Proton Chemical Shifts of Water in Cationic Hydration Complexes and their Contribution to Water Shifts in Electrolyte Solutions

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The proton chemical shift of water in hydration complexes of the cations Sn^{4+}, Al^{3+}, Ga^{3+}, In^{3+}, Mg^{2+}, and Be^{2+} has been measured at low temperatures. The shifts are strongly downfield and correlate with shift increments calculated to arise from the electric field of the ion. The correlation indicates that the total cationic water shift contains two contributions; a downfield one from the electric field and a smaller upfield one from a structural effect. The correlation is used to estimate the proton shift of hydration water of the larger Group II and Group I cations where proton exchange is always too fast to allow a separate resonance for the co-ordinated water to be observed. The contribution of cationic hydration to the molal shifts of salt solutions is thus obtained and comparison with measured molal shifts allows estimates to be made of the anionic contribution, which is upfield and arises from solvent structure-breaking. A three-site model is developed to explain the solution shifts and previous measurements are shown to be consistent with a hydration number of 6 for all the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, of 4 for the alkali-metal ions, and of zero for Me_4N^+. The sulphate anion is also probably tetrahydrated.

MANY studies have been made of the effect which dissolved electrolytes have on the chemical shift of the water solvent.[1-11] Because rapid proton exchange occurs between the various possible water environments, a singlet resonance is invariably observed in dilute solutions between 0 and 100 °C, which may be displaced upfield or downfield from the pure water resonance, the direction depending on the electrolyte and, in a few cases, on temperature. Interpretation of the results is difficult since the contributions made by anionic and cationic hydration, ion-pairing, and solvent-structure changes are not individually known and the different effects oppose one another so making the overall shifts small.[3] Recently separate resonances have been observed for protons in the bulk solvent and in the cationic hydration complexes of concentrated solutions of some Group IV, Group III, and Group II electrolytes at low temperatures and the cationic hydration numbers have been estimated.[12-14] In addition, the chemical shift of the hydration water relative to some suitable standard such as Me_4N^+ can be measured, the contribution to the solution shift of cationic hydration alone can be calculated, and an estimate made of the contribution of the other factors. Results of measurements on six salts are reported and a model is developed which predicts the molar shifts of a large number of salts at all temperatures.

EXPERIMENTAL

Measurements were made as for $Al(H_2O)_6^{3+}$.[15] Concentrated aqueous solutions of the chlorides were used for measurements with $Ga(H_2O)_6^{3+}$, $In(H_2O)_6^{3+}$, and $Be(H_2O)_4^{2+}$. An aqueous acetone solution of the perchlorate was used for $Mg(H_2O)_6^{2+}$. In this case sufficient standard would not dissolve and the acetone had to be used as a secondary standard.

A measurement was also made for the aquotin(IV) ion $Sn(H_2O)_x^{4+}$ in order to study the effect of ionic charge over as wide a range of charge number as possible. Unfortunately the measurements are complicated by hydrolysis and by the formation of co-ordination complexes with the anions. However, a resonance was detected in aqueous $Sn(SO_4)_2$ solution considerably to low field of any other resonance measured and is attributed to $Sn(H_2O)_6^{4+}$. The hydration number could not be measured owing to interfering reactions. Fratiello *et al.* have also measured the chemical shift of the water in $Sn(H_2O)_6^{4+}$ using $SnCl_4$ in aqueous acetone and report it as 11·0—11·3 p.p.m. to low field of internal tetramethylsilane,[12] which is close to the lowest-field resonance seen in $Sn(SO_4)_2$ solution.

The precision of the measurements is not high since the resonances are broad and there is exchange perturbation of their positions.[15] In addition they may also be sensitive to hydrolysis, temperature, or concentration, and some investigation of these effects was made for solutions of Al^{3+} and Be^{2+}.

No large changes in shift have been observed in highly hydrolysed 3M-aluminium salt solutions[16] though the proportion of bound water decreased. Addition of small quantities of acid on the other hand reduces the extent of hydrolysis and slows the rate of proton exchange[17] so that a separate and well resolved bound-water resonance can be observed near 0 °C in 1M solutions.[18] The bound-water shift in 1M-$Al(NO_3)_3$ is $-8·67 \pm 0·1$ p.p.m. and is not significantly different from the previous result for 3M-$AlCl_3$. The similarity of the bound-water shifts in 1M-$Al(NO_3)_3$ at

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-3 °C and 3M-$AlCl_3$ at -40 °C also indicates that neither temperature nor concentration have significant effects. Similarly hydrolysis of beryllium chloride solution did not alter the position of the bound-water resonance.[18] Data are not available for the other solutions but it seems reasonable to suppose that they equally may not suffer significant effects.

RESULTS

The results are in the first two columns of Table 1. Those obtained in pure aqueous solution agree closely with estimates made on the basis of Fratiello's work.[12–14] The bound-proton resonances are all to low field of the pure water resonance and in general move increasingly to low field as the ionic charge increases or as the ionic radius decreases. This observation suggests that the proton shifts may be caused by the electric field of the ions and could perhaps be calculated by use of Buckingham's equation,[19] although the fact that the gallium complex has a larger shift than the slightly smaller aluminium complex needs to be rationalised.

TABLE 1

Model and calculated chemical shifts for the water hydrogen in complex aquo-cations

	Chemical shifts/p.p.m.						
		Calculated					
Cation	Measured[a]	Total	AE term	BE^2 term	Model	M–O distance/pm	∠MOH/°
$Sn(H_2O)_6^{4+}$	$-10{\cdot}1$[b,c]	$-8{\cdot}51$	$-3{\cdot}96$	$-4{\cdot}55$	Planar	211	128
$Al(H_2O)_6^{3+}$	$-8{\cdot}74$	$-6{\cdot}99$	$-3{\cdot}48$	$-3{\cdot}51$	Planar	191	128
$Ga(H_2O)_6^{3+}$	$-8{\cdot}98$	$-6{\cdot}54$			Planar	195	128
		$-6{\cdot}96$	$-3{\cdot}20$	$-4{\cdot}39$	Pyramidal[e]	195	119
$In(H_2O)_6^{3+}$	$-7{\cdot}22$	$-5{\cdot}06$	$-2{\cdot}78$	$-2{\cdot}28$	Planar	221	128
$Be(H_2O)_4^{2+}$	$-8{\cdot}04$	$-5{\cdot}80$	$-2{\cdot}95$	$-2{\cdot}85$	Pyramidal	162	119
$Mg(H_2O)_6^{2+}$	$-5{\cdot}55$[d]	$-3{\cdot}33$	$-2{\cdot}08$	$-1{\cdot}25$	Planar	206	128
Pure water at 25 °C	$-4{\cdot}13$						

[a] Corrected to ethane gas standard. [b] Includes data of ref. 10. Three sets of data averaged. [c] $SnCl_4$ in aqueous acetone and $(SnSO_4)_2$ in water. [d] In aqueous acetone. [e] Assumed similar to Be $^{2+}$. In fully pyramidal Ga^{3+}, the MOH angle is 110° and the shift is increased by 0·5 p.p.m.

Calculation of the Chemical Shift due to Electric-field Effects.—The contribution of the electric field E to the screening $\Delta\sigma_E$, can be found from the Buckingham equation[19] (1), where θ is the angle between the direction

$$\Delta\sigma_{\mathrm{E}} = -AE\cos\theta - BE^2 \qquad (1)$$

of the field and the O–H bond axis of the water and A and B are constants characteristic of the bond. Because of the spherical symmetry of the ion it is possible to ignore solvent-polarisation effects and make a straightforward calculation of E as if arising from a point charge.

The calculation depends upon the correct choice of values for A and B and critically upon knowing accurately the distance between the centre of the ion and the water protons. These two factors are discussed below. The constants A and B are not known for the O–H bond of water though B does not vary greatly for protons and it is reasonable to take B as $0{\cdot}75 \times 10^{-18}$ e.s.u.[20–23] Estimates of A however vary widely, values of 25×10^{-12} e.s.u.[20] and $2{\cdot}55 \times 10^{-12}$ e.s.u.[3] being given. The former is too large, in this case leading to far too large calculated shifts [*ca.* 90 p.p.m. for $Al(H_2O)_6^{3+}$]. In addition the temperature dependence of the chemical shift of water vapour is believed to be small[24] and this is in accord with a small value of A.[21–23] A value of $2{\cdot}0 \times 10^{-12}$ e.s.u. has been chosen in this case since it gives good agreement with the experimental results. A and B are however not to be regarded as accurate parameters although fortunately the further treatment of the results is not markedly affected by the values chosen. (In SI the Buckingham equation is best written:

$$\Delta\sigma_{\mathrm{E}} = -4\pi\varepsilon_0 AE\cos\theta - 16\pi^2\varepsilon_0^2 BE^2$$

where $A = 0{\cdot}6 \times 10^{-6}$ m^2 C^{-1} and $B = 0{\cdot}0675 \times 10^{-6}$ m^4 C^{-2}. Writing the equation in this way considerably simplifies the calculations since the $4\pi\varepsilon_0$ terms cancel with those in the expression for E.)

The position of the hydrogen atoms in the complexes may lie between two extremes, either with the metal ion, the oxygen atom, and hydrogen atoms all planar, the so-called dipolar model, or else an oxygen lone pair of electrons may co-ordinate the ion so that the stereochemistry is pyramidal around oxygen and the hydrogen atoms are brought appreciably closer to the centre of the complex.[3,25–27] The water molecules may of course not be static but, in the case of the small, highly charged cations where the presence of some covalency in the metal–oxygen bond now seems established,[28] it is likely that their motion is fairly constrained. We may thus use the crystal-structure data for the hydrated salts as a guide as to the structure of the complex in solution. We find in the case of $Mg(H_2O)_6^{2+}$

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and $Al(H_2O)_6^{3+}$ and in their related oxygen-bridged compounds that the co-ordination is invariably near planar[29–37] whereas in $Be(H_2O)_4^{2+}$ the co-ordination is of an intermediate pyramidal form.[38,39] Few data are available for gallium though it is believed it may be a pyramidal complex also,[40,41] a conclusion in accord with its electronegativity being larger than that of aluminium, and which can explain the anomalously large observed gallium shift. Crystal data are not available for indium or tin hydrates and planar co-ordination has been arbitrarily assumed in both cases.

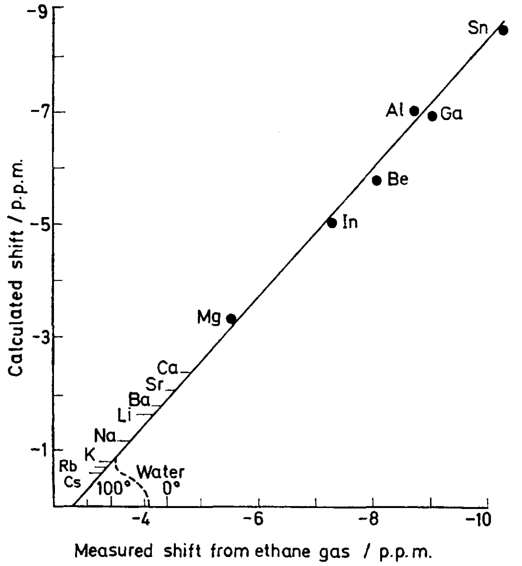

FIGURE 1 Calculated proton chemical shifts $\Delta\sigma_E$ in aquo-ions due to the electric field of the ion as a function of the measured chemical shifts (ethane standard). The horizontal lines indicate the calculated shifts of the more weakly hydrated ions. The broken line suggests how the correlation may break down as we pass from structure-forming to structure-breaking cations

The calculated values of $\Delta\sigma_E$ based on the above data are also in Table 1 and are plotted as a function of the measured chemical shifts in Figure 1. The correlation between the calculated and measured chemical shifts is an extremely good straight line with a slope of 1·15. That the slope differs from unity is of little importance since it depends upon the rather arbitrary values chosen for A and B and since other factors such as the anisotropy of the metal–oxygen bond or motion of the co-ordinated water may also contribute to the shifts.

Extension to other ions. Since these calculations appear to give such a good description of the shifts of the above ions it is an attractive proposition that they might also give an equally good description of the shifts of the larger cations and anions where exchange is always so fast that the hydration shift cannot be measured. The correlation of Figure 1 could then be used to read off a series of ' measured ' shifts corresponding to the shifts calculated from the dimensions of the ions. These have been calculated by use of the planar model favoured by the X-ray data[26,27] and on the assumption that the hydration water is stationary relative to the ion. The results are in Table 2 which also shows the ' measured ' shifts estimated from Figure 1. The shift calculated as introduced by the electric field of an anion is not upfield since both charge and water molecule orientation are reversed.

TABLE 2

Calculated $\Delta\sigma_E$ and estimated chemical shifts for some weakly hydrated ions

	Complexed water proton shifts/p.p.m.	
Ion	Calculated [a]	Estimated [b] δ_S
Ca^{2+}	−2·38	−4·78
Sr^{2+}	−2·07	−4·52
Ba^{2+}	−1·78	−4·26 [d]
Li^+	−1·44	−3·98 [d]
	−1·63 [e]	−4·15 [d]
Na^+	−1·17	−3·72 [d]
K^+	−0·80	−3·40
Rb^+	−0·70	−3·32
Cs^+	−0·61	−3·26
F^-	−1·20	−3·80 [d]
Cl^-	−0·80	−3·40
SO_4^{2-}	−1·05 [c]	−3·70 [d]

[a] The planar model and octahedral crystal radii being used. [b] ' Measured ' shift derived from Figure 1 (ethane scale). [c] Calculated for one proton of the water hydrogen bonded to a sulphate oxygen. [d] Chemical shifts in the same range as pure water, *i.e.*, −3·42 to −4·38 p.p.m. [e] Calculated by use of the pyramidal model and a tetrahedral radius of 51 pm. This value was used to obtain the results of Figure 3.

Hindman has previously carried out electric-field calculations for the alkali-metal cations.[3] He regarded the shifts however as absolute increments to that of pure water, *i.e.*, as always downfield, whereas the correlation of Figure 1 suggests that some cations may have small upfield shifts.

DISCUSSION

The correlation between calculated and measured chemical shifts shown in Figure 1 strongly supports the contentions that the electric fields of the cations make the major contribution to the chemical shift of the hydration water and that different cations may be co-ordinated differently. Figure 1 also reveals the interesting feature that the straight line drawn through the points intercepts the measured shift axis a little to high field of the range within which liquid water is found to resonate. This implies that a pseudo-cation of zero charge would cause an upfield shift. This will arise because the formation of a complex will modify the extent to which the hydration water is hydrogen bonded to the bulk solvent, *i.e.*, there is a structural cationic effect as

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suggested by Hindman[3] which opposes the electric-field effect and appears to be the same for all the ions measured. Such structure-breaking is consistent with the shift of the hydration complex being temperature-independent, as observed.

Knowledge of both hydration number and hydration shift for some cations enables us to calculate the contribution made to the solution shifts by cationic hydration. In the case of $Al(H_2O)_6^{3+}$ this surprisingly accounts for almost the whole of the shift.[15] In the case of $Mg(H_2O)_6^{2+}$ however the cationic contribution is about double that actually observed at 25 °C so that the anion must introduce an opposing shift. This is illustrated by the figures in Table 3. The calculated hydration shift of $Ca(H_2O)_n^{2+}$ is close to that of the magnesium salt and a ' measured ' shift can be read off from Figure 1 with some confidence. The calcium ion is probably also hexahydrated and calculations based on these figures confirm the upfield anionic contribution. The fact that anions introduce an upfield water shift has been inferred by many previous workers, who have assigned positive molar ion shifts to the majority of anions.[1-11] This is however the first unequivocal demonstration of the effect.

TABLE 3

Anion contribution to solvent shift at 25 °C; elimination of cation contribution (all values in p.p.m.)

Molal shift of $Mg(ClO_4)_2$ solution (H_2O standard)	+0·021
Shift of $Mg(H_2O)_6^{2+}$ from water	−1·42
Cation contribution to water shift	−0·153
Anion contribution , by difference	+0·174

The upfield anionic contribution is in strong contrast to the calculated electric-field effect. It thus cannot arise because of a hydration interaction of the same type as observed with cations but must result from the well known structure-breaking effect of the anions which reduces the hydrogen bonding of the solvent and so leads to the required upfield shift. The enhanced water motion around anions,[42] which are relatively large, will in fact tend to reduce the contribution of the $AE \cos \theta$ term to $\Delta\sigma_E$ and may well reduce the electric-field effect to near zero.

If we postulate that each anion causes the breaking of F hydrogen bonds then we can construct a three-site model giving the observed shift δ_{obs} for these solutions as follows.

$$55{\cdot}5\delta_{obs} = \delta_S mh + \delta_N(55{\cdot}5 - mh - Fmz/2) + \delta_F Fmz/2 \quad (2)$$

In equation (2) the δ's are referred to some standard, preferably the ethane gas chosen by Malinowski *et al.*,[4] δ_S is the chemical shift of the cationic hydration water and is assumed temperature-independent, δ_N the shift of the normal water component of the system, $\delta_N = -4{\cdot}38 + 0{\cdot}00958T$,[7] δ_F the shift of the hydrogen atoms freed from hydrogen bonding by the structure-breaking effect, h the cationic hydration number, z the cationic charge, and m the molality. Thus $Fmz/2$ is the quantity of effectively free water molecules produced by a concentration zm of anions. All these factors are known for solutions of Mg^{2+} or Ca^{2+} except for F and δ_F. The shift δ_F can be estimated as follows: a downfield chemical shift of the proton in a water molecule occurs when a hydrogen bond is formed between it and an oxygen atom of another water molecule. The second hydrogen atom is much further removed from the bonded oxygen and so will experience a much smaller shift. We can thus make the assumption that the shift δ_F of this hydrogen atom approximately equals that of the completely free water molecule. Thus δ_F is close to the shift of steam or of trace water in hydrocarbon solvents. These values bracket that of ethane gas[30,43,44] so that we can put $\delta_F = 0$ in equation (2) with only slight error and thus simplify the equation. We can now calculate anion F factors using the shifts observed at 25 °C for some magnesium and calcium salt solutions. These are given in Table 4 and the average F factors for the unicharged anions are plotted as a function of ionic volume in Figure 2; F factors for other unicharged ions can also be obtained from the Figure. The order of effectiveness of structure-breaking found for the unicharged anions is similar to that obtained by other

TABLE 4

F factors for some anions at 25 °C

Salt	$(\delta_{obs} - \delta_N)$/p.p.m.[g]	F	$\frac{\text{Anion volume}}{\text{O}^{2-}\text{ volume}}$
$MgSO_4$	−0·172 [a]	−0·5 [h]	
$MgCl_2$	−0·035, 0·065 [a,e]	1·40 } 1·33	
$CaCl_2$ [c,d]	+0·048, +0·025, +0·005	1·27 }	2·16
$Ca(NO_3)_2$ [c]	+0·0345 [f]	1·42	3·2
$Mg(ClO_4)_2$	+0·021 [f]	2·35 } 2·49	7·4
$Ca(ClO_4)_2$ [c]	+0·125 [f]	2·63 }	
Bromide		1·40 [b]	2·70
Iodide		1·62 [b]	3·67

[a] Ref. 9. Estimated F factors. [c] Assumes the cation is $Ca(H_2O)_6^{3+}$. A shift of −4·78 p.p.m. for the water in this ion can be obtained from Figure 1. [d] Ref. 7. [e] Ref. 1. [f] Ref. 8. [g] Calculated for a 1 molal solution. [h] F was taken as zero for the purposes of calculation.

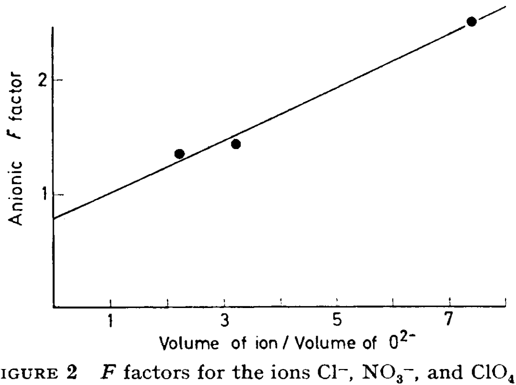

FIGURE 2 F factors for the ions Cl^-, NO_3^-, and ClO_4^- plotted as a function of anionic volume

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[42] H. G. Hertz, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 159.

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[44] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 1958, **28**, 601.

techniques.[42,45-48] In addition the structural enhancement caused by sulphate ion which has been detected by Raman spectroscopy [46] is well demonstrated.

Walrafen [46,47] has shown that dissolution of perchlorate ion (as $NaClO_4$) to give a 1M solution is equivalent to raising the water temperature by 34 °C. Estimates of the proportion of hydrogen bonds present in water at various temperatures suggest that between 0·04 [25] and 0·06 [49] of the total possible hydrogen bonds in the system are broken by a 34 °C temperature rise. These figures are quite close despite the fact that the two models used predict very different degrees of hydrogen bonding in the liquids. Since in a molar solution there are about 50 water molecules per anion (about four may be involved in cation hydration) then the perchlorate anion must break between four and six hydrogen bonds. This estimate agrees quite well with the F factor of 2·49. Exact agreement would not be expected since the chemical-shift calculation lumps all the anion effects into one. Thus the small remnant electric-field effect of the anion and any hydrogen bonding in which it is involved [46-48] will tend to introduce low-field shifts and so reduce the apparent F factor.

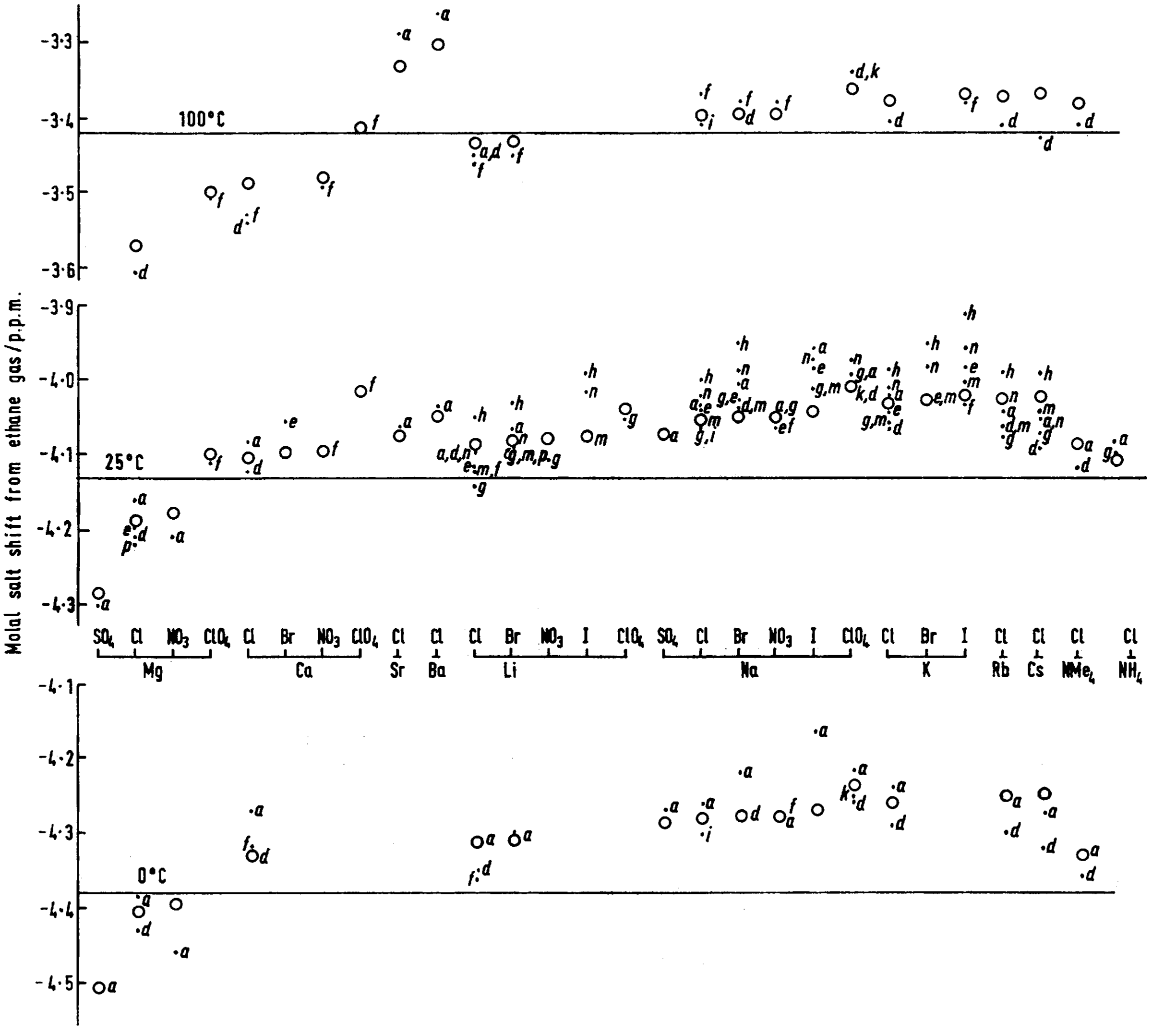

FIGURE 3 Calculated chemical shifts (○) of molar aqueous salt solutions at 0, 25, and 100 °C. The points and letters indicate the experimental results and their origins. Some of the scatter of results arises because some molal shifts have been determined by extrapolation to zero concentration while others have been scaled down from a determination at high concentration. A letter beside a calculated point indicates coincidence of calculated and experimental shifts. The horizontal lines show the shift of pure water at each temperature: [a] Ref. 9; [b] Ref. 5; [d] Ref. 7; [e] Ref. 1; [f] Ref. 8; [g] Ref. 3; [h] Ref. 2, obtained at 21 °C and adjusted to 25 °C; [i] Ref. 4; [m] Ref. 10; [n] Ref. 11; [p] A. LoSurdo and H. E. Wirth, *J. Phys. Chem.*, 1972, **76**, 130.

Figure 2 has a positive intercept at zero volume implying that even a very small anion has a structure-breaking effect. This will arise because the hydrogenic part of the water is turned towards the anion and cannot

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[45] C. Deverell, *Progr. N.M.R. Spectroscopy*, 1969, **4**, 235.

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[49] G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, 1962, **36**, 3382.

hydrogen bond to other water oxygen atoms. The cations have a smaller structural effect because the hydrogenic part of the water is not turned away from the surrounding water molecules. The increase in F factor with ionic volume on the other hand may arise partly because the bulky ions cause more disturbance of the surrounding water though the reduction in hydrogen bonding will also contribute to the slope of the line.

The variable-temperature measurements recently reported by Malinowski and others [4-9] provide a very sensitive test of our model. The chemical shift of pure water varies with temperature by 0·00958 p.p.m. per kelvin [7] and this is reduced if an electrolyte is added. The change can be related to a reduction in the proportion of normal water caused by hydration effects, and can be used to obtain effective hydration numbers, which however tend to be larger than the cationic hydration numbers where these are known, an observation which can easily be explained on the basis of our model (2). The change in slope means that the molar shifts are different at different temperatures and we should see if we can satisfactorily predict these changes. In a few cases [*e.g.*, $Mg(ClO_4)_2$, $CaCl_2$, and LiCl] the solution shift changes sign as the temperature is raised [7-9] and it would be particularly satisfying if equation (2) could reproduce this result.

The model is compared with experiment in Figure 3. The low- and high-temperature predictions for the Group II cations are generally satisfactory, the only exception being $CaCl_2$ at 100 °C and $Mg(NO_3)_2$ at 0 °C. Gratifyingly the model predicts the change in sign of salt shift observed for $Mg(ClO_4)_2$, $CaCl_2$, and $Ca(NO_3)_2$ between 25 and 100 °C. The model was also found to be successful for strontium and barium chloride solutions at 25 °C.

Alternatively we can compare measured and calculated shift–temperature dependences. Differentiation of equation (2) with respect to temperature gives:

$$\frac{d(\delta_{obs})}{dT} = \frac{d(\delta_N)}{dT}\left[1 - \frac{m}{55\cdot5}(h + Fz/2)\right] \qquad (3)$$

i.e. the change in slope of the shift-temperature plot at a given m is determined by the hydration number and the anion structural effect. This equation does not contain δ_S and so can be expected to give more meaningful hydration numbers where $\delta_S \approx \delta_N$. Equation (3) has been used to predict the slopes for a number of these electrolyte solutions and the predictions are compared with experimental slopes in Table 5. The predictions were satisfastory for the Group II metals. We thus conclude that a three-state model can explain the behaviour of the chemical shifts of these solutions on the basis of a constant cationic hydration number with the hydration water having a temperature-independent chemical shift.

The Alkali Metals.—In view of the success of the model for the Group II cations it is of interest to see if it can be applied to alkali-metal salt solutions where considerably more experimental data have been obtained. The alkali-metal solutions differ from those just discussed in that no long-lived cationic solvation complex is formed [50] and therefore the hydration number is more difficult to define. Since we are interested in the effect of hydration upon chemical shifts and their temperature dependence we are forced to define the cationic hydration number as that number of water molecules which are sufficiently constrained by the cation so as to markedly reduce their shift–temperature dependence. Such water molecules will then also have a characteristic δ_S which is given in Table 2. Since the ion–water interaction is entirely electrostatic [3,46-48] there is no reason for choosing any particular h though we can take the view that h is determined primarily by the water structure and will be *ca.* 4.[51,52] This assumption

TABLE 5

Measured and calculated shift–temperature dependences of aqueous electrolyte solutions

Salt	Concn./ molal	Cation h	Slope $d(\delta_{obs})/dT$ / p.p.m. K^{-1} Measured	Slope $d(\delta_{obs})/dT$ / p.p.m. K^{-1} Calculated	Error % measured slope
Pure water			0·00958		
$MgSO_4$	1·00 [a]	6	0·0077 *	0·00855 †	+11·0
		6 + 4 †		0·00785 †	+2·0
$MgCl_2$	2·92 [b]	6	0·00545	0·00588	+7·9
$Mg(ClO_4)_2$	1·95 [c]	6	0·00691	0·00675	−2·3
$CaCl_2$	0·95 [c]	6	0·00793	0·00838	+5·7
	2·92 [c]	6	0·00537	0·00588	+9·5
	2·37 [b]	6	0·00575	0·00658	+14·4
$Ca(NO_3)_2$	1·74 [c]	6	0·00723	0·00736	+1·8
$Ca(ClO_4)_2$	2·27 [e]	6	0·00619	0·00626	+1·1
LiCl	0·89 [c]	4	0·00922	0·00886	−3·9
	1·00 [a]	4	0·00858	0·00878	+2·3
	2·93 [c]	4	0·00777	0·00722	−7·1
LiBr	0·97 [c]	4	0·00824	0·00879	+6·7
	2·91 [c]	4	0·00724	0·00722	−0·3
Na_2SO_4	1·00 [a]	4 × 2	0·00746 *	0·00827 †	+10·9
		4 × 2 + 4 †		0·00758 †	+1·6
NaCl	1·00 [d]	4	0·00900	0·00880	−2·2
	1·00 [a]	4	0·00862	0·00880	−2·1
	3·00 [d]	4	0·00720	0·00726	+0·8
NaBr	3·01 [b]	4	0·00729	0·00724	−0·7
$NaNO_3$	1·00 [a,c]	4	0·00894	0·00880	−1·6
	3·00 [c]	4	0·00787	0·00724	−8·0
$NaClO_4$	1·00 [e]	4	0·00894	0·00871	−2·6
	3·00 [e]	4	0·00787	0·00697	−11·4
KCl	1·00 [a]	4	0·00853	0·00880	+3·9
	2·99 [b]	4	0·00719	0·00726	+1·0
RbCl	1·00 [a]	4	0·00871	0·00880	+1·0
	3·2 [b]	4	0·00737	0·00711	−3·5
CsCl	1·00 [a]	4	0·00866	0·00880	+1·6
	3·2 [b]	4	0·00756	0·00711	−5·9
Me_4NCl	2·66 [b]	0	0·00929	0·00928	−0·1
KI	1·00 [c]	4	0·00877	0·00878	+0·1
	2·00 [c]	4	0·00819	0·00799	−2·4

[a] Ref. 9. [b] Ref. 7. [c] Ref. 8. [d] Ref. 4. [e] Ref. 6.

* Slope obtained from results at two temperatures only and therefore less reliable than the remainder which were obtained from results at several temperatures. † Second calculation includes hydration of sulphate ion. $F = 0$ in both cases.

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[50] J. W. Akitt, *J. Chem. Soc.* (*A*), 1971, 2347.

[51] A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, 1967, **43**, 97.

[52] I. V. Radchenko and A. I. Ryss, *Zhur. strukt. Khim.*, 1965, **6**, 731 (English translation).

means also that we can no longer regard the proton–ion distance as constant but that this must vary with temperature. The X-ray data suggest that this distance will increase by *ca.* 6 pm between 0 and 100 °C leading to a small reduction in δ_S. Shifts were thus calculated by use of different δ_S values for each temperature and the slopes were calculated for Li^+ and Na^+ from a modified form of equation (3), namely (4). The correction factor

$$d(\delta_{obs})/dT = [d(\delta_N)/dT]\left[1 - \frac{m}{55\cdot5}(0\cdot95h + Fz/2)\right] \quad (4)$$

was negligible for the larger alkali-metal cations.

This approach gave generally satisfactory agreement between experimental and calculated shifts for many salts of sodium and potassium (Figure 3) with the calculated result falling close to the densest part of the clusters of experimental results, usually the most recent work. The exceptions were NaI, for which no reason can be given, lithium salts, RbCl, and CsCl.

The crystallographic octahedral radii of the ions were used for the calculations of δ_S. The tetrahedral radii will be slightly less but this introduces negligible error for all but lithium. Accordingly the lithium water shift was recalculated taking a radius of 51 pm, the smallest radius which can be suggested on the basis of the measured Li–O distance in Li_3PO_4 where the lithium is four-co-ordinate.[53] In addition it was found necessary to postulate pyramidal co-ordination. This model then gave very good agreement with experiment and predicted the changes in sign of salt shift observed between 25 and 100 °C, Figure 3.

The measured shifts for rubidium and caesium chloride are lower than the calculated ones. That these two salts do not follow the trend of the earlier alkali metals has been recognised previously.[9] This is presumably associated with the generally accepted structure-breaking properties of these cations which will lead to a reduction in the high-field cation structural shift and consequent reduction in molal salt shifts. The line of Figure 1 can thus be redrawn to curve as shown broken to accommodate this change in ionic properties.

The slopes calculated by use of equation (4) for a number of solutions at various concentrations are given in Table 5. In interpreting Table 5 it should be borne in mind that a change in h of ±1 alters the slope by *ca.* 2·1% for a 1 molal solution and 7·4% for a 3 molal solution. The slopes have typically been determined within a quoted error of $\pm2\cdot5\%$. Only four of the values in Table 5 fall outside the combined limits (0·95m- and 2·37m-$CaCl_2$, 0·97m-LiBr, and 3m-$NaClO_4$). The slopes therefore are consistent with a hydration number of 4 for the alkali metals. Interestingly the slopes of the sulphate solutions are too small to be accounted for in terms of cationic hydration alone and give confirmatory evidence of the formation of strong hydrogen bonds to four molecules of water. The contrast with the apparently very similar perchlorate anion is as marked in the n.m.r. results as in the Raman and i.r. spectra.[46-48]

Slopes have been determined for lithium bromide solutions up to very high concentrations where there can be virtually no normal water present and the model breaks down. Here the chemical shift is only slightly temperature-dependent (slope *ca.* 0·002 p.p.m. K^{-1}) suggesting that most of the water hydrates the cations and confirming that this water is certainly much less affected by temperature than is the normal water. ^7Li shift measurements are in accord with this picture in that they indicate that the hydration changes very little over a large range of concentration.[54]

The plots of chemical shift against temperature obtained at different salt concentrations have been shown all to intersect for each salt close to a single point.[4-8] The chemical shift δ_I at which this occurs has been suggested as being equal to the chemical shift δ_S of the hydration water, though a measurement of an actual shift for $Al(H_2O)_6{}^{3+}$ has shown that this is not the case.[15] Equation (2) gives the relation (5). Thus δ_S is always to

$$\delta_S = \delta_I\left(1 + \frac{Fz}{2h}\right) \quad (5)$$

low field of the shift at which the intersections occur. Equation (5) in general gives values of δ_S in agreement with those estimated here (Table 2) although for lithium δ_S is larger if obtained in this way, an observation which justifies the manner in which the shift of the lithium hydration water was recalculated above.

Thus we can summarise these results as follows: chemical shifts of the alkali-metal solutions reflect mainly the ionic structure-breaking effects and are insensitive to the actual cationic hydration number. Hydration numbers can however be estimated from the temperature dependence of the shifts if the anionic structural effect is taken into account and this suggests that h is close to 4 and certainly not greater than 5 or less than 3. N.m.r. thus presents a model where the ionic co-ordination number is relatively constant but where the intensity of the ion–water interaction decreases as the ionic size increases.

Ammonium Ions.—The two ions Me_4N^+ and H_4N^+ are both large and like Rb^+ and Cs^+ do not follow the trend of increasing high-field water shift with increasing ion radius which is shown by the earlier members of the alkali-metal series. In the case of Me_4N^+ it appears that the hydration is so weak that normal water persists right up to the surface of the ion. There is no hydration in the sense that this may be detectable by n.m.r. shift data and this view is substantiated by the small effect that Me_4NCl has upon the shift–temperature dependence of the solvent and which can be accounted for purely on the basis of an anion effect.

In the case of the simple ammonium ion, which one would expect to be tetrahydrated, the shift from pure water is even less. This must arise because the ammonium cation possesses exchangeable protons which

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[53] R. W. G. Wyckoff, 'Crystal Structures,' Wiley, New York, 1965, vol. 3.

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will also perturb the water shift. Exchange is retarded in acidic solution and a measurement in 2M-hydrochloric acid indicates that the ammonium protons resonate 2·26 p.p.m. to low field of pure water. Inclusion of the ammonium protons in a calculation based on a tetrahydrated NH_4^+ leads to good agreement with the experimental results. This correction appears to have been overlooked in previous work.

Anomalous Salts.—A number of salts give water shifts which are appreciably to low field of the calculated values. These are invariably salts of cations which undergo extensive hydrolysis, such as aluminium and beryllium,[55] or are salts of weak acids which have decidedly alkaline solutions such as phosphates, or which raise the solution pH by hydrolysis such as acetates and fluorides. The chemical shift of the hydrated proton and of the hydroxide ion are both strongly to low field and hydrolysis must contribute to the observed shifts. Hydrogen bonding to the anions of the weak acids may also be important,[46] while the small, highly charged cations may induce shifts in a second hydration sphere. The model (2) would not however be expected to apply to such solutions. The absolute shift of the proton is considered in the following paper so that its effect on hydrolysis can be accurately estimated and detailed consideration will then be given to the problem of the shift in solutions of Al^{3+}.

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