Proton Chemical Shift and Hydration of the Hydronium Ion in Aqueous Acids

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A new four-site model is developed to describe the chemical shifts of aqueous acid solutions which takes into account the structure-breaking effect of ions. The model predicts the differing values obtained from different acids for the chemical shift of H_3O^+ and also predicts closely the apparent variations with temperature of the measured shift. The electric field of the ion H_3O^+ produces only small chemical shifts in any hydrogen-bonded water and n.m.r. chemical-shift studies are probably insensitive to the presence of such species as $H_5O_2^+$ or $H_9O_4^+$. Measurements at different temperatures are consistent only with the formulation H_3O^+.

THE chemical shift of the hydronium cation has been estimated in dilute aqueous solutions of several strong acids.[1–13] The shift is obtained from the slope of a plot of solution chemical shift (measured relative to pure water) against the Gutowsky parameter p, which gives the concentration of protons in H_3O^+ in the system [1] [equation (1)], where x is the stoicheiometric mole

$$p = 3x/(2 - x) \qquad (1)$$

fraction of acid. The plot is linear at low concentrations of acid where dissociation is complete. Unfortunately, different acids give very different values of hydronium shift varying from −9·14 ($HClO_4$) to −14·5 p.p.m. (toluene-*p*-sulphonic acid), the principal cause of the variation being attributed to the anions.[12] All acids give increased values of H_3O^+ shift in deuterium oxide solutions, up to −16·6 p.p.m.,[9,10] and this is ascribed to a preference of H to reside on the hydronium ion.[14,15] (The shifts are all to low field of water and are given a negative sign in this paper.) The H_3O^+ shift also apparently increases with temperature.[9] This is not surprising since it is well known that the shift of the water standard moves upfield with increasing temperature. However, the observed change in hydronium shift is 2—3 times greater than the change in the pure water shift over the same temperature range and this has never been explained.

The preceding paper showed that the proton chemical shifts of many aqueous salt solutions can be accounted for on the basis of cationic hydration together with an anionic structure-breaking effect.[16] The anion structure-breaking F factors found to fit the salt solution data correlate strongly with the hydronium shifts obtained for different acids and it is the purpose of this paper to indicate how these can be introduced into Gutowsky's model and what modifications this introduces into previous interpretations.

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RESULTS AND DISCUSSION

Hydration and Structural Effects of H_3O^+.—The hydronium ion is hydrogen bonded with the solvent and this bonding will be enhanced by the positive charge of the ion. For this reason it is often formulated as being trihydrated, *i.e.*, $H_9O_4^+$. Any increase in the bond strength between the ion and its hydration water will presumably be due to electrostatic forces, the hydrogen-bonding interaction being similar to that between ordinary water molecules. For this reason the only difference between normal water and the water close to the ion that is likely to be detected by ^1H n.m.r. shift measurements is probably a small electric-field shift. I have calculated this for a static water molecule bonded to H_3O^+ in the pyramidal configuration [16] and find that the electric field induces a downfield shift increment of only 0·7 p.p.m. in the hydration water. This represents a maximum value since the water is in a rapid state of motion so as to reduce the contribution of the $A \cos \theta$ term. The chemical shift of the hydration water is thus very much smaller than that of the protons in H_3O^+ and a ^1H n.m.r. shift measurement is unlikely to be capable of separating the influence of the hydration water from that of the central ion, H_3O^+.

The hydronium cation may, however, possess a structural influence on the solvent. A normal water molecule can form four hydrogen bonds to its neighbours. If a water molecule is protonated then the three protons can hydrogen bond to three other water molecules but formation of the fourth bond *via* its remaining oxygen lone pair, which should be to the hydrogenic, positive part of another water molecule, will be inhibited by the positive charge of the ion. Thus we can assume that the protonation of water breaks one hydrogen bond in the system per proton.[17] This will be added to the anionic F factor.

Since we are about to consider temperature effects we must also consider briefly whether the shift of H_3O^+ itself is temperature dependent. If its hydrogen bonding is strengthened by its electric field then it seems possible that an increase in temperature will not reduce the bonding to the same extent as that which occurs in the bulk solvent. We can assume with confidence that the shift will be less temperature dependent than that of water and can regard it as being absolutely constant without too much error. The second sphere of hydration water in $H_9O_4^+$ will of course behave like normal water since the involvement of its oxygen in hydrogen bonding to H_3O^+ probably has a relatively small effect on the shift of its own protons.

The Four-site Equation for Dilute Aqueous Solutions of Strong Acids.—The chemical shift of aqueous acids is normally quoted relative to that of pure water. This simplifies the form of the equations used since the shift of the pure water part of the equation can be put equal to zero and a term eliminated. Unfortunately this step has been made at too early a stage by previous workers with the result that a useful term has been lost from the final equation. That this should be so can be realised if we note that the equation must contain temperature-dependent terms but that the pure water shift is the only temperature-dependent quantity we have to deal with.

In the following calculations it is necessary to use two different chemical-shift scales: (*a*) based on the temperature-independent standard ethane gas (though any other standard would serve equally well) for which I will use the term δ with subscripts as introduced by Malinowski and his co-workers; [16] and (*b*) the water scale for which I shall use the letter S used commonly in previous work. All low-field shifts are given a negative sign on both scales in the present paper.

If we have an acid HA dissolved in water to a stoicheiometric mole fraction x, then if α is the degree of dissociation of the acid we have the following mole fractions of species in solution: αx of H_3O^+ and A^- (shift is $\delta_{H_3O^+}$); $(1 - \alpha)x$ of HA (shift is δ_{HA}); $\alpha x(1 + F)/2$ of additional free, or non-hydrogen-bonded water due to the structural effect of the anion and hydronium ion (shift is δ_F); and $(1 - x) - \alpha x - \alpha x(1 + F)/2$ of ordinary water (this has the temperature-dependent shift δ_N, where $\delta_N = -4{\cdot}38 + 0{\cdot}00958t$; t in °C [18]). The quantity F has been defined previously [16] as the number of water hydrogen bonds broken per anion. The total number of protons in the system is $2 - x$. We have then equation (2) for the observed shift δ_{obs}. Converting to the water

$$\delta_{obs} = \frac{3\alpha x\delta_{H_3O^+} + 2\delta_N[1 - x - \alpha x - \alpha x(1 + F)/2] + \alpha\delta_F x(1 + F) + (1 - \alpha)x\delta_{HA}}{2 - x} \qquad (2)$$

scale we have equation (3). I have argued that δ_F is

$$S_{obs} = \delta_{obs} - \delta_N = \frac{3\alpha x\delta_{H_3O^+} - \delta_N x[1 + 2\alpha + \alpha(1 + F)] + (1 - \alpha)x\delta_{HA} + \alpha x\delta_F(1 + F)}{2 - x} \qquad (3)$$

ca. 0 on the ethane scale.[16] Making this substitution and introducing Gutowsky's parameter,[1] we have equation (4). When $\alpha = 1$ then the limiting slope of

$$S_{obs} = p\left\{\alpha\delta_{H_3O^+} - \left[\frac{1 + 2\alpha + \alpha(1 + F)}{3}\right]\delta_N + \frac{(1 - \alpha)}{3}\delta_{HA}\right\} \qquad (4)$$

the plot of S_{obs} against p is given by equation (5), which

$$\lim_{p \to 0}(S/p) = \delta_{H_3O^+} - \frac{(4 + F)}{3}\delta_N \qquad (5)$$

predicts a different and temperature-dependent limiting slope for each acid, as is observed. We can also obtain from (2) expression (6) for the dependence on temperature of the shift observed at any concentration in

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

[18] J. I. Musher, *J. Chem. Phys.*, **1961**, **35**, **1989**.

acidic solutions which, if we put $\alpha = 1$ and express

$$\frac{d(\delta_{\mathrm{obs}})}{dT} = \frac{d(\delta_{\mathrm{N}})}{dT}\,\frac{2 - 2x - 2\alpha x - \alpha x(1 + F)}{2 - x} \qquad (6)$$

concentration as molality, m, gives (7).

$$\frac{d(\delta_{\mathrm{obs}})}{dT} = \frac{d(\delta_{\mathrm{N}})}{dT}\left(1 - \frac{m[4 + F]}{111 + m}\right) \qquad (7)$$

Comparison with Experimental Results.—Effect on estimates of $\delta_{\mathrm{H_3O^+}}$. Equation (5) can be used to obtain values of $\delta_{\mathrm{H_3O^+}}$ corrected for structural effects. The results are given in Table 1 for a temperature of 25 °C.

TABLE 1

Observed and absolute values of $\delta_{\mathrm{H_3O^+}}$ for acids at 25 °C in H_2O

Acid	Limiting slope/ p.p.m.	F [b]	$\delta_{\mathrm{N}}\dfrac{(4 + F)}{3}$ [c] / p.p.m.	$\delta_{\mathrm{H_3O^+}}$ [d] / p.p.m.	$S_{\mathrm{H_3O^+}}$ [e] / p.p.m.
$HClO_4$	−9·18 [a]	2·49	−8·94	−18·12	−13·99
HNO_3	−11·08 [f]	1·42	−7·46	−18·54	−14·41
HCl	−11·64 [g]	1·33	−7·34	−18·98	−14·85
H_2SO_4	−13·10 [h]	0	−5·51	−18·61	−14·48
Toluene-*p*-sulphonic	−14·5 [i]				

[a] Ref. 9. [b] Ref. 16. [c] $\delta_{\mathrm{N}} = -4{\cdot}13$ p.p.m. at 25 °C. [d] Ethane scale. [e] Water scale. [f] Ref. 10. [g] Ref. 12 and papers quoted therein. [h] Ref. 3. [i] This is the largest value so far recorded in ordinary water, R. W. Creekmore and C. N. Reilly, *J. Phys. Chem.*, 1969, **73**, 1573.

Application of the correction reduces the range of observed hydronium shifts from 5·3 to only 0·86 p.p.m., a range which might be considered to be within the bounds of the approximations inherent in the present model. It therefore seems reasonable to conclude that the absolute shift of H_3O^+ is constant and lies within the range $-14{\cdot}4 \pm 0{\cdot}4$ p.p.m. from water at 25 °C or $-18{\cdot}5 \pm 0{\cdot}4$ p.p.m. from gaseous ethane.

Of course any series of F factors which differed by the same amounts as the ones used here would give equal improvement in the results but very different absolute shifts. The F factors were however derived from a quite independent set of measurements so that we can accept that the quoted shift is probably close to the true absolute shift. Further confirmation that this is so comes from the variable-temperature results, which are summarised in Table 2. Equation (5) predicts the temperature variation of the limiting slopes for perchloric acid almost exactly on the basis of a constant hydronium shift. A set of larger F factors would give a worse shift prediction. The data are less good for nitric and hydrochloric acids. In the case of the first there is a change in acid dissociation with temperature which will affect the results, while for the second there does appear to be a discrepancy between the variable-temperature results and previous results obtained at only 25 °C, which may indicate an overestimation of the temperature dependence. The difference presumably arises because of the larger susceptibility corrections needed with hydrochloric acid. This result thus cannot be held to invalidate the present approach. Indeed a change of only 1 p.p.m. in the estimate of $\delta_{\mathrm{H_3O^+}}$ over the temperature range studied can probably be accepted as reasonable proof of its relative invariance with temperature.

TABLE 2

Observed and absolute values of $\delta_{\mathrm{H_3O^+}}$ in H_2O at different temperatures

Acid	F	t/°C	Limiting slope/ p.p.m.	$\delta_{\mathrm{N}}\dfrac{(4 + F)}{3}$/ p.p.m.	$\delta_{\mathrm{H_3O}}/+$ p.p.m.
$HClO_4$ [a]	2·49	0	−8·67	−9·48	−18·15
		25	−9·18	−8·94	−18·12
		65	−10·01	−8·14	−18·15
HNO_3 [a]	1·42	0	−10·25	−7·82	−18·07
		25	−11·08	−7·46	−18·54
		65	−12·18	−6·80	−18·98
HCl [b]	1·33	10	−11·37	−7·63	−19·00
		30	−12·27	−7·28	−19·55
		50	−12·74	−6·95	−19·69
		70	−13·27	−6·60	−19·87
		90	−13·75	−6·25	−20·00

[a] Ref. 10. [b] Ref. 11. These results are *ca.* 0·4 p.p.m. larger than would be expected on the basis of other results at 25 °C; ref. 12. This probably arises because only two points have been obtained at sufficiently low concentrations; determination of $\delta_{\mathrm{H_3O^+}}$ was not the prime interest of ref. 11.

The absolute shift from water of −14·4 p.p.m. can be calculated as described previously[18] by use of the correlation between calculated and measured chemical shifts obtained for cation hydration water[16] and corresponds to a proton–oxygen distance in H_3O^+ of 106 pm. This is close to the larger distances observed in nitric acid hydrate.[19]

The protonic hydration number. Malinowski and his group[11] have estimated the hydration number h of the hydrogen ion by observing the effect that dissolved acid has upon the shift–temperature dependence of water. His results give typically $h = 3$ which is similar to the estimate of 1·6—2 for H_3O^+ made by Redlich and his co-workers.[10] Equation (7) can be used to calculate the slopes expected on the basis of the present model and the results are set out in Table 3. The results for perchloric

TABLE 3

Measured and calculated shift–temperature dependences for some aqueous acids

Acid	m	F	$\dfrac{d(\delta_{\mathrm{obs}})}{dt}$/p.p.m. K^{-1} Measured	Calc. for $h = 1$	Error % measured
$HClO_4$ [a]	1·62	2·49	0·00873	0·00869	−0·5
	3·50		0·00784	0·00768	−2·1
	5·25		0·00672	0·00677	+0·7
HNO_3 [b]	0·703	1·42	0·00911	0·00925	+1·5
	1·506		0·00861	0·00889	+3·3
	2·36		0·00825	0·00850	+3·0
$HClO_4$ [c]	0·904	2·49	0·00906	0·00908	+0·2
	1·85		0·00861	0·00856	−0·6
	2·73		0·00823	0·00809	−1·7
HCl [a]	0·94	1·33	0·00907	0·00915	+0·9
	1·90		0·00805	0·00872	+8·3
	2·84		0·00750	0·00831	+10·8
	3·89		0·00712	0·00785	+10·2
	4·77		0·00630	0·00747	+18·5

[a] Ref. 11. [b] Ref. 13. [c] Ref. 9.

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[19] V. Luzzati, *Acta Cryst.*, 1953, **6**, 152, 157.

acid can be accounted for well within experimental accuracy on the basis of the monohydrate H_3O^+ and anion and hydronium structural effects. The fit for nitric acid is not as good but remains adequate. The measured slopes in the case of hydrochloric acid are always less than predicted and the model is not satisfactory in this case though it does seem strange that the hydration of the proton should apparently be greater in hydrochloric acid than in the other two. It may again be significant that the hydrochloric acid results require the largest susceptibility corrections.

Specific shifts of hydronium ions. Duerst has derived specific shifts for the different forms of hydrated proton $H_9O_4^+$, $H_5O_2^+$, and H_3O^+. The specific shift of the latter (*ca.* −6·0 p.p.m.) differs considerably from the value found here. It was obtained from the limiting slope of the shift curve obtained in concentrated perchloric acid solutions and on the assumption of the absence of free water molecules in such solutions. In view of the strong structure-breaking effect of the perchlorate ion it is not unreasonable to suppose that concentrated acid solutions should contain free hydronium ions and that some of the water present should exist as free (non-hydrogen-bonded) molecules. The shift of the latter is some 9·7 p.p.m. upfield of the anhydrous acid and of the former (which will presumably be shifted by, say, 4 p.p.m. upfield by the loss of $H_3O^+–H_2O$ hydrogen bonding) perhaps only 4·7 p.p.m. downfield. The presence of a small proportion ($\not> 1/3$) of free water in the concentrated acid solutions could thus easily explain the rather small limiting slope observed and indeed can explain the quite small shift variation which occurs for perchloric acid between 0·5 and 1·0 mole fraction. That small quantities of free water may exist in this high concentration range does appear to be likely in view of the spread of the i.r. results.[9,20] The conclusion based on Table 3 of the presence of only monohydration, together with the small electric-field effect expected for the outer hydration sphere, indicates that n.m.r. chemical-shift determinations are quite insensitive to the degree of involvement of any second hydration sphere. The allocation of specific shifts to the other polyhydrated protons is therefore probably unnecessary.

Estimates of dissociation constants. The inclusion of anionic effects in the calculations does not alter the dissociation constants estimated from the data since the new terms cancel out. Recognition of structural effects does however remove some uncertainty from the results. While different acids gave such widely different values of $S_{H_3O^+}$ it was always possible that regular small changes of α with concentration, or changes in the degree of hydration of the proton with concentration, might effect the limiting slopes obtained from dilute acids. The attribution of the differences almost solely to anionic effects means that we can have more confidence in previous results derived on the basis of the three-site version of equation (4).

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