Temperature Dependence of Proton Chemical Shifts of Aqueous Sodium Fluoride, Sodium Hydroxide, and Tetramethylammonium Hydroxide: The Internal Tetramethylammonium Ion Standard

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Proton chemical shifts have been determined over a range of temperature for water, and for aqueous sodium fluoride and sodium or tetramethylammonium hydroxide solutions using Me_4N^+ as an internal standard. The water results agree closely with those of Hindman and confirm that the shift temperature dependence is not constant over the range 0—100 °C. The shifts of NaF solutions can be explained by including a downfield shift increment arising from the electric field of the fluoride ion; the latter is the only unicharged anion for which such an effect has been detected. The absolute shift of the hydroxide ion was estimated from the results assuming it introduces the same low-field increment in its co-ordinated water. It is 14·2 p.p.m. low field of C_2H_6 and is probably slightly less descreened than H_3O^+. The presence of ion-pairing in sodium hydroxide solutions is confirmed.

THE measurement of proton chemical shifts of aqueous electrolyte solutions has generally been undertaken using external standardisation. True shifts are small, in many cases smaller than the necessary and somewhat uncertain bulk diamagnetic susceptibility corrections, and precise values are difficult to obtain. Published results thus contain a high degree of scatter, demonstrated by figure 1 of ref. 1. Recently, satisfactory results appear to have been obtained using Me_4N^+ as an internal standard.[2-4] This allows precise measurements to be made with ease and, if low concentrations of standard are used, should not measurably effect either the absolute shift or the shift temperature dependence.[1,3] This cation also has the advantage of being soluble in acidic media and gives results identical with those for aluminium salt solutions and an external standard.[5]

The utility of the Me_4N^+ standard can best be checked by using it to redetermine the shift of water. There is however some controversy regarding the exact form of the water shift temperature dependence; it may be constant between 0 and 100 °C,[6,7] or it may fall as the temperature increases.[8] The different sets of results are very close and the different interpretations arise from differences between only two or three experimental points. It is possible that internal standardisation might resolve this controversy.

Proton chemical shifts of sodium fluoride solutions are low field of water, whereas the other sodium halide salts all introduce high-field shifts.[3] It was not possible to account for this in terms of a previous model,[1] since the fluoride ion should introduce a high-field shift due to solvent structure-breaking effects, just as do the larger unicharged anions. Refinement of the model is however frustrated by existing data which differ considerably,[3,9,10] so that the shifts have had to be redetermined.

Chemical shifts of sodium hydroxide solutions are even further to low field [9,10] due to the large low-field contribution of the proton in the hydroxide ion; this has been estimated previously as having the same shift as that of H_3O^+.[10] However, just as the true shift of H_3O^+ is obscured by anion effects,[11] so that of OH^- is obscured by cation effects and realisation of this, together with the adoption of internal standardisation, should allow a much more accurate estimate to be made of the true shift of OH^-.

EXPERIMENTAL

Measurements were made at 90 MHz using a Bruker HFX90 frequency-swept spectrometer equipped with a Bruker variable-temperature device. This was calibrated using ethylene glycol. The spectrometer was locked to the water signal using an internal-lock facility and the chemical shift measured of the Me_4N^+ triplet (J 0·6 Hz), care being taken to select the centre resonance for each measurement. The spectrometer was set on the resonance peak and the frequency difference between lock and spectrum channels measured to 0·1 Hz with a counter. The process was repeated several times until steady readings within 0·2 Hz were obtained. The errors in a single measurement were ±0·1 Hz from the counter round-off, and ±0·1 Hz in selecting the resonance maximum, giving a random error of ±0·002 p.p.m. A larger error arose from the temperature measurements. This may be expressed as a shift error based on a shift temperature dependence of 0·01 p.p.m. per degree. The temperature could be read to 0·5 °C and seemed reproducible to this figure, implying an error of ±0·005 p.p.m. In addition a systematic error was possible, specified by the makers at up to 2 °C, a possible error of 0·02 p.p.m. However measurements made on separate days, with and without liquid-nitrogen cooling of the heat-exchanger gas, and while progressively raising or lowering the temperature, almost invariably fell within ±0·005 p.p.m. of the average shift and this is probably a good estimate of the error on each measurement.

Work with hydroxide solutions is fraught with the difficulty of excluding carbon dioxide. The chemical shift of a 0·5M solution of sodium carbonate was found to be in the same direction as that of 1M-sodium hydroxide, though smaller by a factor of 0·59. A 5% CO_2 contamination of a 1M solution thus should produce only a 2% error

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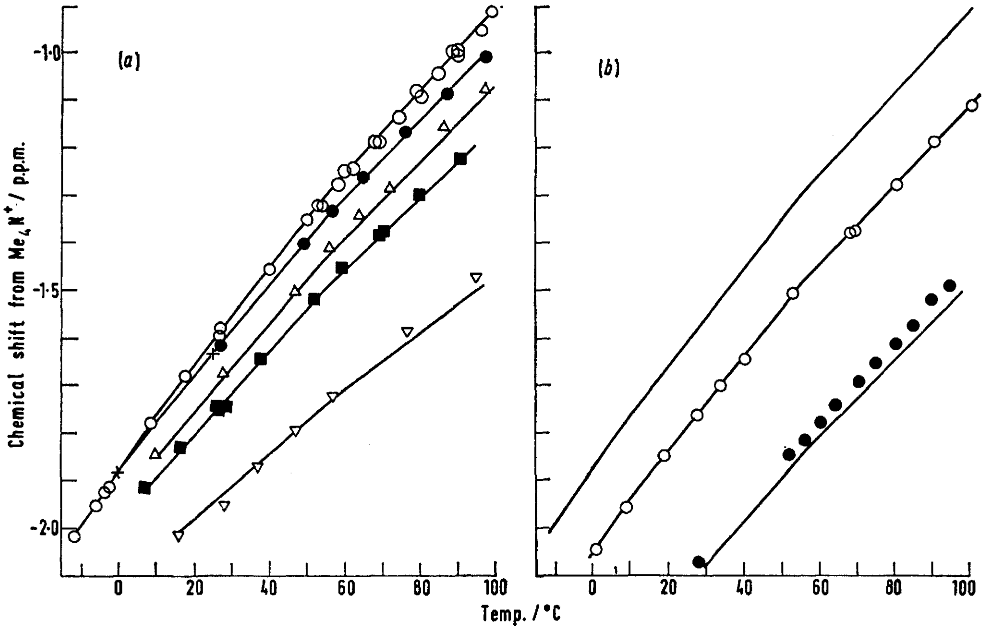
in the shift, or only *ca.* 0·002 p.p.m. For this reason no rigorous efforts were made to exclude CO_2, though fresh solutions were used and stored in stoppered vessels. Results are shown in the Figure.



Proton chemical shifts of water and some electrolyte solutions as a function of temperature using Me_4N^+ as standard: (*a*) (○), 0·1 and 0·037M-Me_4NCl, (●), 1·0 mol kg^{-1} NaF, (+), Symons' results, (△), 1·00 mol kg^{-1} NaOH, (■), 1·58 mol kg^{-1} NaOH, (▽), 3·99 mol kg^{-1} NaOH; (*b*) (—), the Me_4NCl results of (*a*) redrawn, (○), 1·287 mol kg^{-1} Me_4NOH, (●), 3·78 mol kg^{-1} Me_4NOH

RESULTS AND DISCUSSION

Chemical Shifts of Water.—This was determined for two solutions of Me_4NCl with concentrations of 0·037 and 0·10M, the latter concentration being used in the electrolyte solutions also. Both sets of results show unequivocally that the shift temperature dependence is reduced above 55 °C. Hindman's smoothed, corrected data,[8] normalised to coincide with the present results at 30 °C where temperature errors should be least, are almost identical with the present data, except below 10 °C. A curious feature of the present results is that they do not follow a smooth curve, the gradient changing quite abruptly at 55 °C, and possibly at 10 °C, a feature also observed on all the dilute electrolyte solutions and also evident in Hindman's results before susceptibility correction. The plot in the Figure was thus drawn as a series of connected straight lines, so simplifying the calculations. The gradient of the line for water was 0·0119 p.p.m. K^{-1} below 10 °C, 0·0103 p.p.m. K^{-1} from 10 to 55 °C, and 0·00855 p.p.m. K^{-1} above 55 °C, all ±2%. The overall gradient at 0—100 °C was 0·00968 p.p.m. K^{-1}, very similar to values quoted by those workers who believe the gradient to be a constant, *i.e.* 0·00956 [7] or 0·00958 p.p.m. K^{-1}.[6]

These results confirm that Me_4N^+ can be used with some confidence as an internal standard in dilute aqueous solutions and should give satisfactory results both for absolute shifts and shift temperature dependence, though salt effects may reduce the accuracy of the results.[12] The change in gradient observed does not invalidate previous variable-temperature measurements of electrolyte solutions, since the average gradient was virtually unchanged, though it may require that a small correction be made to the absolute shifts in the region of 30—40 °C.

The breaks in the gradient do not correspond to any marked changes in the properties of water,[13] and the chemical-shift plot seems unique in this respect. The region below 10 °C could correspond to a rapid increase in ice-like structure as the temperature falls, while above 55 °C the proportion of fully hydrogen-bonded water might be substantially reduced. These changes in $d\delta/dT$ indicate quite appreciable structural changes between 0 and 100 °C and would support a fairly large change in the degree of hydrogen bonding such as that suggested by Walrafen.[14]

Chemical Shifts of Electrolyte Solutions.—(a) *Sodium fluoride.* The results for NaF (1 mol kg^{-1}) agree closely with those of Symons [3] and earlier workers.[15-18] Malinowski's shifts all seem displaced to low field by about 0·1 p.p.m.[9] The rate at which the shift moved to low field relative to that of pure water as the temperature increased, is consistent with an effective total hydration

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number slightly greater than 4. This is consistent with a recent model [1] which shows that the change in gradient of these lines is determined by the sum of the cationic hydration number (about 4 for Na^+) and an anion structural factor F (F varies from 1 for F^- to 2·35 for ClO_4^-, see figure 2 of ref. 1) which is compounded from various solvent–anion interactions, and leads to a marked upfield shift. F is at a minimum for F^- because this ion is similar in size to a water molecule, and fluoride-ion solutions should exhibit the lowest field shifts of all the alkali-metal halide salts. However this cannot account for the reversal of the sign of the shift, which is some 0·09 p.p.m. to low field of its calculated position.[1]

The fluoride ion differs from the larger halide ions in that it is believed to interact with the solvent in some way. It may indeed form relatively strong hydrogen bonds,[19] and the rate of motion of water around the ion is reduced.[20] It is also the smallest unicharged anion and this, coupled with the restriction of motion around the ion, suggests that it should be considered whether any significant electric-field chemical shift, $\Delta\sigma_E$, may be induced in the surrounding water molecules. The quantity $\Delta\sigma_E$ has been calculated for the following four models.

(i) The water molecule is co-ordinated in the dipolar or planar configuration. This gave $\Delta\sigma_E = -1{\cdot}20$ p.p.m.[1] (the negative sign indicates a downfield shift).

(ii) The water molecule is rotating anisotropically with the hydrogen atoms remaining in the hemisphere closest to the ion. This gave $\Delta\sigma_E = -1{\cdot}23$ p.p.m.[5]

(iii) One hydrogen atom of the water molecule is specifically hydrogen-bonded to the ion. The average for the two hydrogen atoms was $\Delta\sigma_E = -2{\cdot}13$ p.p.m. The specific interaction should thus lead to a much larger observable shift. In view of the short time scale any interaction must have,[20] this situation seems less likely than that of (i) or (ii).

(iv) If full isotropic rotation of water molecules occurs then $\Delta\sigma_E$ is reduced dramatically to $-0{\cdot}04$ p.p.m.

The formation of a specific hydrogen bond stronger than the water–water hydrogen bond would of course also lead to a low-field shift. It is generally accepted however that the ultimate source of the hydrogen-bond shift in water is probably an electric field, in which case the argument as to whether the low-field component of the shift is purely electric field, or is a specific effect, reduces to finding what influence orientation has on the calculated electric-field shift increment. The net electric-field shift of course is given by the effect of the fluoride-ion field less that of the dipole field of another water molecule. In the present treatment this latter term is accounted for in the F factor for the anion.[1]

F Factors have been determined previously by separating empirically contributions to the water chemical shift of cations and anions.[1] The latter give a strong upfield contribution which can be quantified by assuming that each anion breaks F hydrogen bonds to produce half water molecules with the chemical shift of steam. The quantity F of course contains contributions from many sources, *e.g.* the bulk of the ion, the electric field of the ion, and any hydrogen-bonding interactions, but is nevertheless of use in carrying out calculations with ionic solutions. Its particular significance is that it indicates that the hydration of anions and cations should be considered quite differently.

Values of $\Delta\sigma_E$ calculated in (i)—(iv) can be taken simply as an increment to the shift of the water co-ordinating the ion. The water structure will limit this to *ca.* 4 and a simple calculation indicates that the excess of low-field shift can be easily accounted for by $\Delta\sigma_E$ (i), (ii), or (iii). In carrying out detailed calculations, however, it is necessary also to take account of the ion-pairing which probably occurs in sodium fluoride solutions.[21] * The effect of this, discussed in detail in the following section, is to destroy the anion low-field increment for paired anions and to slightly reduce the cation hydration number. Using the previous notation,[1-3] equation (1) is obtained for the chemical shift of sodium

$$55{\cdot}5\,\delta_{\mathrm{obs}} = mh_1\delta_1 + mh_aS_a + \delta_N\,[55{\cdot}5 - mh_1 - (Fm/2)] \qquad (1)$$

fluoride solutions in the absence of ion-pairing, where the δ's are shifts referred to ethane gas and S is a shift increment from water, h_1 (*ca.* 4) and δ_1 are cation hydration number and shift respectively, h_a (*ca.* 4) and S_a are anion co-ordination number and shift increment, δ_N is the shift of pure water, m is the molality, and F is the anionic structural factor. Equation (1) can be recast to give the shift S_{obs} from pure water. This is probably the most useful quantity to consider where δ_N varies non-linearly with temperature. Equation (2) is thus obtained.

$$S_{\mathrm{obs}} = \frac{m}{55{\cdot}5}\,[h_1\delta_1 + h_aS_a - \delta_N\,(h_1 + F/2)] \qquad (2)$$

If ion-pairing occurs and α is the degree of dissociation of NaF then h_1 is replaced by $4\alpha + 3(1 - \alpha)$ and h_a by 4α [see equation (4)]. If $\delta_1 = -3{\cdot}72$ p.p.m.[1] is inserted in (2), then it is found that the experimental results are well reproduced for $S_a = -1{\cdot}43$ p.p.m. [see line drawn on Figure (*a*)]. The value of S_a is larger than those calculated for models (i) and (ii), but much smaller than that for (iii). These results are thus consistent with the proposition that the fluoride ion introduces considerable restriction of water motion in its vicinity, sufficient for a large electric-field increment in chemical shift to result, perhaps even with a small proportion of longer-term specific hydrogen bonding, but nevertheless insufficient to reduce the temperature dependence of the chemical shift of neighbouring water. Finally it should be noted that, while hydrolysis may also contribute to the chemical shift,[1] the data presented in the following section indicate that the effect will be insignificant.

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* I am indebted to a referee for drawing my attention to this paper.

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(b) *The shifts of the aqueous hydroxide salts.* The shifts were all further to low field, though gradients of chemical shift against temperature plots for equimolal NaOH and NaF were almost identical. Gradients for Me_4NOH solutions were much steeper and this is attributed to lack of hydration of Me_4N^+.[1] Examination of the results, assuming that OH^- is hydrated in the same way as F^-, gave different values of the shift of the hydroxide ion, δ_{OH^-}, depending upon whether the NaOH or Me_4NOH results were used, the latter giving the larger shifts. This can be explained by the formation of ion-pairs in sodium hydroxide solutions; these are present to the extent of 7% at 0·4M.[22-24]

The effect of ion-pairing on the electric field around each ion has been calculated. The field is reduced so that (*a*) water co-ordinated to Na^+ experiences fields similar to those produced by Cs^+ (the water shift will thus be unchanged[1] though the cationic hydration number will fall to three), and (*b*) water co-ordinated to OH^- experiences fields similar to those produced by Cl^-. The water close to the anion will thus probably lose its low-field shift increment. This change is in the correct sense to explain the discrepancies in δ_{OH^-} values. It should be noted that it can be concluded from these calculations that ion-pairing in the alkali-metal halide salts, other than fluoride, will produce very little effect on the solution shifts and only a small effect on the shift temperature dependence. Solution proton shifts are thus probably not sensitive to ion-pairing except for hydroxide or fluoride salts. This accounts for the closely linear shift against concentration plots which are obtained up to about 4 mol kg^{-1} for most uni-unielectrolyte solutions.[25]

Ion-pairing would be expected to be at a minimum in Me_4NOH solutions. For this reason δ_{OH^-} can be probably obtained most accurately from them. Equation (2) has to be modified to allow for the proton introduced with OH^- and equation (3) is obtained, where δ_{OH^-} is the shift

$$S_{obs} = \frac{m}{0{\cdot}5m + 5{\cdot}55}\,[h_1\delta_1 + h_aS_a + 0{\cdot}5\,\delta_{OH^-} - \delta_N(h_1 + F/2 + 0{\cdot}5)] \qquad (3)$$

of the OH^- proton on the ethane scale. The values of h_a and S_a can be taken as similar to that of F^- (the calculated S_a value was used) and $h_1 = 0$. It is possible to argue that OH^- can only co-ordinate the hydrogenic part of three water molecules and that h_a should be three. This however implies that one should add 1 to the F factor, whereas the results do not appear to support such an increase. Substituting $\delta_{OH^-} = -14{\cdot}73$ p.p.m. in equation (3) generates the lines drawn on Figure (*b*). The fit is good for 1·287 mol kg^{-1} Me_4NOH and remains adequate for the 3·78 mol kg^{-1} solution. The value of δ_{OH^-} can thus be taken as being −14·7 p.p.m. The random errors in this value are very small, the major cause of uncertainty being the values of h_a, S_a, and F which are used, and limits of perhaps ±1·0 p.p.m. may be estimated.

Equation (3) does not reproduce the shifts or gradients of shift against temperature plots for sodium hydroxide solutions and has to be modified to take into account the existence of ion-pairing. If α is the proportion of sodium hydroxide which is dissociated, new values for h_1 and h_a can be written, as in equation (4). Values of α were

$$S_{obs} = \frac{m}{55{\cdot}5 + (m/2)}\,\{[4\alpha + 3(1-\alpha)]\delta_1 + 4S_a\alpha + 0{\cdot}5\,\delta_{OH^-} - \delta_N[1 + 4\alpha + 3(1-\alpha)]\} \qquad (4)$$

calculated at each molality for a dissociation constant of 5 mol l^{-1}, and, when inserted into equation (4), gave the lines drawn on Figure (*a*). Values of α are 0·854 (1·0), 0·799 (1·58), and 0·659 (3·97 mol kg^{-1}). Remarkably, this approach gave an extremely close fit to the experimental results, indicating that the dissociation constant of NaOH varies very little either with temperature or concentration.

A few measurements were also made at 28 °C with potassium hydroxide solutions, which appear to have shifts almost identical to those of sodium hydroxide solutions.[10] Potassium hydroxide is believed to be much less associated than is sodium hydroxide,[22] though the resulting low-field increment in shift will be opposed by the rather higher field shift of the hydration water around K^+.[1] A calculation with $\alpha = 1$ gave shifts close to the measured ones, namely at 1·6M-KOH $S_{meas} = -0{\cdot}163$ ($S_{calc} = 0{\cdot}142$), and at 3·97M-KOH $S_{meas} = 0{\cdot}351$ ($S_{calc} = -0{\cdot}346$ all in p.p.m.). These data thus support a negligible degree of association of KOH.

Chemical Shifts of Hydroxide and Oxonium (*Hydronium*) *Ions*.—These ions were originally believed to exhibit approximately equal chemical shifts.[10] The corrected result for δ_{OH^-} is −14·7 p.p.m. and that for $\delta_{H_3O^+}$ is −15·7 p.p.m. The shifts from H_2O are $S_{OH^-} = -10{\cdot}0$ p.p.m. and $S_{H_3O^+} = -11{\cdot}0$ p.p.m. The latter figure has been reduced from that previously reported[11] to allow for the electric-field effect of H_3O^+ on co-ordinated water, (about −0·7 p.p.m.) so making the two results comparable. The shifts are thus similar, but probably not exactly equal, and δ_{OH^-} is the smaller of the two, as might be expected on the basis of equation (5),[26] which can only account for the shifts if the charge

$$\Delta\sigma_E = -AE\cos 0 - BE^2 \qquad (5)$$

centres of the ions are displaced from the oxygen nucleus, towards the proton for OH^- and away from the protons in H_3O^+. This is not unreasonable and lends some support to the suggestion that the shift is mainly due to electric fields in the ions,[27] though it is doubtful whether it is really valid to apply equation (5) to a shift induced within an ion by its own electric field.

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