

Tetra-alkylammonium Fluorides and Chlorides in Glacial Acetic Acid Solution: Nuclear Magnetic Resonance Studies, Deuterium Fractionation Factors (ϕ), and Anion Hydrogen Bonding

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The salts NMe_4F , NEt_4F , and NBu_nF dissolve very readily in MeCO_2H and cause downfield shifts of the acid proton that are linearly related to the fluoride concentration. From these measurements and those in MeCO_2D the fractionation factors (ϕ) have been calculated and give an average value of 0.55, indicative of anion solvation involving strong hydrogen bonding. The corresponding tetra-alkylammonium chlorides produce upfield chemical shifts and average ϕ of 1.26, which indicates much weaker anion solvation.

The curious properties of alkali and other metal fluorides in glacial acetic acid have aroused considerable interest.¹⁻⁶ The unexpectedly high solubility of fluorides in this apparently low-polarity medium is attributed to very strong solvation of the anion, an interaction which involves hydrogen bonding. The strength of this hydrogen bonding has been estimated by a variety of methods based on thermochemical,² i.r.,² ion cyclotron,⁷ and *ab initio* data,^{8,9} in addition to ¹H n.m.r. analysis which has shown that the chemical shift of the proton in the species $\text{F}(\text{MeCO}_2\text{H})_n^-$ is ca. 14.5 p.p.m.³ The degree of solvation of the fluoride ion in these solutions is not known but there is evidence to suggest that $n = 2$.¹⁰ Solid state X-ray crystal structure determinations on $\text{KF}\cdot(\text{CH}_2\text{CO}_2\text{H})_2$,¹¹ $\text{CsF}\cdot(\text{CH}_2\text{CO}_2\text{H})_2$,¹² and $\text{KF}\cdot\text{CH}_2(\text{CO}_2\text{H})_2$ ¹³ show the fluoride ion to be hydrogen bonded to two carboxylic acid groups in each case.

Earlier ¹H n.m.r. studies on fluoride solutions noted the downfield shift of the resonance of the acidic proton of the solvent on addition of the fluoride.^{3,4} It was also observed that, whereas for the alkali metals Na, K, Rb, and Cs the linear relationship between chemical shift and concentration was independent of the cation, for tetramethylammonium fluoride a different gradient was obtained. In the work reported here we have returned to this problem and extended the n.m.r. investigations to other tetra-alkylammonium fluorides and to the corresponding chlorides. In addition we have investigated these salts in MeCO_2D solvent in such a way as to obtain fractionation factors (ϕ) for the distribution of D and H between the solvent and solvated fluoride hydrogen bonds.

Experimental

Materials.—Acetic acid was dried by azeotropic distillation with benzene and stored over A4 molecular sieves. Only acid with a water content of less than 50 p.p.m. was used. The deuterium derivative, MeCO_2D , supplied by Aldrich as 98 atom %, was dried over 4A molecular sieves prior to use until the water content was less than 150 p.p.m. The deuterium content was checked by comparison of the CH_3 and residual OH signals.

Tetra-alkylammonium fluorides were supplied as hydrates (Aldrich). Complete dehydration in the solid state leads to decomposition.¹⁴ After preliminary drying under reduced pressure the solids were used to prepare solutions which were dried by azeotropic distillation with benzene. The moisture content was thereby reduced to 150 p.p.m. Solutions in MeCO_2D were prepared as above and then the requisite

amount of MeCO_2D was added. The mole fractions of NR_4F were measured from integrations of the NR_4^+ and CH_3CO signals of the most concentrated solutions. These solutions were then diluted with known weights of MeCO_2H or MeCO_2D . The fluorides KF and CsF were dried at 200 °C. All manipulations of solutions were carried out in a nitrogen-purged P_2O_5 -dried glove-box. Fluoride solutions were handled in polyethylene containers. Tetra-alkylammonium chlorides were commercial samples dried to constant weight under reduced pressure over P_2O_5 in a drying pistol.

Instruments.—Proton n.m.r. spectra were run on a Bruker WM250 spectrometer operating at 250 MHz. The water content of solutions was measured on a Mitsubishi CA-02 coulometric moisturemeter.

Theory

The chemical shift of the acidic proton of MeCO_2H was referenced to the methyl signal of the acid which is only marginally affected by changes to the system, when compared to an external reference.¹⁵ The observed signal of the acid proton, δ_{obs} , varies linearly with the concentration of added NR_4F , KF, or CsF in both MeCO_2H and MeCO_2D . The mole fraction of solute x and the corresponding δ_{obs} , δ_0 (neat acid), and the fractionation factors (ϕ) are given in Table 1 for the fluoride solutions and Table 2 for the chloride solutions.

The general equation (1) for the linear downfield shift, in which δ is the gradient, and its counterpart (2) for MeCO_2D , can be related to equation (3), in which n is the atom fraction of deuterium in the deuteriated solvent.¹⁶ The fractionation factor

$$\delta = \delta_0 + \delta_x \quad (1)$$

$$\delta_n = \delta_0 + \delta_n x \quad (2)$$

$$\delta/\delta_n = 1 - n + n\phi \quad (3)$$

$$\phi = \frac{(\text{D/H}) \text{ solute}}{(\text{D/H}) \text{ solvent}} \quad (4)$$

ϕ is defined according to equation (4). The above relationships all rest on the assumption that the physical structure of the system does not depend on the value of n . This assumption has been shown to be valid in $\text{D}_2\text{O}-\text{H}_2\text{O}$ solutions¹⁷ and $\text{MeOD}-\text{MeOH}$ solutions.¹⁸ Thus ϕ can be determined simply from the ratio of the gradients of the changes in chemical shift caused by

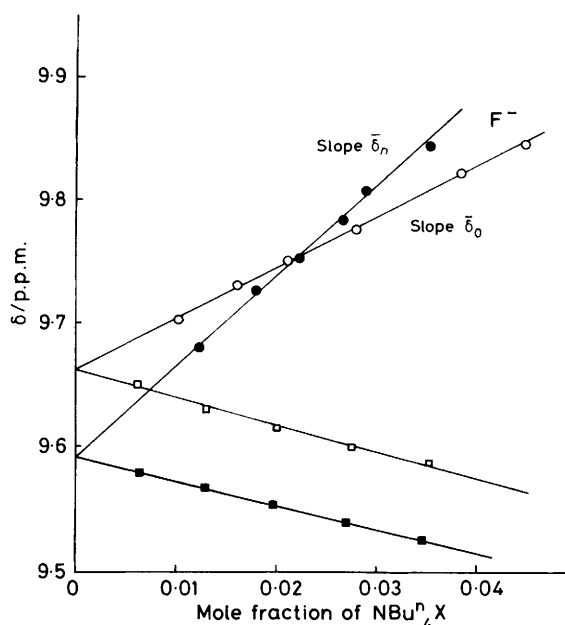


Figure 1. Plots of $\delta(\text{CH}_3\text{CO}_2\text{H})$ against x (mole fraction) for NBu_4F in MeCO_2H (○) and MeCO_2D (●), and for NBu_4Cl (□, ■ respectively)

the solute, if they are linear. That this is so is illustrated in Figure 1 for the tetra-*n*-butylammonium salts, and the other systems exhibit similar behaviour.

The solvation of the anion is assumed to be the only alternative hydroxyl environment to that of the solvent itself which is mainly cyclic dimers and trimers.³ Solvation of the cation has been ignored and there are good precedents for this, although not specifically for glacial acetic acid. The work of Butler and Symons¹⁷ on methanol solutions of a large range of salts, and of Gold and Grist¹⁵ on NaOMe solutions in methanol, showed that solvation of cations in a solvent with an extensive hydrogen-bond structure did not result in a deshielding of the protons of the primary solvation sphere. For large univalent cations of the type used here the cation solvation can be ignored and the best evidence for this is our observations of the insensitivity of δ and δ_n to the nature of the cation.

Thus in our analysis of the n.m.r. data we are assuming that D and H distribution is occurring between two environments: bulk solvent and solvated anions. If the hydrogen bonds are similar in terms of their potential-energy wells and zero-point energies (z.p.e.s) then there should be no D/H fractionation between them, *i.e.* $\phi = 1$. On the other hand if there is a marked difference, and if the hydrogen bond in the solvated anion is much stronger than that of the solvent dimers, then ϕ will be less than unity since the deuterium will prefer to remain in the solvent where the hydrogen bond is weaker and where consequently the force constant of the covalent hydroxyl bond is stronger.

Discussion

The previous work by us³ which claimed a difference between the chemical shifts of alkali-metal fluoride-acetic acid solutions and $\text{NMe}_4\text{F}-\text{MeCO}_2\text{H}$ is contradicted by the present results which show no difference in behaviour between KF , CsF , or NR_4F where $\text{R} = \text{Me}$, Et , or Bu^n . The previous results for $\text{NMe}_4\text{F}-\text{MeCO}_2\text{H}$ were probably distorted by incomplete drying.

The effect of added water was tested for the $\text{KF}-\text{MeCO}_2\text{H}$

Table 1. ^1H N.m.r. chemical shifts of solutions of NR_4F in MeCO_2H and MeCO_2D at 25 °C and fractionation factors ϕ

MeCO_2H		MeCO_2D	
$10^3x(\text{NR}_4\text{F})^a$	$\delta_{\text{obs.}}^b$	$10^3x(\text{NR}_4\text{F})^a$	$\delta_{\text{obs.}}^b$
NMe_4F ($\phi = 0.543 \pm 0.019$)		$n = 0.968^c$	
3.2	9.697	4.2	9.616
6.6	9.702	8.9	9.642
9.7	9.717	17.9	9.707
14.5	9.738	23.7	9.747
20.0	9.758	27.5	9.779
27.3	9.790	31.2	9.814
33.6	9.820	36.0	9.848
$\delta_{\text{obs.}} = 9.678 + 4.060x$		$\delta_{\text{obs.}} = 9.577 + 7.276x$	
NEt_4F ($\phi = 0.554 \pm 0.010$)		$n = 0.933$	
7.3	9.704	6.0	9.647
10.8	9.717	11.6	9.680
13.3	9.734	17.7	9.711
20.3	9.756	21.2	9.744
24.0	9.775	28.3	9.783
30.8	9.798	31.5	9.830
$\delta_{\text{obs.}} = 9.676 + 3.999x$		$\delta_{\text{obs.}} = 9.600 + 6.849x$	
NBu_4F ($\phi = 0.555 \pm 0.018$)		$n = 0.976$	
10.5	9.703	12.5	9.680
16.3	9.731	18.2	9.727
21.5	9.750	22.5	9.753
28.2	9.777	27.1	9.783
38.8	9.824	29.3	9.809
45.1	9.846	35.7	9.845
$\delta_{\text{obs.}} = 9.661 + 4.126x$		$\delta_{\text{obs.}} = 9.590 + 7.331x$	
KF ($\phi = 0.541 \pm 0.027$)		$n = 0.978$	
5.7	9.696	5.7	9.638
11.4	9.721	11.4	9.681
17.1	9.742	17.1	9.720
22.8	9.767	22.7	9.763
30.1	9.802	28.4	9.806
$\delta_{\text{obs.}} = 9.671 + 4.097x$		$\delta_{\text{obs.}} = 9.595 + 7.435x$	
CsF ($\phi = 0.532 \pm 0.009$)		$n = 0.971$	
5.7	9.701	5.8	9.638
11.4	9.720	11.5	9.674
17.1	9.738	17.2	9.718
22.8	9.763	22.9	9.758
28.5	9.785	28.6	9.734
34.2	9.808	35.0	9.845
$\delta_{\text{obs.}} = 9.677 + 3.797x$		$\delta_{\text{obs.}} = 9.595 + 6.964x$	

^a Mole fraction. ^b ± 0.001 . ^c Atom fraction of deuterium in MeCO_2D .

system. Addition of water to neat MeCO_2H results in the expected upfield shift and $\delta(\text{H}_2\text{O}) = -14.762$ p.p.m. x^{-1} . On adding equimolar amounts of water to $\text{KF}-\text{MeCO}_2\text{H}$ the upfield shift was reduced, $\delta(\text{KF}, \text{H}_2\text{O}) = -10.811$ p.p.m. x^{-1} . The reduction in slope, 3.951 p.p.m. x^{-1} , is nearly that of $\delta(\text{KF})$, 4.097 p.p.m. x^{-1} .

From the data in Table 1 the fractionation factors for the various fluorides were calculated using equation (3) and these all fall in the narrow range of 0.532–0.555 with an average value of 0.545. This shows significant preference of the H for the anion solvent species which in turn shows that the hydrogen bonding in $\text{F}(\text{MeCO}_2\text{H})_n^-$ is strong. This accords with other evidence on $\text{RCO}_2\text{H} \cdots \text{F}^-$ hydrogen bonding which shows it to be exceptionally strong.^{8,9}

The link between ϕ and the strength of a hydrogen bond $A-H \cdots B$ is not immediately obvious, although a simple inverse relationship might have been expected. When a molecule AH forms a hydrogen bond its stretching vibration changes dramatically, falling to much lower wavenumbers. The extent of this change has often been quoted as a measure of the bond energy $E(A-H \cdots B)$.¹⁸ As the force constant of AH weakens so the molecule becomes even less attractive to deuterium than to protium and hence ϕ decreases.

The shift to lower wavenumbers for $\nu(\text{MeCO}_2\text{H} \cdots \text{F}^-)$ is over 2000 cm^{-1} yet ϕ is not as small as in other, less strongly hydrogen-bonded systems. This lack of a simple relationship between these parameters is rather like that of the observed chemical shifts of hydrogen-bond protons, where the most downfield protons are not those of the strongest hydrogen bonds. The explanation of this behaviour in terms of three distinct types of hydrogen bond can also be used to interpret ϕ values.¹⁹

The three kinds of hydrogen bond, weak, strong, and very strong, are distinguished by their potential-energy wells and the relative z.p.e. for H and D.¹⁹ Normal or weak hydrogen bonds have two potential-energy wells with a high energy barrier between them which constrains the proton to one well, usually that of the atom of the hydrogen-bond donor. The type of hydrogen bond with the biggest difference between the protonated and deuterated forms is that in which the z.p.e.(H) is above the energy barrier between the two potential-energy wells but the z.p.e.(D) is still confined to the well nearest its parent atom [Figure 2(b)]. This type of hydrogen bond is referred to as strong. In this case the downfield chemical shift reaches a maximum and by the same token we would expect ϕ to be at a minimum. As the hydrogen bond gets stronger, *i.e.* $R(A \cdots B)$ further decreases, δ starts to move upfield again. An even stronger bond, referred to as very strong hydrogen bonding, is reached when z.p.e.(D) is also above the internal barrier, at which point the difference between the protium and

deuterium force constants is less marked and ϕ will not be as small as in strong hydrogen bonds. This type of hydrogen bond is like the truly single p.e. minimum of which HF_2^- is the prime, and maybe only example.

The value for $\phi(\text{HF}_2^-)$ has been estimated to be 0.60 by Kreevoy and Liang²⁰ using the data of Kresge and Chiang.²¹ In the same paper²⁰ the fractionation factors of other HA_2^- ions were reported, some as low as 0.30 for $\text{H}[\text{3,5-(NO}_2)_2\text{C}_6\text{H}_3\text{-CO}_2]_2^-$. Even the nitrophenol-nitrophenolate $\text{H(4-NO}_2\text{C}_6\text{-H}_4\text{O)}_2^-$ ion has ϕ 0.31 and clearly the hydrogen bonding of these ions cannot rival that of HF_2^- . The explanation that these are strong hydrogen bonds would explain their low ϕ values. This being the case then a value of 0.55 for $\text{F(MeCO}_2\text{H)}_n^-$ would suggest a stronger bond, perhaps even of the very strong class. This is supported by other evidence which shows the measured enthalpy of the $\text{RCO}_2\text{H} \cdots \text{F}^-$ bond to be $> 59 \text{ kJ mol}^{-1}$,² the computed bond energy to be 110 kJ mol^{-1} ,²² δ to be 14.5 p.p.m. ,³ $\Delta\nu$ to be 2000 cm^{-1} ,⁴ and $R(\text{O} \cdots \text{F})$ to be 2.44 \AA .¹³

Unfortunately in comparing ϕ values for the above systems no allowance has been made for the fact that they were measured for species in different solvents. That this is important is shown by the fractionation factor of 0.72 for H(MeO)_2^- obtained from solutions of NaOMe in MeOH.^{15,23,24} Again this almost certainly involves a strong hydrogen bond. What ϕ for a strong hydrogen bond is describing is the difference between its potential-energy well and z.p.e.s and those of the medium. For most solvents the exchanging hydrogen will be involved in a weak hydrogen bond such that both z.p.e.(H) and z.p.e.(D) are deep within one well. For such a solvent medium ϕ should vary as in Figure 2 and we would like to suggest this type of relationship between ϕ and bond energy or $R(A \cdots B)$ as an explanation for the behaviour of ϕ . Similar relationships have also been proposed for variations in δ ¹⁹ and $\nu_{\text{H}}/\nu_{\text{D}}$.²⁵

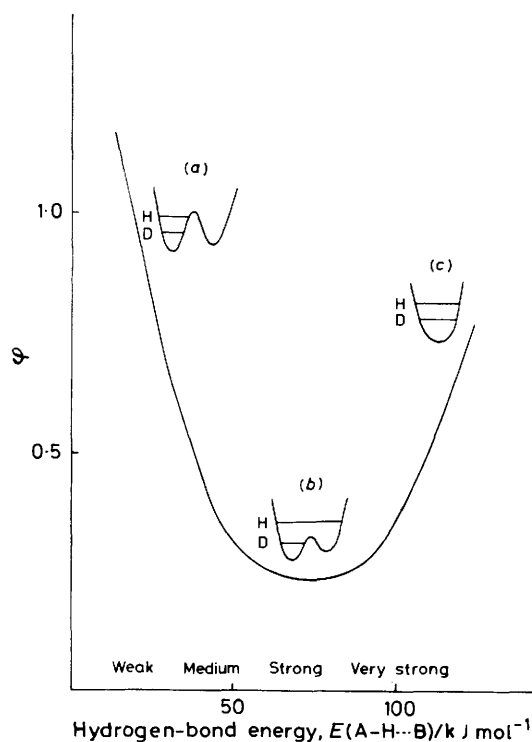


Figure 2. Relationship between the fractionation factor ϕ and hydrogen-bond strength $E(A-H \cdots B)$. Insets (a)–(c) show the potential-energy curves for the three kinds of hydrogen bond

Table 2. ^1H N.m.r. chemical shifts of solutions of NR_4Cl in MeCO_2H and MeCO_2D at 25°C and fractionation factors ϕ

MeCO_2H		MeCO_2D	
$10^3x(\text{NR}_4\text{Cl})^a$	$\delta_{\text{obs.}}^b$	$10^3x(\text{NR}_4\text{Cl})^a$	$\delta_{\text{obs.}}^b$
$\text{NMe}_4\text{Cl} (\phi = 1.200 \pm 0.044)$		$n = 0.979^c$	
5.8	9.647	5.8	9.572
11.6	9.619	11.7	9.546
17.5	9.583	17.6	9.520
23.5	9.564	23.6	9.498
29.6	9.533	29.5	9.477
$\delta_{\text{obs.}} = 9.673 - 4.803x$		$\delta_{\text{obs.}} = 9.593 - 4.016x$	
$\text{NEt}_4\text{Cl} (\phi = 1.292 \pm 0.027)$		$n = 0.973$	
5.8	9.661	5.8	9.588
11.7	9.636	11.8	9.569
17.7	9.607	17.8	9.545
23.8	9.585	24.0	9.528
30.1	9.561	30.4	9.510
$\delta_{\text{obs.}} = 9.684 - 4.194x$		$\delta_{\text{obs.}} = 9.605 - 3.268x$	
$\text{NBu}_4\text{Cl} (\phi = 1.290 \pm 0.031)$		$n = 0.966$	
5.9	9.659	6.0	9.581
12.0	9.640	12.2	9.567
18.5	9.623	18.8	9.556
25.3	9.605	25.7	9.543
32.5	9.590	33.0	9.531
$\delta_{\text{obs.}} = 9.673 - 2.552x$		$\delta_{\text{obs.}} = 9.591 - 1.992x$	

^a Mole fraction chloride, concentrations (± 0.001) 0.100, 0.200, 0.300, 0.400, and 0.500 mol kg^{-1} respectively for each chloride solution.

^b ± 0.001 . ^c Atom fraction of deuterium in MeCO_2D .

NR_4Cl .—The hydrogen-bonding ability of the chloride ion compared to that of fluoride is dramatically demonstrated by the negative gradients obtained for NR_4Cl solution in MeCO_2H and MeCO_2D , Table 2 and Figure 1. The fractionation factors of 1.200–1.292, average 1.26, show that $\text{Cl}(\text{MeCO}_2\text{H})_n^-$ has a weaker hydrogen bond than have the solvent dimers. A similar divergence of behaviour between these ions in methanol solutions was reported by Butler and Symons.¹⁷

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