Strong Hydrogen Bonding in Aliphatic Diol Solutions of Alkali-metal Fluorides

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Heavy alkali-metal fluorides are soluble in low-molecular-weight liquid aliphatic diols. Low-field shifts in the proton magnetic resonances of selected fluoride–diol solutions may be interpreted as being due largely to strong hydrogen bonding between the fluoride anion and the diol hydroxyls, although cation effects are also evident. Variable-temperature ^{1}H n.m.r. studies on KF–1,2-ethanediol, CH_3CN–1,2-ethanediol, and neat 1,2-ethanediol have been carried out and values of $-(50 \pm 10)$ kJ mol^{-1} for $\Delta H^\ominus$ and $-(130 \pm 25)$ J K^{-1} mol^{-1} for $\Delta S^\ominus$ have been determined for the $(F \cdots HO)^-$ hydrogen bond.

ONE of the recent developments in hydrogen-bonding research is the growing interest in complexes of the type $AH \cdots B^-$ where AH is an electron acceptor bonded to an electron-donor anion B^-.[1] Studies of these complexes have often revealed many unusual properties which may be interpreted as exaggerated manifestations of hydrogen bonding.

The effects of hydrogen bonding on the chemical reactivity of associated molecules are poorly understood and their importance in chemistry has been overshadowed by the study of better known physical and spectroscopic hydrogen-bonding manifestations. For complexes of the type $AH \cdots F^-$ however, it has been shown that the hydrogen bonding is often strong enough to reveal itself not only in the modified physical and spectroscopic parameters of the associated molecules but also in their changed behaviour in chemical reactions.[2] The recognition of this has provided a basis for the understanding and utilisation of the base-like properties of the fluoride ion.[3]

Before the advent of tetra-alkylammonium fluorides, crown ether-solubilised potassium fluoride, and other modern-day sources of the fluoride ion, aliphatic diol solutions of alkali-metal fluorides were often used as reagents for organofluorination and base-assisted condensation reactions.[3,4] Reported reaction products often included those derived from solvent attack on the reactant electrophile. Results such as these have prompted us to investigate the solubility of alkali-metal fluorides in some aliphatic diols and to attempt to determine the nature and strength of the salt–solvent interaction. Recent analysis of the bonding in ethanoic acid solutions of potassium fluoride has revealed the presence of very strong hydrogen bonds[5] and has shown that n.m.r. spectroscopy is a particularly useful technique for the study of such phenomena.[6,7] Interpretation of the apparently anomalous reaction chemistry of KF–ethanoic acid systems was greatly aided by the complementary spectroscopic studies.[8,9] We have therefore chosen ^{1}H n.m.r. as our technique for the investigation of the diolic systems, with ^{19}F n.m.r. studies to be reported in a subsequent paper.

EXPERIMENTAL

Proton n.m.r. spectra were recorded on a Bruker WP-60 FTNMR spectrometer operating at 60 MHz with a sweep width of 750 Hz in quad detection mode using 30° pulses. The average deviation was ± 0.19 Hz. The samples were referenced externally to tetramethylsilane.

Reagent-grade 1,2-ethanediol, 1,2- and 1,3-propanediols, and 1,4-butanediol were dried over 5-Å molecular sieves until they gave a constant δ(OH) shift. Commercial anhydrous potassium fluoride (99%), rubidium fluoride (99.9%), and caesium fluoride (99.9%) were dried by heating under vacuum before use.

Saturated solutions of fluorides in diols were prepared by stirring excesses of fluoride for about 24 h followed by removal of the excess by centrifugation. Solutions of lower concentration were prepared by dilution of saturated samples. All manipulations were carried out in a glovebox.

DISCUSSION

Table 1 lists the solubilities, in moles of fluoride per kilogram of solvent, of KF, RbF, and CsF in 1,2-ethanediol and of KF in 1,2- and 1,3-propanediols and 1,4-butanediol. Lithium fluoride is insoluble and NaF has only slight (<0.5 mol kg^{-1}) solubility in these solvents and they were not studied further. The three fluorides studied have outstanding solubilities in 1,2-ethanediol and in saturated solutions the molar ratios MF : 1,2-ethanediol are 1 : 2.8 (KF), 1 : 1.9 (RbF), and 1 : 1.7 (CsF). Thus the room-temperature mole-to-mole solubilities of these fluorides in 1,2-ethanediol are actually greater than those in ethanoic acid, liquid hydrogen fluoride, and water, the other three common

TABLE 1

Solubilities of metal fluorides in diols at 298 K

Metal fluoride	Solubilities/moles fluoride per kg solvent			
	1,2-ethanediol	1,2-propanediol	1,3-propanediol	1,4-butanediol
KF	5.73	3.37	1.05	0.36
RbF	8.60			
CsF	9.24			

solvents in which these fluorides show appreciable solubility.[10] The fluorides do not, however, dissolve in the diols with any significant evolution of heat.[10]

The effect of heavy alkali-metal fluorides on the $\delta(\mathrm{OH})_{\mathrm{obs.}}$ of 1,2-ethanediol is shown in Figure 1. The effect of KF on the $\delta(\mathrm{OH})_{\mathrm{obs.}}$ of the four diols studied is shown in Figure 2. In all cases the OH-proton chemical shift increased with molality of metal fluoride, as has been observed for solutions of heavy alkali-metal fluorides in ethanoic acid.[6] Methyl, methylene, and methine proton shifts were generally unaffected by the change in concentration of metal fluorides.

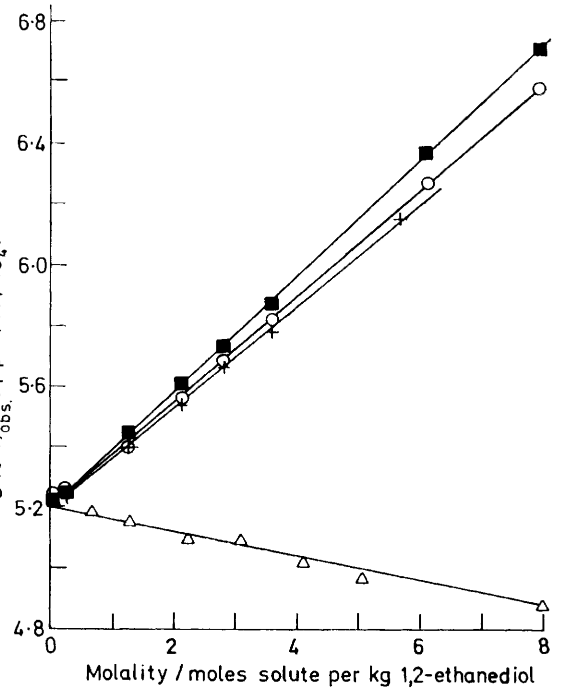

FIGURE 1 Plots of hydroxyl ^{1}H n.m.r. shifts, $\delta(\mathrm{OH})_{\mathrm{obs.}}$, against the molality of fluorides and acetonitrile in 1,2-ethanediol: (+), KF; (○), RbF; (■), CsF; and (△), acetonitrile

Diols are extensively self associated in the liquid state and form intramolecular[11] as well as intermolecular hydrogen bonds[12] so that $\delta(\mathrm{OH})_{\mathrm{obs.}}$ for pure diols will be a time-averaged resonance of the diol in all environments. Addition of a metal fluoride will disturb the equilibria existing in the pure diol and the fluoride ion will be surrounded by diol molecules which are presumably mostly polymerised since it would seem unreasonable to suppose that monosolvated fluoride ions will exist as discrete entities,[13] although we cannot as yet rule out the possible occurrence of species involving hydrogen bonding of both hydroxyl groups in a diol molecule to one fluoride ion. If we ignore the effect of F^- on diol molecules not directly attached to it, then we can say that the $\delta(\mathrm{OH})_{\mathrm{obs.}}$ values are time-averaged signals of the bulk solvent, the cation solvation sphere, and the anion solvation sphere. Each of these aspects will be briefly considered below.

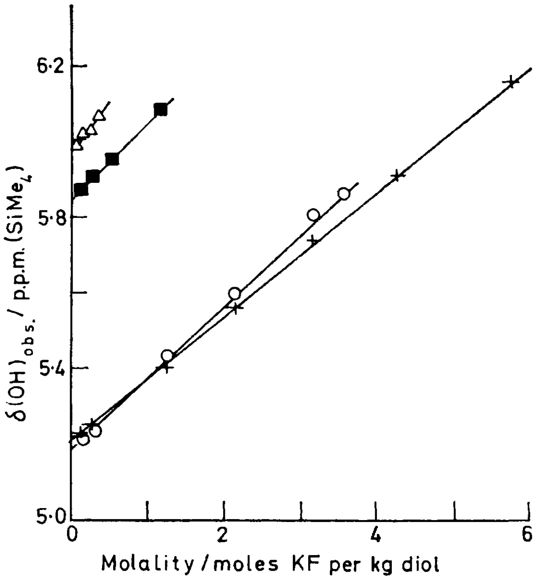

FIGURE 2 Plots of hydroxyl ^{1}H n.m.r. shift against the molality of KF in diols: (+), 1,2-ethanediol; (○), 1,2-propanediol; (■), 1,3-propanediol; and (△), 1,4-butanediol

The addition of any solute to a diol will disturb the hydrogen-bonding equilibria in that diol and we need to consider the effect of a non-hydrogen-bonding solute on $\delta(\mathrm{OH})$ so as to correct the values observed for the fluoride solutions by allowing for non-specific dilution effects. Unfortunately, solubility problems prevent the use of obvious solutes such as cyclohexane or carbon tetrachloride and in an attempt to discover the best solute for our purposes we studied the effect of several organic compounds on $\delta(\mathrm{OH})$. The results are summarised in Figure 3. At infinite dilution of the diol, acetonitrile gives the value most closely in agreement with the calculated value for an isolated diol molecule[12] and we therefore selected this compound for our studies. A

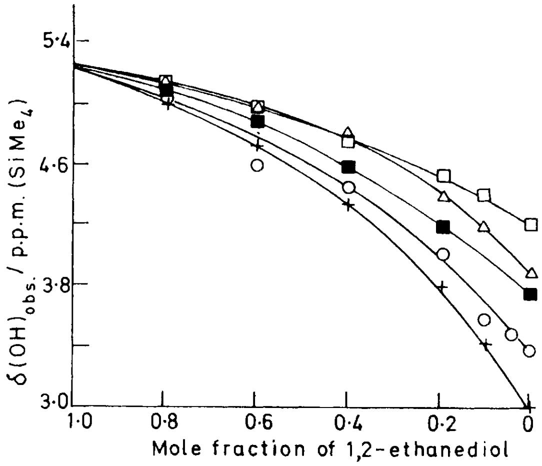

FIGURE 3 Plots of hydroxyl ^{1}H n.m.r. shift against the mole fraction of 1,2-ethanediol in various solvents: (+), acetonitrile; (○), acetone; (■), 1,4-dioxan; (△), tetrahydrofuran; (□), dimethylformamide

linear variation of $\delta(OH)_{obs.}$ over the range 0—8 mol kg^{-1} was observed for CH_3CN–1,2-ethanediol (Figure 1) and this plot was used to correct the $\delta(OH)$ value obtained for the fluoride–1,2-ethanediol systems by using equation (1) where m is the molality of the solute.

$$\delta(OH)_{sol.} = 5{\cdot}20 - 0{\cdot}05\, m \qquad (1)$$

Inspection of Figure 1 reveals a cation effect which is small at low concentrations but significant at higher concentrations. Presumably, direct contact ion pairs, as opposed to solvent-separated ion pairs, become more important as the MF concentration increases and smaller cations would be expected to form tighter ion pairs resulting in a greater weakening of the hydrogen bond [14] and lower hydrogen-bond chemical shifts.

The third, and most important, aspect which makes the largest contribution to $\delta(OH)_{obs.}$ is the formation of a strong hydrogen bond with fluoride anions. If we assume that all the dissolved anions are solvated and that the hydroxyl proton under these conditions has a shift denoted by $\delta(OH)_{OHF}$, we can use the same weighted equation for $\delta(OH)_{obs.}$ employed by Clark and Emsley [6] for KF in ethanoic acid, (2), where in our case a is the

$$\delta(OH)_{obs.} = \delta(OH)_{sol.} + (a/b)[\delta(OH)_{OHF} - \delta(OH)_{sol.}] \qquad (2)$$

number of moles of F^- and b is the number of moles of hydroxyl (twice the number of moles of diol). This equation predicts a linear relationship between $\delta(OH)_{obs.}$ and concentration where the slope of the curve is $[\delta(OH)_{OHF} - \delta(OH)_{sol.}]/b$. Evaluation of $\delta(OH)_{OHF}$ gives values of 11.00 (KF), 11.32 (RbF), and 11.96 p.p.m. (CsF). Correction of these values using (1) gives 12.22 (KF), 12.54 (RbF), and 13.18 p.p.m. (CsF). The last of these values, 13.18 p.p.m., is probably the most realistic one for $\delta(OH)_{OHF}$ since it allows for non-specific disruption of the solvent structure and represents the least amount of cation weakening of the hydrogen bond among the systems studied.

A similar approach to that described above may be applied to the systems involving heavier diols. Evaluation of uncorrected $\delta(OH)_{OHF}$ values gives 11.20 (KF–1,2-propanediol), 13.22 (KF–1,3-propanediol), and 13.97 p.p.m. (KF–1,4-butanediol).

It has usually been assumed that the stronger the hydrogen bond the less shielded is the proton, although most workers in the field agree that qualitative indications of relative hydrogen-bond strengths are only provided by considering relative magnitudes of downfield shifts for a series of bonds involving a common hydrogen-bond electron acceptor or donor. Even this qualified interpretation does not always seem to be valid: a comparison of the ethanoate–ethanoic acid and fluoride–ethanoic acid hydrogen bonds, for example, has shown that the observed $\delta(OH)_{OHO}$ value for the former is appreciably greater than the $\delta(OH)_{OHF}$ value for the latter, despite overwhelming evidence pointing to a stronger hydrogen bond in the latter system.[6] Downfield shifts in the proton resonance signals of associated hydroxyl hydrogens are thought to be due to the relative influence of anisotropic magnetic currents in the electron donor and polarisation of the O–H bond by the electron donor. Thus, in the ethanoic acid systems, the larger downfield shift induced by the ethanoate anion is probably due to the magnetic anisotropy of the ethanoate anion [6] and its greater ability to polarise the O–H bond relative to the fluoride anion.[13]

Comparison of our $\delta(OH)_{OHF}$ values with other such values would, however, seem justified. The observed values for the diol systems are less than those observed for ethanoic acid [6] and 2,2,2-trifluoroethanoic acid systems,[15] suggesting that the former systems contain the weaker hydrogen bonds. In an attempt to confirm this conclusion, while at the same time showing that diol–F^- bonds are strong and therefore likely to have a significant effect on the properties of the diols, we have carried out variable-temperature ^1H n.m.r. studies with the object of estimating the thermodynamic parameters of association.

Temperature dependency of hydrogen-bond-associated molecules has been reported by many workers. Dilution with non-hydrogen-bonding solvents or raising the temperature of the system causes breaking of hydrogen bonds, resulting in movement of the hydroxyl proton resonance to higher magnetic fields. We have observed a similar temperature effect for diol systems.

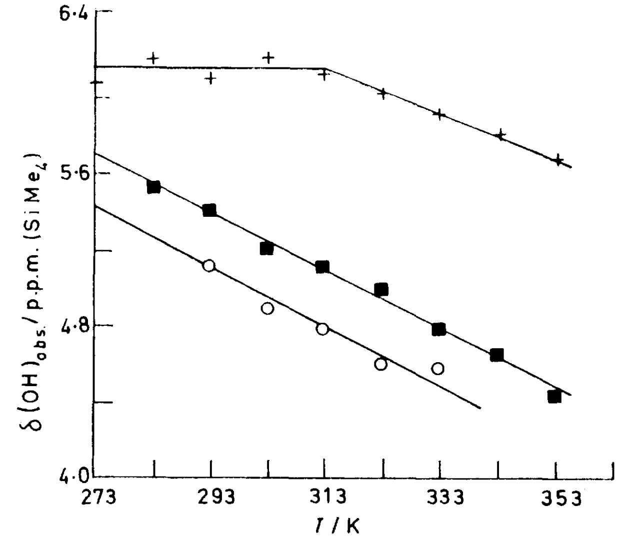

FIGURE 4 Plots of hydroxyl ^1H n.m.r. shift against temperature for a 5.73 mol kg^{-1} solution of KF in 1,2-ethanediol (+), a 5.73 mol kg^{-1} solution of acetonitrile in 1,2-ethanediol (○), and neat 1,2-ethanediol (■)

Figure 4 is a plot of $\delta(OH)_{obs.}$ *versus* temperature for neat 1,2-ethanediol and 5.73 mol kg^{-1} solutions of KF and CH_3CN in 1,2-ethanediol. The plot shows linear correlations for both neat diol and CH_3CN–diol systems. For KF–diol, $\delta(OH)_{obs.}$ is temperature independent below *ca.* 313 K, suggesting that at temperatures below this value there is complete solvation of all dissolved fluoride anions.

Since near the freezing point it is assumed that a completely hydrogen-bonded state is realised for diols in the pure liquid state,[16] we assumed such a state in 1,2-ethanediol at 273 K and between dissolved fluoride anions and 1,2-ethanediol at 273 K. From Figure 4 it is possible to estimate the fraction of ' free ' fluoride ion in KF–1,2-ethanediol at any temperature using (3) where $\delta(OHF)_{273}$ is the observed proton chemical shift

$$\frac{[F^-]_{\text{free}}}{[F^-]} = \frac{\delta(OHF)_{273} - \delta(OHF)_T}{\delta(OHF)_{273} - \delta(OHO)_T} \qquad (3)$$

of a 5.73 mol kg^{-1} solution of KF in 1,2-ethanediol at 273 K (total solvation of F$^-$ is assumed), and $\delta(OHF)_T$ and $\delta(OHO)_T$ are the observed proton chemical shifts at a given temperature T of a 5.73 mol kg^{-1} KF solution and a 5.73 mol kg^{-1} CH_3CN solution respectively.

In KF–diol solutions, where the diol is assumed to be

$$F^- + \text{diol} \rightleftharpoons (F \cdots \text{diol})^- + \text{diol} \qquad (4)$$

in excess, the equilibrium (4) will be set up and to a first approximation we may write (5) for the equilibrium

$$K_c = [F^- \cdots \text{diol}]/[F^-] \qquad (5)$$

constant for association where K_c is used rather than K based on activities as the charge is the same on both sides of equilibrium (4). Combining (3) and (5) enables us to determine values for 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 $\ln K$ *versus* $1/T$ should yield $\Delta H^\ominus$ for association (Figure 5). This approach provides us with a value of *ca.* $-(32 \pm 5)$ kJ mol^{-1} which represents the heat change on breaking the OH $\cdots$ F$^-$ bond in the bulk 1,2-ethanediol solvent. It does not, however, provide us with an estimation of the heat change in breaking the OH $\cdots$ F$^-$ bond in isolation, since we must allow for the possibility of the diol molecule, which is released on breaking the OH $\cdots$ F$^-$ bond, forming a new hydrogen bond to another diol molecule or diol polymer. In order to determine the probability of released diol molecules forming new hydrogen bonds and to arrive at an estimate of the $\Delta H^\ominus$ of self association it is necessary to treat the data for pure diol from Figure 4 in a manner similar to that described for the KF–diol system.

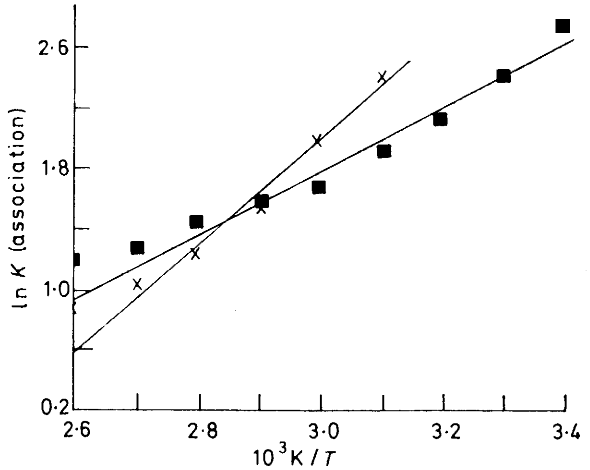

FIGURE 5 Plots of reciprocal temperature against logarithm of the equilibrium constant for association for a 5.73 mol kg^{-1} solution of KF in 1,2-ethanediol (×) and neat 1,2-ethanediol (■)

In the neat diol, at any given temperature, we assume there is an equilibrium (6) set up between monomers and polymers. Here, polymers represent all species except

$$\text{monomers} + \text{polymers} \rightleftharpoons \text{polymers} \qquad (6)$$

monomers because it is not possible to distinguish higher polymers from dimers similar to the case in alcohols.[17] Hence K_c' for association equals $1/c_m$ where c_m is the concentration of the monomer. The fraction of monomer at any temperature is given by (7) where $\delta(OHO)_{273}$ and $\delta(OHO)_T$ are the observed proton chemical shifts at

$$\frac{[\text{monomer}]}{[\text{diol}]} = \frac{\delta(OHO)_{273} - \delta(OHO)_T}{\delta(OHO)_{273} - \delta_m} \qquad (7)$$

273 K (at which temperature the diol is assumed to be in a completely hydrogen-bonded state) and a given temperature T respectively; δ_m is the proton chemical shift of the diol monomer which is less readily available. Infinite-dilution shifts derived from studies in non-polar, non-hydrogen-bonding solvents are normally considered to be acceptable approximations of monomer shifts, but we do not consider the infinite-dilution shift of 1,2-ethanediol in CH_3CN to be a reasonable estimation of the monomer shift and prefer to use the calculated value of 0.34 p.p.m.* The monomer fractions calculated from (7) varied from 0.030 at 283 K to 0.299 at 373 K and are low enough even at the higher temperature range of our studies to indicate a high probability of bulk-solvent recapture of a diol molecule released on breaking the F$^-$ $\cdots$ HO bond. The plot of $1/T$ against $\ln K_c'$ for the self association of 1,2-ethanediol is given in Figure 5 and provides a value of $\Delta H^\ominus$ of $-(18 \pm 5)$ kJ mol^{-1}. We may therefore represent the breaking of F$^-$ $\cdots$ HO bonds in bulk diol by two simultaneous equations (8) and (9) giving an improved $\Delta H^\ominus(F^- \cdots HO)$ value of $-(50 \pm 10)$ kJ mol^{-1}.

$$F^- \cdots HO \longrightarrow F^- + HO; \quad \Delta H^\ominus = 32 \pm 5 \text{ kJ mol}^{-1} \qquad (8)$$

$$HO + HO \longrightarrow HO \cdots HO; \quad \Delta H^\ominus = -(18 \pm 5) \text{ kJ mol}^{-1} \qquad (9)$$

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* An attempt was made to measure the chemical shift of the diol in the vapour state using a ^{11}B probe and the ^1H decoupling coil for ^1H observations at 373 K, with an external D_2O lock signal derived from the Bruker probe modified for external lock with a D_2O sample and coil. Two drops of 1,2-ethanediol were placed in the tube which was sealed under vacuum. An unresolved doublet at *ca.* 0.6 p.p.m. was attributed to signals due to free and intramolecular hydrogen-bonded hydrogens of the monomer. This value is in good agreement with the calculated value used in our calculations.

This value is significantly less than that obtained for carboxylic acid –F^- systems (*ca.* 120 kJ mol^{-1}) [5,6] and is slightly smaller than those estimated for phenol–F^- (62 ± 5 kJ mol^{-1}) [2] and catechol–F^- (63 ± 5 kJ mol^{-1}),[2] but is certainly outside the range of ' normal ' hydrogen-bond enthalpies (12—40 kJ mol^{-1}). The plots of ln K_c *versus* $1/T$ on which our results are based show significant deviation from linearity, especially for the fluoride system, but the coefficient of correlation (using a least-squares fitting routine) was found to be 0.98 for both curves.

Changes in the free energies and entropies of the two systems at the temperatures studied are readily obtained from standard thermodynamic relationships and are given in Table 2. The relative ΔS values for the two systems are in keeping with a large increase in system order resulting from the formation of stronger hydrogen bonds on adding KF to 1,2-ethanediol.

TABLE 2

Calculated changes in the free energies and entropies of association for 1,2-ethanediol and KF–1,2-ethanediol at different temperatures

T/K	$\Delta G \pm 0.5$ kJ mol^{-1}		$\Delta S \pm 20$ J K^{-1} mol^{-1}	
	F^-–diol	diol–diol	F^-–diol	diol–diol
323	−6.5	−5.1	−135	−40
333	−5.1	−4.8	−135	−40
343	−4.3	−4.5	−133	−39
353	−3.6	−4.2	−131	−39
363	−3.2	−4.0	−129	−39
373	−2.7	−3.8	−127	−38

In conclusion, we have shown that the dissolution of an alkali-metal fluoride in a liquid diol results in disruption of the solvent structure and the formation of strong hydrogen bonds between the fluoride anions and the diol hydroxyls which are comparable in strength to those formed between F^- and phenolic compounds. The formation of this type of hydrogen bond will result in a significant shift in electron density, from the electron-donor anion to the electron-acceptor diol. The nucleophilicity of the fluoride will be reduced by this effect while that of the diol will be enhanced. Reaction of MF–diol systems with electrophiles such as halogenoalkanes might therefore be expected to result in products derived from fluoride-anion attack (fluoroalkanes) and solvent attack (ethers), as well as possible elimination products (alkenes), as has indeed been observed to be the case.[3]

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