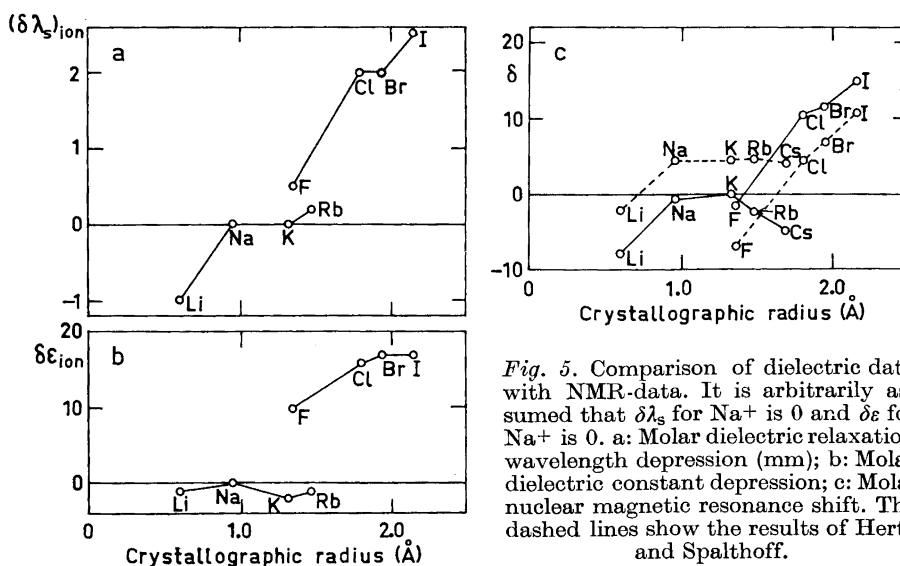

Fig. 5. Comparison of dielectric data with NMR-data. It is arbitrarily assumed that $\delta\lambda_s$ for Na+ is 0 and $\delta\varepsilon$ for Na+ is 0. a: Molar dielectric relaxation wavelength depression (mm); b: Molar dielectric constant depression; c: Molal nuclear magnetic resonance shift. The dashed lines show the results of Hertz and Spalthoff.

a hydration number, we think it wise to postpone such direct statements about δ. It should finally be remarked, that a similar sequence of the ions in question is found from Raman spectra [74,79].

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