Temperature Dependence of Proton Chemical Shifts in Aqueous Silver Salts. The Association Shift of Water

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^1H N.m.r. chemical shifts are reported for aqueous $AgNO_3$ and $AgBF_4$ between 15 and 100°. The salts have a very small influence on the chemical shift of water and the cationic hydration number is apparently less than unity. The small shift is attributed to almost exact cancellation of upfield anionic and downfield cationic contributions. The calculated cationic hydration water shift is unusually large and cannot be accounted for by the ionic electric field alone. Since the hydration complex cannot have spherical symmetry it is proposed that the dipole moment induced in the hydration water by the ionic field cannot be ignored and acts as an anti-screening mechanism which increases the hydration water chemical shift. The introduction of this anti-screening effect into calculations of the association shift of water results in close agreement between calculation and experiment. The results appear to support bond bending and stretching rather than bond breaking as affecting the temperature dependence of the association shift.

THE nature of hydration of the argentous ion is uncertain.[1] A large proportion of the reported measurements, made using different techniques, give small hydration numbers in the range 0·3 to 1·05 and it seems generally agreed that the water is not strongly held.[2-6] Linear AgL_2 complexes are common in the inorganic chemistry of silver(I) and it is possible that the aquo complex is a member of this family, the effective hydration number being reduced by the lability of the complex.

Only one study of the effect of argentous salts on the water ^1H n.m.r. resonance appears to have been made [7] and this indicates that at 25 °C silver salts introduce very little change, in marked contrast to salts of sodium or potassium, molar solutions of which move the water resonance up to 0·1 p.p.m. upfield. It is generally agreed that the cations Na^+ and K^+ probably introduce only a small upfield contribution to the water shift, the major proportion of the upfield shift arising from structure breaking associated with the anions.[8] We have therefore to conclude that Ag^+ must introduce a downfield contribution to oppose the anionic shift. It will be shown that since the hydration number of Ag^+ is small then the calculated shift is surprisingly large, very much larger than can be accounted for by the ionic electric field alone.[8]

Previous calculations of the electric field induced chemical shifts of aquo complexes reported in the present series of papers [8-10] used the very simple model where the electric field arises entirely from the ion co-ordinated to the oxygen of the water. This model gives a good correlation between calculation and experiment for the octahedral or tetrahedral aquo complexes of Sn^{4+}, Al^{3+}, Ga^{3+}, In^{3+}, Be^{2+}, and Mg^{2+} but does not give accurate, absolute results. This is hardly surprising since it ignores the contribution of the water electric moments to the electric fields and these are appreciable.[11] The simple model can nevertheless be justified on the grounds that all the complexes so far considered have pseudo-spherical symmetry about the ion so that the electric moments of first and second hydration sphere form essentially closed, neutral spherical charge distributions and so have no net effect. If however Ag^+ forms a linear 1 : 2 or a 1 : 1 complex then the local symmetry is not spherical, the previous simplifying assumptions are no longer valid and we must expect to have to take account of all local electric fields.

We examine first the temperature dependence of the proton chemical shift and estimate a hydration number using Malinowski's method [12] with an anionic correction [8] and then construct a model which gives the correct absolute shift. The details thus revealed make it possible for the first time to calculate a good value for the association shift of water. The significance of the results for the spherical aquo complexes is also discussed.

EXPERIMENTAL

^1H N.m.r. chemical shifts were measured with Me_4N^+ as standard,[10] on a Bruker HFX3 spectrometer operating at 90 MHz. Sample temperatures were measured using the Bruker temperature controller. The accuracy of an individual measurement is ±0·005 p.p.m. and has been discussed previously.[10] Solutions were made up by weight from $AgBF_4$ (G.P.R.) and $AgNO_3$ (AnalaR) as received.

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[1] Gmelin, Handbuch der Anorganischen Chemie, No. 61 A3, p. 70.

[2] E. Darmois, *J. Chim. Phys.*, 1946, **43**, 1.

[3] G. Sutra, *J. Chim. Phys.*, 1946, **43**, 189.

[4] H. M. Feder and H. Taube, *J. Chem. Phys.*, 1952, **20**, 1335.

[5] G. Journet and J. Vadon, *Bull. Soc. chim. France*, 1955, 593.

[6] A. N. Campbell, J. B. Fishman, G. Rutherford, T. P. Schaefer, and L. Ross, *Canad. J. Chem.*, 1956, **34**, 151, 158.

[7] J. C. Hindman, *J. Chem. Phys.*, 1962, **36**, 1000.

[8] J. W. Akitt, *J.C.S. Dalton*, 1973, 42, and references quoted therein.

[9] J. W. Akitt, *J.C.S. Dalton*, 1973, (a) p. 49, (b) p. 1177.

[10] J. W. Akitt, *J.C.S. Dalton*, 1973, 1446.

[11] C. A. Coulson and D. Eisenberg, *Proc. Roy. Soc.*, 1966, **A291**, 445.

[12] E. R. Malinowski, P. S. Knapp, and B. Feuer, *J. Chem. Phys.*, 1966, **45**, 4274.

The internal standard was Me_4NNO_3 used at 0·05—0·1M and prepared from Me_4NOH and HNO_3. The chemical shifts of deuterium in D_2O and of hydrogen in H_2O were compared over a range of temperatures between 30 and 100° using a Bruker deuterium lock and proton Fourier Transform equipment. The deuterium resonance from a D_2O capillary was used to lock the magnetic field and the position of the H_2O resonance determined in a series of single pulse experiments with a resolution of 0·05 Hz per address. The results at any one temperature fell within $\pm 0{\cdot}001$ p.p.m. though errors are likely to be greater than this due to distortions of the capillary and changes of resolution with temperature. Calculations were carried out on the Leeds ICL 1906A computer using a short programme designed to obtain the electric field strength and direction relative to any O–H bond due to an assembly of any number of point charges.

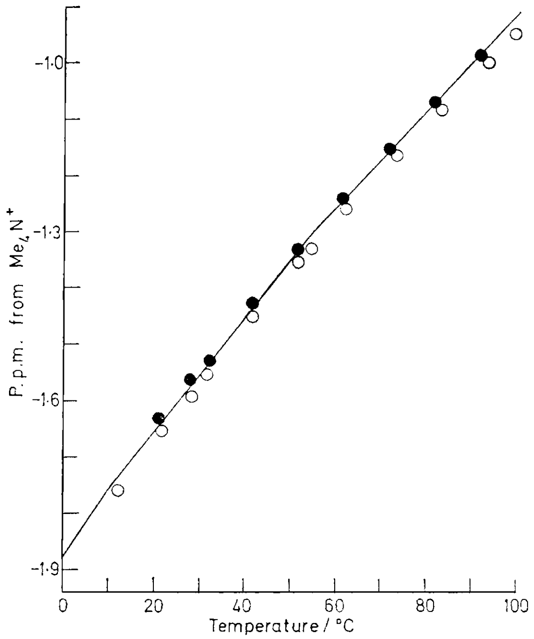

FIGURE 1 ^1H N.m.r. chemical shifts of molar silver nitrate (●) and fluoroborate (○) at different temperatures. The full line is the chemical shift of pure water

RESULTS

The chemical shift results for the silver salts are in Figure 1. The result for $AgNO_3$ at 25° is close to Hindman's value.[7] The marked change of chemical shift temperature coefficient that occurs between 25 and 75° is again evident in these results.[10] Hydration numbers may be estimated from the gradients of the lines using the expression (1),

$$h + F/2 = -\left(\frac{d(S_{obs})}{dT} \cdot \frac{55{\cdot}5}{m}\right) \Big/ \frac{d\delta_N}{dT} \qquad (1)$$

where h is the cationic hydration number, F is an empirically determined anionic factor which quantifies the anionic upfield and structural influences,[8] $d\delta_N/dT$ is the gradient of the plot for pure water, and $d(S_{obs})/dT$ the rate at which the observed shift for the solution deviates with temperature from that of pure water, both at temperature T; m is the molality. F is 1·42 for NO_3^- and can be estimated as 2·0 for BF_4^- using Symons' results.[13] The results are summarised in Table 1 and indicate a hydration number of less than unity. The results might possibly be influenced by ion pairing in $AgNO_3$ but this is too small in extent significantly to affect the figures,[14] indeed even the extensive formation of a linear ion pair $(NO_3^-)(Ag^+)(H_2O)$ would be expected to have little effect on either h or the co-ordinated water shift.

TABLE 1

Hydration number of Ag^+

		Hydration numbers	
Solute	$F/2$	Total	Cationic
$AgNO_3$	0·7	1·4	$0{\cdot}7 \pm 0{\cdot}3$
$AgBF_4$	1·0	1·54	$0{\cdot}54 \pm 0{\cdot}35$

An experimental value for the shift δ_S of the hydration water may be estimated in two ways,[8] either (a) from equation (2) where S_{obs} is the shift from pure water, and δ_N that of pure water from ethane gas at the same

$$S_{obs} = \frac{m}{55{\cdot}5}\,[h\delta_S - \delta_N(h + F/2)] \qquad (2)$$

temperature or (b) from the shift δ_I (ethane scale) where the plots for pure solvent and solution intersect, *i.e.* where $S_{obs} = 0$. We use equation (3). The results for δ_S are summarised in Table 2, for $h = 0{\cdot}7$, 1·0, and 2·0.

$$\delta_S = \delta_I(1 + F/2h) \qquad (3)$$

The comparison of the shifts of H_2O and D_2O indicated that between 31 and 93° the H_2O shift moves upfield slightly more slowly with increase in temperature than does that of D_2O, the relative change amounting to $0{\cdot}017 \pm 0{\cdot}001$ p.p.m. Thus the shift temperature coefficients of the two liquids are the same within 1·7%. The change observed is similar in magnitude to that which occurs for the ^1H resonance of HOD in D_2O,[15,16] and may be a small isotope effect due to the small differences in the dimensions of H_2O and D_2O.

TABLE 2

Chemical shifts of water co-ordinated to Ag^+

Estimated from experimental data

	Chemical shift/p.p.m.[a,b]		
Solute	$h = 0{\cdot}7$	$h = 1$	$h = 2$
$AgNO_3$	−9·0, −8·6	−7·5, −7·3	−5·8, −5·8
$AgBF_4$	−9·0, −8·7	−7·6, −7·2	−5·8, −5·4

Calculated from different models

Model [c]	$\Delta\delta_E$/p.p.m.[d]
(a) Shift due to field of Ag^+ alone	−0·98
(b) Includes induced dipole of water A	−6·32
(c) Includes total dipole of water A	−26·38
(d) Field due to Ag^+ and water B (no own dipole)	−2·72
(e) As (d) but includes own induced dipole of A	−8·48

[a] Ethane standard. [b] The first figure of each pair was obtained using equation (2) and the second from equation (3). [c] Refer to Figure 2. The models are lettered as in the text. [d] This figure gives the shift relative to the free water molecule. The chemical shift of steam is *ca.* 0·2 p.p.m. upfield of ethane.

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[13] J. Davies, S. Ormondroyd, and M. C. R. Symons, *Trans. Faraday Soc.*, 1971, **67**, 3464.

[14] A. N. Campbell and E. M. Kertznark, *Canad. J. Chem.*, 1955, **33**, 887.

[15] A. Merbach, *J. Chem. Phys.*, 1967, **46**, 3450.

[16] R. L. Duerst, *J. Chem. Phys.*, 1968, **48**, 2275.

The proton resonance of 6M $AgBF_4$ was also obtained at temperatures down to $-50°$ where solidification took place. No separation of a resonance due to bound water was observed, as would be expected for a labile complex.

DISCUSSION

The Silver Salt Solutions.—The n.m.r. results emphasise that the hydration of Ag^+ should be regarded as quite different to that of the alkali metals. In the case of the latter the co-ordination appears to be determined by the surrounding tetrahedral water structure whereas Ag^+ may reject this stereochemistry, presumably because of its tendency to linear co-ordination. It is not possible therefore to extend the previous calculations of the electric field induced shifts to the case of Ag^+ since the complex is no longer spherical. Instead we have to attempt the much more difficult task of calculating the absolute shift of the water co-ordinating the ion.

Values of δ_S were calculated for several simple models using Buckingham's equation (4), where $\Delta\sigma_E$ is the electric field shift increment, E is the electric field at the

$$\Delta\sigma_E = -AE\cos\theta - BE^2 \qquad (4)$$

hydrogen nucleus and θ is the angle between field direction and OH bond.[17] A and B are constants whose values have been discussed previously.[8] In order to obtain a roughly 1 : 1 correlation between calculation and experiment the value of A used in earlier papers was $2{\cdot}0 \times 10^{-12}$ e.s.u. If an absolute value of shift is required however it is probably better to adopt the more generally accepted value for A of $2{\cdot}5 \times 10^{-12}$ e.s.u., B remains at $0{\cdot}75 \times 10^{-18}$ e.s.u. [in S.I. $A = 0{\cdot}75 \times 10^{-6}$ m^2 C^{-1} and $B = 0{\cdot}0675 \times 10^{-6}$ m^4 C^{-2} provided equation (4) is written $\Delta\sigma_E = 4\pi\varepsilon_0 AE\cos\theta - 16\pi^2\varepsilon_0{}^2BE^2$]. The models used for calculation were based on Figure 2.

The electric field at molecule A will arise from the ion and from the surrounding water molecules, primarily those in the second hydration sphere. These latter will be polarised in the same way as bulk water but with an additional component with spherical symmetry around the ion. To a first approximation therefore we can ignore the dipoles induced by the ion in the second hydration sphere molecules and consider them as having only the normal total dipole moment of liquid water. The electric field at the centre of molecule A due to co-ordinated molecules can also be surprisingly small. If two molecules are co-ordinated to the hydrogens of A and oriented with the negative ends of their dipoles pointing towards the ion then the field is only $0{\cdot}0028 \times 10^6$ e.s.u. and any polarisation of A by this field can be neglected. The field at the hydrogens of A due to the co-ordinated molecules is of course much larger since they are very much closer to the dipole centre. Results are presented in Table 2 for shifts in A due to (a), the field of the ion alone, *i.e.* the usual simple model; (b), the field of the ion plus that of the dipole μ_I induced in A by the ionic field; (c), the field of the ion plus that of the total dipole moment of A; (d), the field of the ion plus that of the total dipole moment of B; (e), as (d) but including the dipole induced in A by the ionic field.

The electric dipole moment of the water molecule was represented as a simple extended dipole 50 pm in length situated at the centre of the molecule so that the ends of the dipole lie in volumes of high charge density. The model gives a higher electric field at short distances than a point dipole and is probably the best representation for the present purpose, particularly where we calculate the effect of the induced dipole moment on the hydrogen in the same molecule—we will call this the own hydrogen and own dipole in what follows. The model is not realistic for the total moments of neighbouring water molecules[18] but some estimate of the error involved can be made using previous calculations[11] and is small compared with the effect of the own dipole. The permanent dipole moment μ_P was taken as $1{\cdot}83$ D, $\mu_I = 0{\cdot}416$ D in molecule A and $0{\cdot}62$ D in molecule B.

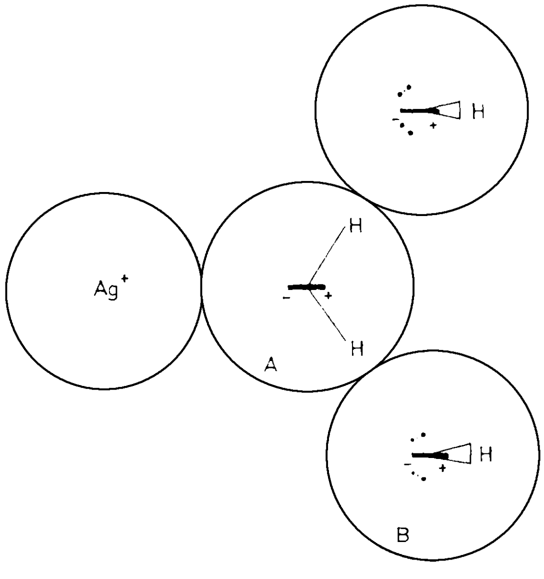

FIGURE 2 Model used for the calculation of the chemical shift of $Ag(OH_2)^+$

A further assumption is also implicit that μ_I is collinear with μ_P though there is no reason why this should be so except that on average this situation produces an energy minimum.

In the absence of any knowledge of the detailed structure of the solvent around Ag^+ we can only expect these calculations to suggest which model may be most likely. The picture most consistent with the known facts seems to be that a linear but labile complex $[H_2OAgH_2O]^+$ is formed in which the hydration water motion is to some extent integrated with that of the bulk solvent so that it has a rather large temperature dependence of shift and an absolute shift which is an average of bulk and hydration shifts. The models used

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[17] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

[18] D. Eisenberg and W. Kauzmann, 'The Structure and Properties of Water,' Clarendon Press, Oxford, 1969, p. 21.

are based on $h = 1$ and therefore represent an instantaneous picture of the situation which should give the maximum chemical shift. The calculated shift should therefore be somewhat larger than the estimated shift for $h = 1$. Comparison with experiment in Table 2 indicates that a reasonable result is obtained only if the electric fields of the own induced dipole and of the co-ordinated water are included [model (e)]. If the total own dipole moment is used the result is very much too high while if the own induced dipole is ignored the results are far too low. The unusual ability of Ag^+ to counteract the upfield influence of the anions despite its apparent small hydration number may thus be explained primarily in terms of the electric field of the own induced dipole.

The complete separation of the effects of permanent and induced dipoles in the manner indicated above seems somewhat surprising. It can however be justified as follows: The charge distribution, internal electric field, and chemical shift are all interlinked properties of the isolated water molecule which obey the laws of quantum mechanics. We may simply regard the external field as perturbing the molecule so as to cause electron drifts at hydrogen and at oxygen. The dipolar electric field set up by the latter drift augments the drift at hydrogen and acts as an anti-screening mechanism which for instance can account for the very high value of the constant A in equation (4) which has been estimated for some phenolic OH groups.[19] This can be concluded from the following order-of-magnitude calculation. If a uniform electric field E is calculated to exist along an OH bond in an *o*-phenol then the observed shift σ_a between *o*- and *m*-phenols, can be explained by putting A in equation (4) equal to 25×10^{-12} e.s.u. Ignoring the smaller quadratic term and the directional effects we have

$$\sigma_a = -25 \times 10^{-12}E \qquad (5)$$

The field E will however induce a dipole moment μ_I at the centre of the oxygen. $\mu_I = \alpha E$ where α is the polarisability of the OH group. μ_I will also produce an electric field E' at the hydrogen atom which if r is the O–H distance is given by equation (6). Substituting

$$E' = 2\alpha E/r^3 \qquad (6)$$

$\alpha = 1{\cdot}4 \times 10^{-24}$ cm^3 and $r = 0{\cdot}96 \times 10^{-8}$ cm we find $E' = 3{\cdot}16E$ so that the total field at the hydrogen atom is $4{\cdot}16E$. We can now recalculate σ_a from equation (4)

$$\sigma_a = -(4{\cdot}16E)A - 0{\cdot}75 \times 10^{-18}\,(4{\cdot}16E)^2$$

substituting for σ_a from (5) we obtain (7).

$$4{\cdot}16A = 25 \times 10^{-12} - 13 \times 10^{-18}E \qquad (7)$$

This cannot be solved in the absence of details of the calculations of Bernstein *et al.* though the substitution of a typical value of E, say $E = 1 \times 10^6$ e.s.u. gives $A = 2{\cdot}8 \times 10^{-12}$ e.s.u., within the accepted range for H_2O and for CH bonds. The concept of antiscreening the proton in water is of some importance, as will be shown below it can account closely for the association shift of water.

The Association Shift of Pure Water.—It has been suggested that the association shift of water is almost entirely an electric field effect which arises because of its tendency to form directed hydrogen bonds.[20-22] The order of magnitude of the local electric field is correct but detailed calculations give an electric field strength which can account for only a third of the observed shift.[11] Hindman[23] has suggested that in order to support a hydrogen-bond breaking mechanism in water the calculated shift needs to be about $-5{\cdot}4$ p.p.m., though reasonable values of the dipole moment were calculated to provide a chemical shift at a neighbouring molecule of only half this value.

If the electric field hypothesis is to be maintained then it appears that some means of augmenting the electric field has to be found and that the own induced dipolar field may well provide the key to the problem. Some support for this view can be obtained from Figure 3 which is a correlation diagram of dielectric constant and chemical shift over 0—100 °C. Both quantities are distinctly non-linear functions of temperature[10,23,24] but are correlated by an almost precisely straight line between 20 and 100 °C. The relationship between shift and dielectric constant is $\delta = 0{\cdot}030636\varepsilon - 0{\cdot}79046$ and the chemical shift results fall within experimental error of this line, the major part of the deviations shown in Figure 3(b) appearing to arise from the author's practice of representing the chemical shift of water by two straight lines, rather than a continuous curve.

Any calculations of the association shift of water should attempt to reproduce both the correct absolute shift and the correct temperature dependence. There will be several contributions to the absolute shift such as magnetic anisotropy and van der Waals effect but Hindman's calculations indicate that the hydrogen bond shift is the dominant one.[23] Several views exist as to the cause of the variation of shift with temperature and any or all bond bending, bond stretching, and bond breaking may be important.[22,23,25] There is however an important difference between the first two and the bond breaking hypothesis. Bond bending or stretching leads to all the water hydrogen atoms having much the same environment and chemical shift. There will be variations about a mean but these should not be more than, say, 1 p.p.m. If bond breaking is the dominant process then some hydrogen atoms will have a shift appreciably greater than the observed shift while those which partake

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[19] A. D. H. Clague, G. Govil, and H. J. Bernstein, *Canad. J. Chem.*, 1969, **47**, 625.

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

[21] J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.*, 1951, **A205**, 155.

[22] J. A. Pople, *Proc. Roy. Soc.*, 1951, **A205**, 163.

[23] J. C. Hindman, *J. Chem. Phys.*, 1966, **44**, 4582.

[24] C. G. Malmberg and A. A. Maryott, *J. Res. Nat. Bur. Stand.*, 1956, **56**, 1.

[25] N. Muller and R. C. Reiter, *J. Chem. Phys.*, 1965, **42**, 3265.

in broken bonds may have zero, or even upfield shifts, the observed shift being the average over both environments. Thus, if we can calculate reasonable values for the shifts using bending and stretching only, then the existence of marked bond breaking is in question whereas if the calculated shift is unduly large we must accept the presence of bond breaking. To date no calculations have been presented which support a bond breaking hypothesis.

Pople's bent bond model has been successful in predicting several of the properties of liquid water,[22] and the calculations in the present paper are based on this model (Figure 4). Thus two water molecules are situated a distance R apart with an OH bond of one and a lone pair of the other at an angle ϕ to the O–O axis. The dipole moments considered are the induced moment μ_I in A and the total moment $\mu_I + \mu_P$ in B. R, ϕ, and μ_I are all temperature dependent. The value of μ_I is not accessible to measurement but can be estimated *via* calculations of the dielectric constant of water. Eisenberg and Kauzmann have made a correction to Pople's calculations [22,26] which give a good description of the temperature variation of dielectric constant and suggest values for $\mu_P + \mu_I$ of 2·45 D at 0 °C and 2·37 D at 83°. R can be estimated from the X-ray radial distribution curve for liquid water and values of R = 282 pm at 0° and 287 pm at 83° were used.[27] The values of ϕ given by Pople are $\phi = 26°$ at 0 °C and, by interpolation, $\phi = 29{\cdot}3°$ at 83 °C.[22] A dipole length of 50 pm was chosen as above and the H–O–H angle used was 105 °C.

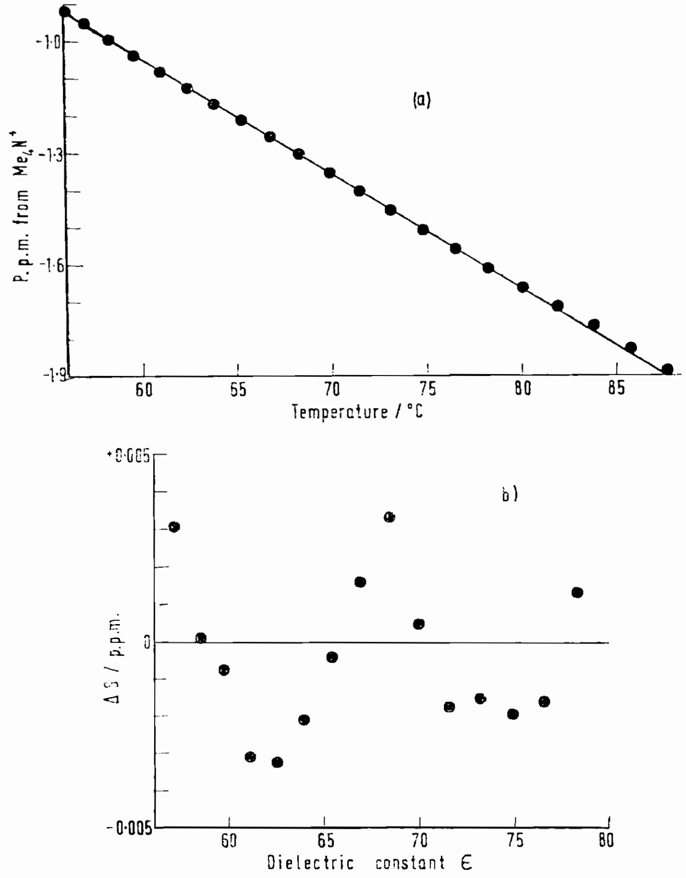

FIGURE 3 (a) Correlation diagram between dielectric constant and chemical shift of pure water over a range of temperatures; (b) deviation of δ from the straight line of (a)

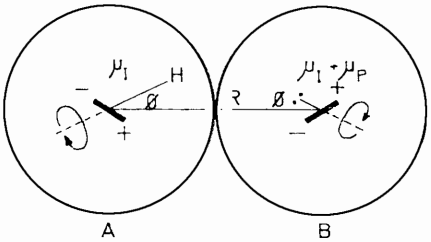

FIGURE 4 Model used for the calculation of the association shift of pure water

The electric field of other water molecules was ignored since by far the greatest contribution to $\Delta\sigma_E$ comes from the own dipole and the nearest neighbouring dipole. The remaining nearest neighbours contribute less than 8% of the field with a component nearly normal to the OH bond. Another possible source of error is that the direction of the induced dipole will fluctuate about that of the permanent dipole as the whole system reorients and the method of calculation implies that these fluctuations will average out and that the bent bond conformation tends to be retained between orientational jumps.

The value of shift calculated varies within a range of ±0·4 p.p.m. depending upon the orientation of each water molecule around the OH and electron pair bond axes, since the orientation of the water dipoles varies and also because the shift depends upon the angle between field direction and OH bond [equation (4), the angular dependence of $\Delta\sigma_E$ in fact provides a most compelling reason why we should test the bent bond model]. The shift was therefore calculated as an average over a rotation of both molecules around the axes shown as dashed lines.

The result of this calculation is compared with experiment in Table 3, where it will be observed that the bent bond-induced dipole model predicts the absolute shift within 0·6—0·7 p.p.m. and the temperature dependence within 15% of the measured value. This

TABLE 3

Calculated chemical shifts of water at 0 and 83°

Temperature/ °C	Chemical shifts/p.p.m.[a] Calc.	Measured	Overall temperature coefficient/p.p.m. K^{-1} Calc.	Measured
0	−3·89	−4·60	0·0084	0·0099
83	−3·19	−3·78		

[a] The calculated shift refers to the free water molecule and the measured shift is referred to steam.

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[26] Ref. 18, p. 193.

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

agreement between calculation and experiment is remarkably good considering the crudity of the model. If one adds to the calculated shift a value for the van der Waals contribution, which Hindman believes lies in the range $-0{\cdot}2$ to $-0{\cdot}54$ p.p.m.,[23] the agreement with experiment becomes very close indeed.

Other models were tested but it was found always essential to include the own induced dipole otherwise shifts and their temperature dependencies were too small. Calculations using a tetrahedrally co-ordinated water molecule with linear bonds gave somewhat lower results and in any case the tetrahedral model is not correct for liquid water. It was not possible to obtain a shift large enough to support a bond breaking hypothesis without assuming a larger total dipole moment $\mu \geqslant 2{\cdot}6$ D, more appropriate to ice.[28] Alternatively A would need to be increased to $3{\cdot}5 \times 10^{-12}$ e.s.u.

These results thus do not support a structure for water in which hydrogen bonds are completely broken but indicate the existence of an extensive though distorted or collapsed ice-like structure with all the water molecules in similar environments. It is difficult to envisage the existence of rapid molecular reorientation in liquid water without hydrogen bond breaking but it appears that the broken bonds must be very short-lived, the structures changing rapidly and co-operatively from one ice-like arrangement to another as envisaged by Frank. This is perhaps not surprising since in order to obtain the necessary zero or upfield shift on bond breaking one has to rotate the water molecule through a large angle (*ca.* 180°) into a position that is very unstable energetically. If this view is correct we can also see that as the temperature increases and the rate of motion increases there is no particular reason why the proportion of time spent in the broken bond state should increase or why bond breaking should markedly affect the temperature dependence of chemical shift. Further support for this view is obtained from the results comparing the temperature dependencies of H_2O and D_2O. If the association shift is purely electrostatic in origin then one would expect little difference between them, as is observed, whereas if a bond with any degree of covalency were formed then we would expect to see an appreciable isotope effect.

Chemical Shifts of Aquo Complexes.—We will now examine how the own induced dipole contributes to the water shift of octahedral and tetrahedral aquo complexes. The field at a hydrogen atom in such a complex arises from the ion, the total dipoles of the other water molecules and from the own induced dipole μ_I. The magnitude of μ_I is smaller than would be expected from the ionic field alone since the total dipoles on the other water molecules oppose the ionic field. The polarisation and calculated chemical shift are reduced some 40% for this reason, though the latter is even then 2·5 times too large in the case of $Al(H_2O)_6^{3+}$. It appears that the polarisation μ_I will depend upon the precise location of charge in the water molecules, that the simple real dipole model is insufficient and that calculations should be based upon a more extended charge distribution that would more nearly approximate spherical symmetry and so reduce the electric fields and the polarisation. In other words the original simplifying assumption of spherical symmetry [8] is probably quite close to reality. The second hydration sphere will have no influence on the first sphere shifts in the case of the highly charged complexes since the ionic field will tend to introduce a degree of spherical orientation around the ion. In the case of the alkali metal cations however this orienting influence will become less and the second sphere will contribute to the polarisation in the first sphere. Thus, we can understand how as we move up the alkali metal series from Li^+ we first see an upfield trend in shift, which indeed probably goes upfield of water since the polarisation of hydration water by the ion is less than the mutual polarisation in bulk water,[8] and then a downfield trend for Rb^+ and Cs^+ where the polarisation of the co-ordinated water by the second sphere starts to become important. At all times of course the second sphere is polarised by the third sphere and so has a shift about equal to or sometimes lowfield of pure water.[9]

The general ability of cations to reduce or eliminate the shift–temperature dependence of co-ordinated water may also be understood using the principles outlined in this paper. The shift–temperature dependence of bulk water arises from changes in the relative orientations of pairs of molecules and from changes in μ_I which occur because of changes in the randomness of water dipole orientations. A cation however constrains the water in its first hydration sphere so that the bond bending effect is much reduced while the pseudo spherical symmetry of the hydration sphere both reduces the contribution of μ_I to the shift and reduces randomness and changes in μ_I. This effect seems to be restricted entirely to the first hydration sphere.[9b]

In the case of large singly charged anions we appear invariably to observe a large upfield shift. These ions increase the rate of motion of the water closest to them. If this results in any degree of isotropic rotation of the water then it is a consequence of the isotropic nature of the polarisability of water that the induced dipole remains stationery in the ionic field while the molecule rotates about it. The field direction along the OH bond can reverse and the chemical shift move upfield and so almost vanish on average.[29] Thus the F factor which quantifies the anionic influence can also be thought of as measuring the reduction in local co-operative motion of water molecules.

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[28] Ref. 18, p. 110.

[29] See equation (2) in ref. 9(b).