A Fluorine-19 Nuclear Magnetic Resonance Study of the Strong Hydrogen Bond between Aliphatic Diols or Acids and Alkali-metal Fluorides

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Solutions of alkali metal fluorides in aliphatic diols or carboxylic acids have been investigated by ^{19}F n.m.r. at concentrations of *ca.* 0.5 mol kg^{-1} and greater. Heats of association of potassium fluoride with ethane-1,2-diol and methanoic acid are obtained from variable-temperature n.m.r. studies. The nature of the strong hydrogen bond and its influence on the n.m.r. spectra are discussed.

Recent developments in the field of strong hydrogen bonding have shown the value of studying physical and spectroscopic properties of complexes of the type $AH \cdots B^-$, where AH is an electron acceptor bonded to an electron-donor anion, B^-.[1,2] Many of these complexes exhibit surprising properties attributed to hydrogen bonding.

Chemical reactivity of such associated species is clearly affected, but chemical studies on the whole have not been correlated with the better known physical and spectroscopic studies. Best studied of these systems are the complexes of the type $AH \cdots F^-$, where it has been demonstrated that strong hydrogen bonding manifests itself as modified physical parameters and in changed chemical reactivity.[3] The recognition of this behaviour has been reviewed recently [4] in terms of the use of the base-like properties of the fluoride ion.

Early sources of solubilised alkali metal fluorides, prior to use of tetra-alkylammonium fluoride or crown-ether solubilised KF, involved use of aliphatic diols as solvent for both organofluorinations and base-assisted condensation reactions.[4,5] Reported reaction products often included those derived from solvent attack on the reactant electrophile. In retrospect, we understand today that these solutions of hydrogen-bonded fluoride make poor fluorinating agents, the competition between fluorination and nucleophilic attack having been studied.[6] Results such as these have prompted us to investigate the solubility of alkali metal fluorides in aliphatic diols and to attempt to determine the nature and strength of the salt-solvent interaction.

We have already reported the ^1H n.m.r. study of these systems.[7] Analysis of the bonding in ethanoic acid solutions of potassium fluoride [8] and caesium fluoride [9] show the presence of very strong hydrogen bonds, with ^1H and ^{13}C n.m.r. proving particularly useful techniques for the study of such systems.[9-11] The anomalous reaction chemistry of such systems was interpreted with spectroscopic studies [12-14] and theoretical calculations.[15,16]

Fluorine-19 n.m.r. studies of very strong hydrogen bonds have been reviewed,[1,2] with most being confined to studies of the hydrogendifluoride ion,[17-19] and heterodihalide ions containing fluoride.[19] A recent ^{19}F n.m.r. relaxation study of fluoride ions in methanol has shown a hydrogen-bonding orientation of the fluoride with four-co-ordination about F^-.[20] In this work we now report some ^{19}F n.m.r. studies of aliphatic diol and carboxylic acid solutions of alkali metal fluorides.

Experimental

Fluorine-19 n.m.r. spectra were recorded on a Bruker WP-60 FT NMR spectrometer operating at 56.45 MHz in quadrature-detection mode using 30° pulses (*ca.* 1.3 μs) and no time delay between acquisitions. The temperature of the samples was 303 K unless otherwise indicated. Typically, a sweep width of 6 024 Hz was used for an 8K data table (0.66 s acquisition time) leading to an average deviation of ± 1.51 Hz in the 4K transformed spectrum. Samples were referenced to external C_6F_6 in a concentric 1.5-mm capillary, which also contained $CDCl_3$ or [$^2H_6$]dimethyl sulphoxide as an external lock, held in place by Teflon spacers. Hydrogen-1 n.m.r. spectra of the solvents were monitored with a Varian A-60 spectrometer.

Reagent grade alcohols and carboxylic acids were dried over 5A molecular sieves until they gave a constant δ(OH) shift in the ^1H n.m.r. spectrum. Commercial anhydrous NaF (99%), KF, RbF (99.9%), and CsF (99.9%) were dried by heating *in vacuo* before use. Saturated solutions of fluorides in acids were prepared by stirring excess of fluoride for about 24 h followed by removal of the excess by centrifugation. Solutions of lower concentration (down to *ca.* 0.5 mol kg^{-1}) were made either by dilution of the saturated solutions or by weighing. All manipulations were carried out in a nitrogen-filled dry-box (P_2O_5 desiccant). For the variable-temperature studies the solutions used had KF concentrations of 5 mol kg^{-1} in ethane-1,2-diol and 16 mol kg^{-1} in formic acid. Representative samples were run in both glass- and Teflon-lined n.m.r. tubes with negligible difference. No etching of n.m.r. tubes was observed as long as the solutions were dry. (It should be noted that new n.m.r. tubes are less susceptible to attack even by wet solutions than are old tubes that were etched by such solutions.) We have deliberately chosen not to use very dilute solutions of alkali metal fluorides in our extrapolation to infinite dilution, so as to minimize any effects due to residual traces of water in the solvents. Similarly, we have chosen to use concentrated solutions for the variable-temperature studies.

Results and Discussion

The solubilities of alkali metal fluorides in ethane-1,2-diol are such that, even taking into account the two hydroxy groups per molecule of diol, the co-ordination of four $^-$OH groups, as in ethanol solutions,[20] about each fluoride, is not possible. This is certainly the case since the solubilities are dependent upon the alkali metal cation, suggesting that it also is extensively solvated. Thus, in concentrated solutions we are presumably looking at one or two strong hydrogen bonds to fluoride rather than the medium-strength hydrogen bonds observed for the case of methanol solution. The ^{19}F chemical shift as a function of alkali metal fluoride concentration in ethane-1,2-diol, ethanoic acid, and water is shown in Figure 1.

For ethane-1,2-diol, δ(^{19}F) does not change appreciably with concentration for KF, whereas a general downfield trend is

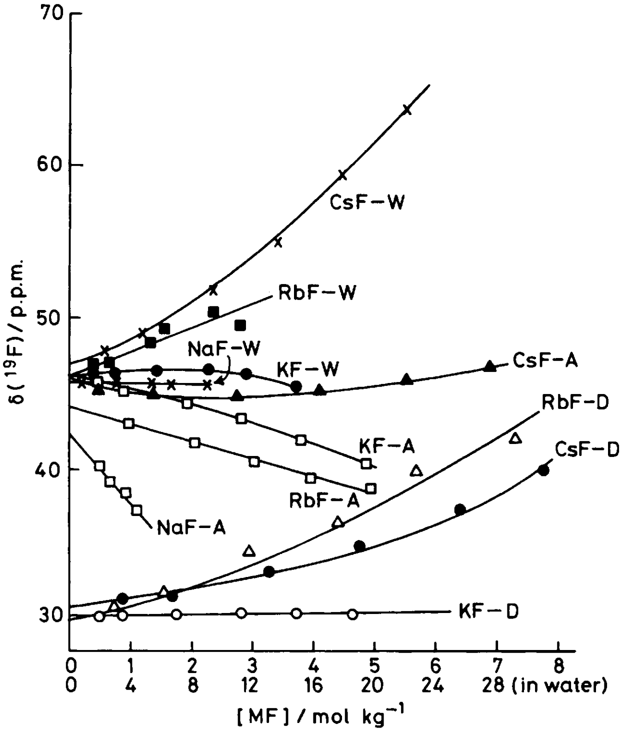

Figure 1. δ(^{19}F) (downfield from C_6F_6) *vs.* concentration for MF (M = Na, K, Rb, and Cs) solutions in ethane-1,2-diol (D), ethanoic acid (A), and water (W)

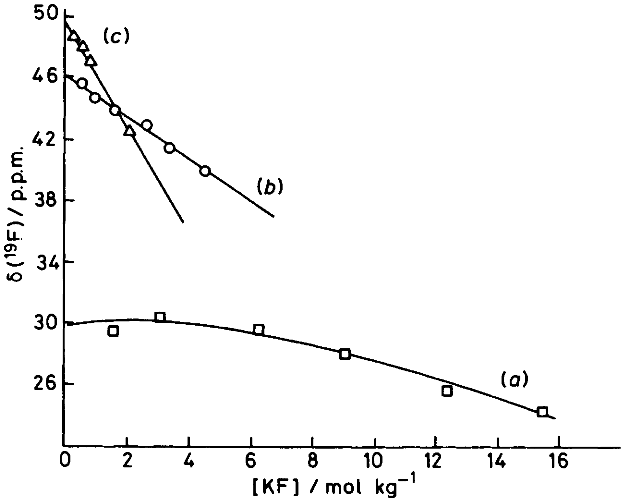

Figure 2. δ(^{19}F) (downfield from C_6F_6) *vs.* concentration of KF in (*a*) methanoic, (*b*) ethanoic, and (*c*) propanoic acids

Table 1. Fluorine-19 chemical shifts (p.p.m.) at infinite dilution * of metal fluorides in diols, carboxylic acids, and water

Compound	NaF	KF	RbF	CsF
$HOCH_2CH_2OH$	—	30.4	30.0	31.0
$HO(CH_2)_3OH$	—	26.3	27.0	26.7
$HO(CH_2)_4OH$	—	29.1	30.0	31.3
HCO_2H	—	29.9	—	—
CH_3CO_2H	42.3	46.1	44.2	46.0
$C_2H_5CO_2H$	—	49.6	—	—
Water	45.8	46.0	46.3	46.9

* Shifts measured relative to C_6F_6.

observed for similarly increasing concentrations of RbF or CsF. In aqueous solutions a similar trend is observed for the rubidium and caesium fluorides; with KF and NaF, δ(^{19}F) is either constant or perhaps decreases at high concentrations in the case of KF. This similarity of the two ' hydroxy ' solvents is to be contrasted with that for ethanoic acid which shows a nearly flat curve for CsF and an upfield shift for RbF, KF, and even NaF. NaF was studied in water and ethanoic acid, but could not be studied in ethane-1,2-diol because of limited solubility (less than one tenth that of KF).

Fluorine-19 chemical shifts can be thought of as reflecting, in part, a range of increasing ionic characters in moving from low-field covalent to high-field ionic shifts. If this were the case, the downfield shifts in the diol and water systems might be considered in terms of increasing polarization of the fluoride ions (*i.e.*, more covalent and more paramagnetic character). The upfield shifts in the ethanoic acid may then indicate the more ionic nature of these solutions. Similar behaviour is observed for methanoic and propanoic acids with KF (Figure 2).

In all the systems reported, there is a significant cation effect, especially great at high MF concentrations. This may be due to the limited amount of solvent available to the fluoride at these concentrations, since the larger cation will be solvated to a greater extent, removing some of the active hydroxy groups from competition for the fluoride. This would suggest that the ^{19}F shift at infinite dilution might reflect the total hydrogen-bonding solvation contribution towards the fluoride. We are, however, dealing with a complex equilibrium including H-bonding effects, cation and ion-pairing effects, and equilibria including various species, as well as bulk magnetic susceptibility effects.[21,22] Though these effects cannot be simply separated, the infinite dilution shifts (Table 1) were determined both for the above systems and also for propane-1,3-diol and butane-1,4-diol.

It is clear from these data that the infinite dilution shifts show no significant cation effects with the exception of the ethanoic acid–NaF system. That NaF should behave differently is not surprising, since this system also behaves differently chemically. In the case of H-bond assisted nucleophilic reactions in the presence of fluoride ion as a base, NaF is ineffectual.[3] Its higher field shift is suggestive of more ionic character, perhaps closer to a solvated NaF ion pair, rather than a solvated cation and strongly hydrogen-bonded fluoride anion. Solvent separated ion pairs in strongly hydrogen-bonding systems have been postulated by Akitt.[23]

Thus it is clear that H-bond strength cannot be simply related to δ(^{19}F) values alone. If we look at a single cation, potassium, then the greater covalent character (stronger hydrogen bond) is reflected by the larger downfield shift with an order for the acids of propanoic > ethanoic > methanoic, consistent with that expected. However, it would be dangerous to read great significance into slight changes in δ(^{19}F) within any class of H-bond electron acceptor, such as acids or diols. Like water, methanoic acid appears rather anomalous. Its shift suggests that there is more ionic character to the fluoride in the methanoic acid–KF system than in the analogous one for ethanoic acid.

In terms of species present at equilibrium, it has been reported that in HCO_2H–KF systems, δ(^{19}F) has contributions mainly from F^- and HF in dilute solutions, while at higher concentrations HF_2^- and $(HF)_n$ also contribute.[24] [It should

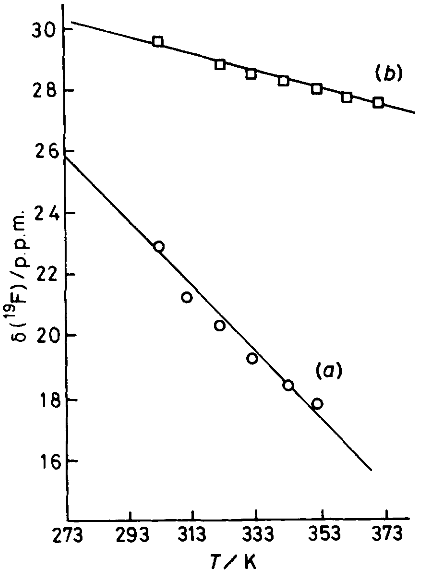

Figure 3. Variation of $\delta(^{19}F)$ (downfield from C_6F_6) with temperature for (*a*) saturated methanoic acid–KF (16 mol kg^{-1}) and (*b*) saturated ethane-1,2-diol–KF (5 mol kg^{-1})

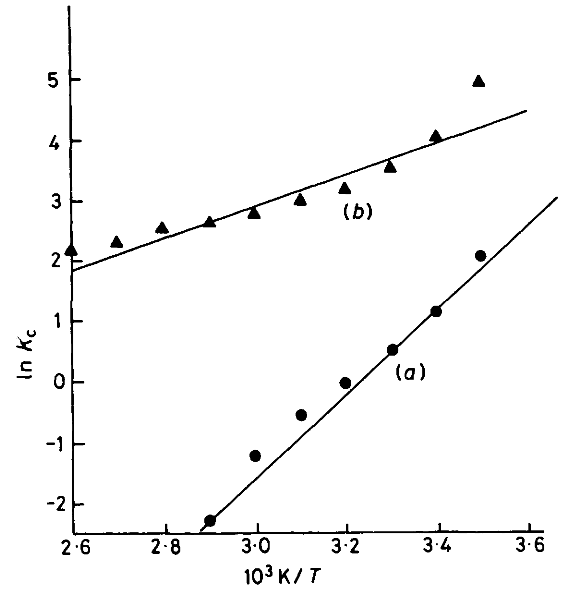

Figure 4. ln K_c *vs.* $1/T$ for (*a*) methanoic acid–KF and (*b*) ethane-1,2-diol–KF

be noted that the sign convention for $\delta(^{19}F)$ in ref. 24 is opposite to that currently accepted, *i.e.* negative δ is used as downfield instead of upfield.]

The postulation of significant HF or HF_2^- contribution may be important for carboxylic acid–MF systems,[16,24,25] but it is clearly not required for alcohol systems.[20] Our ^{13}C n.m.r. studies on the observed nuclear Overhauser effect (n.O.e.)[26] clearly suggested that HF and HF_2^- species were unlikely to be significant in concentrated carboxylic acid–MF systems. This is the case since the presence of HF and HF_2^- also requires the presence of carboxylate anion, which would depress the n.O.e. by an order of magnitude, rather than increasing it as is usually observed for carboxylic acid–KF systems.[11] Similarly, ^{13}C n.O.e. studies[26] of the diol–MF systems considered in this paper show no sign of the behaviour expected if the alkoxy anion required by the formation of either HF or HF_2^- was present. Other work in our laboratory[26] using low-temperature ^{19}F n.m.r. has shown that the H–F coupling constant and ^{19}F chemical shift of the fluorine in the H-bonded complex of F^- with the enol form of pentane-2,4-dione corresponds neither to HF nor HF_2^-. Infrared analysis of a number of strongly hydrogen-bonded complexes involving F^-, including those to uracil[27] and oximes,[28] has shown no evidence for the presence of significant amounts of HF_2^-. Thus, it would appear that, while the contribution from such species as HF and HF_2^- cannot be ignored, the evidence seems to suggest that for the type of systems examined here, strong hydrogen bonding is the principal cause of variation after cation effects are eliminated.

Temperature-dependent spectroscopic parameters are very common for H-bonded associated molecules, raising the temperature leading to breaking of the hydrogen bonds. Similar temperature behaviour is observed for $\delta(^{19}F)$ in the ethane-1,2-diol–KF and methanoic acid–KF systems as shown in Figure 3 for solutions saturated at 298 K. As was shown for the ^1H n.m.r. data,[7] we assume that the ^{19}F chemical shift at 273 K, $\delta(^{19}F)_{273}$, approaches the chemical shift value of fully solvated fluoride ions for this particular solvent system. The calculated value of Deverell *et al.*[29] of −112 p.p.m. (to high field of C_6F_6) has been taken as the chemical shift of free fluoride ions, $\delta(^{19}F)_{F^-(free)}$. Based on such assumptions it is possible to calculate the fraction of free F^- ion at any given temperature by equation (1), where $\delta(^{19}F)_T$ is the observed ^{19}F shift at a given temperature *T*.

$$\frac{[F^-]_{free}}{[F^-]} = \frac{\delta(^{19}F)_{273} - \delta(^{19}F)_T}{\delta(^{19}F)_{273} - \delta(^{19}F)_{F^-(free)}} \quad (1)$$

For both acid and diol systems we would expect equilibria of the type (2).

$$\underset{(x)}{F^-} + R\text{–}OH \rightleftharpoons R\text{–}OH + \underset{(1-x)}{(F^- \cdots H\text{–}OR)} \quad (2)$$

If the assumption is made that net changes in acid or diol concentrations are small over the range of temperatures studied, then the equilibrium constant K_c for association based on concentration rather than activity may be expressed as equation (3) where *x* is the fraction of free fluoride. Combining equations (1) and (3) enables us to determine K_c at the temperatures studied and since K_c is related to the change in enthalpy on association by $\ln K_c = -\Delta H^\ominus/RT +$ constant, a plot of $\ln K_c$ *vs.* $1/T$ gives $\Delta H^\ominus$ for association, for the methanoic acid–KF, and ethane-1,2-diol–KF systems (Figure 4).

$$K_c = \frac{[F^- \cdots H\text{–}OR]}{[F^-]} = \frac{(1-x)}{x} \quad (3)$$

The slope of the curve for HCO_2H yields a value of $\Delta H^\ominus = -58 \pm 5$ kJ mol^{-1}. However, the self-association of the carboxylic acid must also be taken into account. The dimer must be broken before the fluoride solvate can form and therefore the observed $\Delta H^\ominus$ must be corrected by 31 kJ mol^{-1} (ref. 30) to obtain a number representative of the strength of solvate formation. Therefore, an improved $\Delta H^\ominus(F^- \cdots HO)$ of -89 ± 5 kJ mol^{-1} is obtained, which compares with −120 kJ mol^{-1} reported for the ethanoic acid–KF system by Emsley,[8] and theoretically calculated[15] to be −250 and −249 kJ mol^{-1} for the HCO_2H–KF and CH_3CO_2H–KF systems. However, these values are calculated based on either solid KF or gas-phase K^+ and F^- ions. A more appropriate number for comparison, which however includes no calculated lattice or

Table 2. Calculated changes in the free energies and entropies of association for HCO_2H–KF (A) and $HOCH_2CH_2OH$–KF (B) at different temperatures

	ΔG/kJ mol^{-1} [a]		ΔS/J K^{-1} mol^{-1} [b]	
T/K	(A)	(B)	(A)	(B)
283	−4.7	−12	−298	−99
293	−2.6	−10	−295	−102
303	−1.2	−9	−290	−102
313	+0.2	−8	−285	−102
323	+1.6	−8	−280	−99
333	+3.4	−8	−277	−96
343	+6.6	−7	−279	−96
353	—	−7	—	−93
363	—	−7	—	−91
373	—	−7	—	−88

[a] ±0.5 kJ mol^{-1}. [b] ±10 J K^{-1} mol^{-1}.

solvation energies, is a minimum thermochemical value of the hydrogen-bond energy in CH_3CO_2–H ··· F^-, *i.e.* −59.3 kJ mol^{-1}.[15] More recent work of Emsley and Hoyte [31] gives minimum thermochemical bond energies for HCO_2H–KF and CH_3CO_2H–KF of −91.9 and −77.7 kJ mol^{-1} respectively, close to our result, although again values are calculated for the gas phase, having made approximations for lattice energies. In their most recent work, Emsley *et al.*[32] report *ab initio* calculations including solvation effects for fluoride solutions in carboxylic acids. They find that the most stable species in methanoic acid–KF are $F(HCO_2H)_2^-$ and F^-, though solvated F^- in HCO_2H medium is of similar energy and thus presumably of similar composition. These are stabilized by 52 kJ mol^{-1} with respect to $H(HCO_2)_2^-$ + HF + F^-; 58 kJ mol^{-1} with respect to 2 HCO_2HF^-; 84 kJ mol^{-1} with respect to HCO_2^-, HF_2^-, and HCO_2H; 87 kJ mol^{-1} with respect to $H(HCO_2)_2^-$ + HF_2^-; and 99 kJ mol^{-1} with respect to 2 HCO_2^- + 2 HF. These values clearly bracket our observed $\Delta H^\ominus$ value of −89 ± 5 kJ mol^{-1}, but may suggest that the solvated fluoride does not necessarily dissociate to free fluoride.

When we look at the ln K_c *vs.* $1/T$ plot for ethane-1,2-diol (Figure 4) it gives a $\Delta H^\ominus$ value of −21 ± 5 kJ mol^{-1}, although the lowest temperature point deviates significantly from the straight line. Again, this value must be corrected for the self-association of the diol system, whose bonds must be broken before solvate formation can occur:[7] equation (4). On applying this correction, we obtain a corrected $\Delta H^\ominus$ value of −40 ± 5 kJ mol^{-1}. This value of −40 kJ mol^{-1} compares with a corresponding −50 ± 5 kJ mol^{-1} determined previously from ^1H n.m.r. data.[7]

$$HO \cdots HO \rightleftharpoons HO^- + HO^- \qquad \Delta H^\ominus = -18 \pm 5\ \text{kJ mol}^{-1} \quad (4)$$

These values of $\Delta H^\ominus$ for the acid and diol systems suggest that there may be some merit in a crude ordering of H-bond strength based on $\delta(^{19}F)$ (Table 1), with the methanoic acid- and ethane-1,2-diol–KF systems having limiting shifts within experimental error, and $\Delta H^\ominus$ values of −89 and −40 kJ mol^{-1}.

An explanation for the general deviation from linearity of the diol curve could be that contributions from other equilibria at higher temperatures, perhaps those generating HF_2^-, are important: equation (5).

$$2\,F^- \cdots HO^- \rightleftharpoons FHF^- + O^-(\text{solvated}) \qquad (5)$$

Changes in free energies and entropies of the two systems at the temperatures studied can be calculated from standard thermodynamic relationships and are given in Table 2. The value of ΔS for the methanoic acid system is essentially constant (−286 J K^{-1} mol^{-1}) and compares favourably with that for ethanoic acid–KF (+357 J K^{-1} mol^{-1}; positive since it was calculated for dissociation [10]).

Similarly, for the ethane-1,2-diol system, ΔS is reasonably constant at −97 J K^{-1} mol^{-1}. Our ΔS values are thus of larger magnitude than the range of ΔS values seen for 'normal' hydrogen bonds, −(50—70) J K^{-1} mol^{-1},[31] and this suggests that for both the acid and the diol systems studied the hydrogen bonds should be classed as 'strong'.

In conclusion, we have shown that fluorine chemical shifts at infinite dilution can be used only with caution as a very crude estimate of the strength of hydrogen bonding to fluoride. Variable-temperature studies yield thermodynamic parameters that are comparable to those determined by ^1H n.m.r. spectroscopy. Fluorine-19 n.m.r. has good sensitivity and a wide range of concentrations may be studied without interference from the solvent as in the case in ^1H n.m.r., which is usually used to study these systems. Thus we can recommend the cautious use of variable-temperature ^{19}F n.m.r. in the study of strong hydrogen bonding to fluoride.

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