

## Fluoride solvation—the case of the missing ion

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**Abstract** - The thermodynamics of fluoride ion solvation in nonaqueous and mixed aqueous solvents are reviewed. Gibbs energies of transfer,  $\Delta_t G^\circ(F^-)_{H_2O-S}$ , indicate that the solvation of the fluoride ion is dominated by hydrogen bonding. Thus,  $\Delta_t G^\circ(F^-)_{H_2O-S}$  is unfavourable for virtually all solvents, especially dipolar aprotics, and correlates well with solvent acceptor strength. The corresponding enthalpy and entropy data are few and are of low quality but suggest  $F^-$  solvation is entropy controlled: the only ion known to be so. In mixed aqueous solvents the values of  $\Delta_t G^\circ(F^-)_{H_2O-H_2O-S}$  generally increase monotonically with declining water content. However, this results from the fortuitous cancellation of dramatic, but largely opposing, variations in  $\Delta_t H^\circ$  and  $\Delta_t S^\circ$ . The complex changes in these parameters are related to subtle changes in ion-solvent and solvent-solvent interactions. Finally, a relationship between fluoride and hydroxide solvation is proposed.

### 1. INTRODUCTION

The thermodynamics of ion-solvation have been studied intensively over the last 25 years. Although many ions have received attention, most information relates to relatively simple species such as the alkali metal and  $d^{10}$  cations  $Ag^+$ ,  $Tl^+$ , etc., and the halide anions (ref. 1,2,3,4). Such ions, of unambiguous size, charge and electronic structure (ref. 5), are a logical starting point for the qualitative and quantitative understanding of the complex interactions which occur in nonaqueous electrolyte solutions (ref. 1). To fully exploit the varying properties of such ions it is desirable to have data for as many members of the group as possible. Studies of halide ion solvation have, however, been almost entirely restricted to chloride bromide and iodide (ref. 1,2,3). In this sense fluoride is indeed "the missing ion".

The gathering of such information is not mere "stamp collecting", as Ernest Rutherford might have put it, but is vital to the development of our understanding of ion-solvation. This has been illustrated rather nicely by Kundu *et al.* (ref. 6). These workers were interested in checking the validity of the widely used electrostatic extrapolation procedure (ref. 1) and showed that vastly different results were obtained when fluoride data were included along with the other halides.

Fluoride also attracts interest because of its relatively simple electronic structure: with no low-lying d-orbitals its bonding characteristics are reasonably straightforward (ref. 5). Fluoride can also be used as a model for testing simple theories of ion-solvation behaviour (ref. 7) and it is important as a (potentially simpler) isoelectronic model for the important hydroxide ion (ref. 5,7). The use of "active" fluoride in nonaqueous solvents for laboratory scale organic syntheses is well established (ref. 8) but such reactions are also attracting attention industrially.

It is not clear why so little information on fluoride ion solvation is currently available. Measurements of Gibbs energies, as pointed out previously (ref. 9), are restricted by the unavailability of a fluoride-responsive electrode suitable for routine use in nonaqueous solvents, which precludes use of the popular emf method. However, there does not appear to

be any particular reason why solubility measurements have not been more widely employed: apart from their lack of charisma. Certainly, no such restrictions should apply to enthalpy measurements by direct calorimetry and yet the available data are even more limited than for Gibbs energies (ref. 9).

In recent years, my group at Murdoch University has begun a systematic study of the thermodynamics of fluoride ion solvation in nonaqueous and mixed solvents (ref. 9,10,11,12,13). This work has focussed mainly on Gibbs energies (ref. 9,10,11), enthalpies and entropies (ref. 9,12,13) although some work is also being done on volumes and heat capacities (ref. 12,14,15). This paper describes some of our recent work and reviews present knowledge of fluoride ion solvation.

## 2. THERMODYNAMIC BACKGROUND

The standard Gibbs energy of solution,  $\Delta_{\text{sln}}G^\circ(\text{MA})$ , of electrolyte MA in a solvent is a measure of the overall strength of solvation of the ions  $M^+$  and  $A^-$ . As such it is directly related to the activities of the ions in solution

$$\Delta_{\text{sln}}G^\circ(\text{MA}) = -RT \ln a_{M^+} a_{A^-} = -RT \ln K_S^\circ \quad (1)$$

where  $K_S^\circ$  is the standard state solubility product of MA.

However, in comparing ion-solvation characteristics in different solvents it is more convenient to use the Gibbs energy of transfer (ref. 1,3)

$$\Delta_t G^\circ(\text{MA})_{S1-S2} = \Delta_{\text{sln}}G^\circ(\text{MA})_{S2} - \Delta_{\text{sln}}G^\circ(\text{MA})_{S1} \quad (2)$$

which is a direct measure of the differences in solvation of the electrolyte in the solvent (or solvent mixture) S2 and some arbitrary reference solvent S1 (usually  $\text{H}_2\text{O}$ ).

From equations (1) and (2) it follows that, at 298 K,

$$\Delta_t G^\circ(\text{MA})_{S1-S2} = 5.709 \Delta p K_S^\circ \quad (3)$$

where  $\Delta p K_S^\circ$  is the change in the negative logarithm of the standard solubility product in going from S1 to S2. Thus, Gibbs energies of transfer of fluoride salts can be determined from solubility measurements and, in the absence of a suitable electrochemical method, this is how most fluoride data have been generated (ref. 9).

Of course, to obtain  $\Delta_t G^\circ(\text{F}^-)$ , it is necessary to employ an appropriate non-thermodynamic assumption since single ion properties are undefined within the framework of thermodynamics (ref. 1). The widely accepted (ref. 1,3,9) tetraphenylarsonium tetraphenylborate (TATB) assumption has been used throughout our work whenever possible. This assumption may be expressed

$$\Delta_t X^\circ(\text{Ph}_4\text{AsBPh}_4) \equiv 2\Delta_t X^\circ(\text{Ph}_4\text{As}^+) \equiv 2\Delta_t X^\circ(\text{BPh}_4^-) \quad (4)$$

where  $X = G, H, S$ , etc. Fluoride data are thus derived from electrolyte data using

$$\Delta_t X^\circ(\text{F}^-) = \Delta_t X^\circ(\text{MF}) - \Delta_t X^\circ(\text{M}^+) \quad (5)$$

where  $\Delta_t X^\circ(\text{M}^+)$  has been determined, from an appropriate set of measurements, via the TATB assumption.

## 3. GIBBS FREE ENERGIES OF TRANSFER

The available data for the Gibbs energies of transfer of the fluoride ion from water to nonaqueous solvents have been reviewed recently (ref. 9). These values along with more recent data are summarized in Table 1.

TABLE 1. Gibbs energies of transfer of the fluoride ion from water to nonaqueous solvents (TATB assumption, 298.15 K)<sup>a</sup>

Solvent (S) <sup>b</sup>	$\Delta_t G^\circ(\text{F}^-)_{\text{H}_2\text{O}-\text{S}}/\text{kJ mol}^{-1}$
acetone (AC)	84, 79 <sup>c</sup>
acetonitrile (AN)	70
BuOH	(15), 55 <sup>d</sup>
D <sub>2</sub> O	-0.2
1,2-dichloroethane (DCE)	(65)
N,N-dimethylformamide (DMF)	85
dimethylsulphoxide (DMSO)	61, 73 <sup>c</sup>
ethyleneglycol (EG)	17
EtOH	26
formamide (FA)	24
MeOH	17
nitrobenzene (NB)	(44), 70 <sup>d</sup>
propylene carbonate (PC)	58
PrOH	22, 40 <sup>c</sup>
2-PrOH	47 <sup>c</sup>
tert-BuOH (TBA)	60 <sup>c</sup>
tetrahydrofuran (THF)	(62)

<sup>a</sup> Data from (ref. 9) unless otherwise indicated; data in parentheses are probably unreliable. <sup>b</sup> Solvent abbreviations are given in parentheses and are used throughout this paper. <sup>c</sup> Derived from recent measurements of KF solubilities (ref. 13). <sup>d</sup> Estimated value (ref. 13).

### 3.1 Reliability of the data

Although solubility measurements are reasonably straightforward and should in principle provide reliable estimates of  $\Delta_t G$  (an error of  $\pm 1$  in  $\Delta pK_s^\circ$  corresponds only to ca.  $\pm 6$  kJ mol<sup>-1</sup> in  $\Delta_t G^\circ$ , see equation (3)) it must be noted that many of the data in Table 1 are of dubious quality. For example, independent estimates (ref. 9) of the solubility of NaF in AN differ by 10 orders of magnitude or  $\sim 60$  kJ mol<sup>-1</sup>! Even when there is agreement about individual salt solubilities, estimates of  $\Delta_t G^\circ(\text{F}^-)$  based on different salts are often in poor agreement. For example, the values of  $\Delta_t G(\text{F}^-)_{\text{H}_2\text{O}-\text{DMF}}$  derived from alkali metal fluoride salt solubilities (ref. 9) vary by 50 kJ mol<sup>-1</sup>.

There are two obvious potential sources of error in the data in Table 1: activity coefficient and ion-pairing effects. It is readily shown, using any of the common expressions for activity coefficients (ref. 16), that such effects are negligible ( $< 5$  kJ mol<sup>-1</sup>) except in very low dielectric constant ( $\epsilon < 20$ ) solvents. Judicious salt selection, especially if coupled to an appropriate correction can keep errors well below 5 kJ mol<sup>-1</sup>. Ion pairing (association) is a more difficult problem especially as little is known about fluoride complexes in nonaqueous solvents (ref. 17,18). However, plausible estimates of association constants can be shown to have significant effects. For example, a salt with a  $pK_s$  of 6 and an association constant of  $10^4$  will result in an error of  $\sim 5$  kJ mol<sup>-1</sup> in  $\Delta_{\text{sln}}G(\text{MF})$ . Fortunately, the solubilities of most fluoride salts are much lower than this (ref. 9), which reduces the effects of ion association considerably.

Thus it appears that neither activity coefficients nor ion-association account for the wide variations in  $\Delta_t G^\circ(\text{F}^-)$  in the literature. The problem therefore probably lies with experimental errors.

### 3.2 Sources of experimental error

It is unclear why fluoride salt solubilities should be difficult to measure but the following may be noted. (i) Fluoride adsorbs strongly on glass, and possibly on plastics in poorly solvating solvents (ref. 19). (ii) Fluoride salts often form very finely divided suspensions making accurate determination of very low solubilities difficult. (iii) Most fluoride salt solubilities in nonaqueous solvents change dramatically upon addition of small amounts of water (ref. 9,10). Reliable results thus require accurate knowledge of the water content. (iv) The disparity between fluoride salt solubilities in water and most nonaqueous solvents can result in the salting out of even quite small quantities of water (ref. 13). These may be difficult to detect in cloudy solutions and may well be the cause of some of the grosser variations reported in the literature. For example, the apparent solubility of CsF in AN (ref. 13), measured using strict vacuum line techniques, shows the expected increase up to ~ 200 ppm H<sub>2</sub>O and then decreases. Since both Cs<sup>+</sup> and F<sup>-</sup> are preferentially solvated by H<sub>2</sub>O (ref. 1,9) this cannot be due to an increase in  $\Delta_{s,ln}G^{\circ}(\text{CsF})$  but is consistent with phase separation.

## 4. ENTHALPIES AND ENTROPIES

Almost no reliable enthalpy or entropy data exist for fluoride solvation (ref. 9). The available data are summarized in Table 2 but they should be treated with great caution. There is clearly considerable scope for reliable calorimetric studies in this area.

TABLE 2. Molar enthalpies and molar entropies of transfer of the fluoride ion from water to nonaqueous solvents (TATB assumption, 298.15 K)<sup>a</sup>

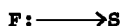
Solvent	$\Delta_{tH}(\text{F}^-)_{\text{H}_2\text{O}-\text{s}}$ kJ mol <sup>-1</sup>	$\Delta_{tS}(\text{F}^-)_{\text{H}_2\text{O}-\text{s}}$ JK <sup>-1</sup> mol <sup>-1</sup>
AC	(50)	(-114)
AN	(30)	(-134)
D <sub>2</sub> O	-1.4	-0.4
DCE	(35)	(100)
DMF	32	(-208)
EG	25 <sup>b</sup>	27 <sup>c</sup>
FA	22	-4
MeOH	20	10
NB	(-4)	(248) <sup>c</sup>
NMA	(42)	-
NMF	(62)	-

<sup>a</sup> Data from (ref. 9) unless otherwise indicated. Values in parentheses are probably unreliable. Solvent abbreviations as for Table 1. <sup>b</sup> Estimated from EG/H<sub>2</sub>O data (ref. 12). <sup>c</sup> Calculated from  $\Delta_{tG} = \Delta_{tH} - T\Delta_{tS}$ , using  $\Delta_{tH}$  data from this table and  $\Delta_{tG}$  from Table 1.

## 5. TRENDS IN FLUORIDE SOLVATION IN NONAQUEOUS SOLVENTS

### 5.1 Gibbs free energies

The outstanding feature of the Gibbs energies in Table 1 is that, compared with water, the fluoride ion is more poorly solvated ( $\Delta_{tG}(\text{F}^-)_{\text{H}_2\text{O}-\text{s}}$  is positive) in virtually all the solvents. This is a reflection of the strong stabilization of F<sup>-</sup> in H<sub>2</sub>O through H-bonding (ref. 9). As shown in Fig. 1 there is an excellent correlation between solvent acceptor properties (expressed, for example, by the Dimroth-Reichardt E<sub>T</sub> parameter (ref. 20)) as would be expected for an anion undergoing a coordinative interaction with solvent molecules



Similar correlations using multivariate analysis have also been noted with related solvent parameters (ref. 21,22). The correlation in Fig. 1 is sufficiently good to act as a data check. Thus it would seem that reported

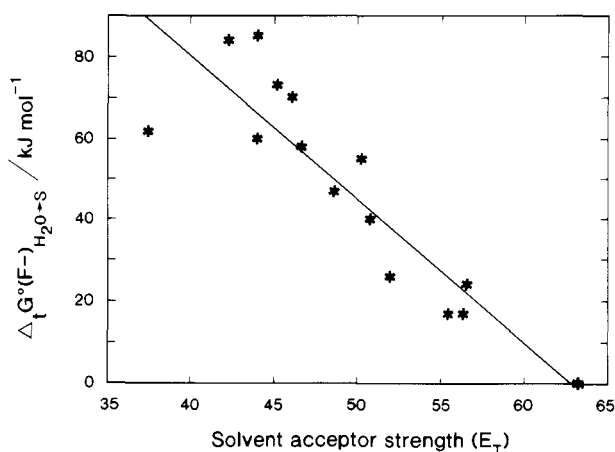


Fig. 1. Gibbs energies of transfer of fluoride (Table 1) as a function of solvent acceptor strength  $E_T$  (ref. 1).

values of  $\Delta_t G(F^-)$  of 44 and 65 kJ/mol for nitrobenzene and dichloroethane (Table 1), both with  $E_T \approx 42$ , are underestimated by many tens of kJ/mol. The data for THF also appears low. A similar conclusion was reached by Luehrs and Godbole (ref. 22) for  $F^-$  in nitrobenzene.

## 5.2 Enthalpies and entropies

Figures 2 and 3 plot most of the available data for enthalpies and entropies of transfer of the halide ions (ref. 9,23). The enthalpies show a more or less uniform increase in going from  $I^-$  to  $F^-$  consistent with the decreasing solvent anion interaction as the anionic charge/radius ratio decreases.

The entropies on the other hand show a spectacular difference between protic and aprotic solvents. Thus,  $\Delta_t S(F^-)_{H_2O \rightarrow S}$  for protic solvents is approximately zero whilst for aprotic solvents it is very strongly negative (unfavourable). This can be explained in terms of the degree of structure of protic as compared with aprotic solvents (ref. 8). It appears therefore that the difference in Gibbs energies (Table 1) is almost entirely due to entropy effects. If this is so, and the inadequacies of the available data should not be overlooked here, fluoride is the first ion whose solvation characteristics appear to be "entropy controlled". This is in marked contrast to other simple ions which, as Parker (ref. 24) pointed out many years ago, are largely "enthalpy controlled"; i.e., their ion-solvation differences could mainly be accounted for by differences in  $\Delta_t H$  or bond strengths between the ion and the solvent.

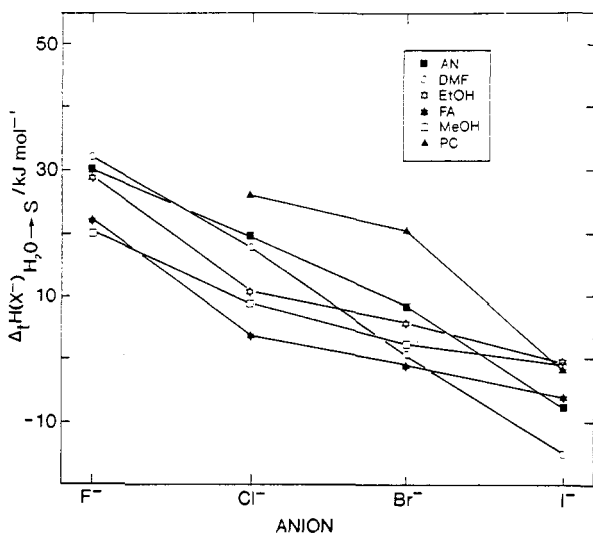


Fig. 2. Enthalpies of transfer of the halide ions at 298K in nonaqueous solvents (after (ref. 9)).

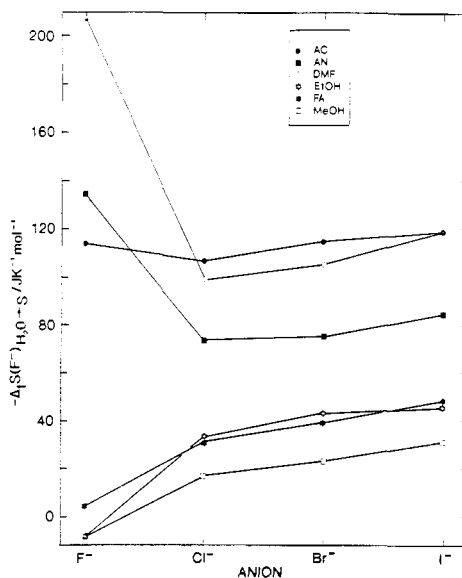


Fig. 3. Entropies of transfer of the halide ions at 298K in nonaqueous solvents (after (ref. 8)).

## 6. SOLVATION IN MIXED SOLVENTS

Mixed solvents are of greater interest than pure nonaqueous solvents for many practical applications because they allow a better selection of solvent properties (ref. 1). Typical examples include the enhancement of lithium battery performance (ref. 25,26), recrystallizations (ref. 27), chemical synthesis (ref. 27,28), hydrometallurgical applications (ref. 29) and so on. Mixed aqueous solvents have some additional advantages: ease of handling and reduced cost. Apart from these considerations, the study of ion-solvation in mixed solvents can provide greater insight into both ion-solvent and solvent-solvent interactions (ref. 1,9,29,30).

### 6.1 Gibbs energies

Table 3 summarizes the Gibbs energies of transfer for solvent mixtures for which data are available over the entire composition range (ref. 10,12,13). In general,  $\Delta_t G(F^-)_{H_2O-H_2O+S}$  show more or less monotonic, although not necessarily parallel, increases (Fig. 4) with decreasing water content. As expected for an ion preferentially solvated by  $H_2O$ , the increase often becomes steep at low water concentrations. Although DMSO appears to be an exception to this rule this may be more a reflection on the reliability of the data at high DMSO concentrations (see below).

TABLE 3. Molar Gibbs energies of transfer of the fluoride ion from water to aqueous solvent mixtures (TATB assumption, 298.15K)<sup>a</sup>

Solvent composition 100 x <sub>s</sub>	$\Delta_t G^\circ(F^-)_{H_2O-H_2O+S}$									Ref
	5	10	20	40	60	80	90	95	100	
AC	4.0	9.5	18.0	28.5	41.0	59.0	68.5	80.5	85 <sup>b</sup>	12
	5.1	10.2	18.0	-	-	-	-	-	-	8
AN	1.5	3.3	8.6	17.0	23.4	32.3	39.0	43	(45)	9
DMSO	3.5	8.5	19.5	39.0	57	(67)	(71)	(72)	(73)	12
	5.2	9.2	18.1	-	-	-	-	-	-	5
EG	2.5	3.8	5.5	9.0	11.7	14.0	15.2	16.0	17.6 <sup>b</sup>	9
EtOH	1.0	2.6	7.4	15.0	18.0	20.3	22.4	24.0	25.8 <sup>b</sup>	9
MeOH	0.7	1.5	3.2	6.8	10.0	13.8	15.0	17.5	18.3	10
	0.7	1.5	3.3	7.2	10.9	15.0	17.8	18.7	20.8	8

<sup>a</sup> Data in parentheses may be unreliable <sup>b</sup> Estimated by extrapolation

Figure 5 plots  $\Delta_t G(X^-)_{H_2O-H_2O+AC}$  for the halides in aqueous acetone mixtures (ref. 13,23,32). There is a remarkably consistent pattern with solvation becoming less favourable in the order  $F^- < Cl^- < Br^- < I^-$  at all compositions with the differences increasing as the water content decreases. This pattern which is found for other solvents (ref. 9,11) is consistent with the decreasing tendency for H-bonding as the charge/radius ratio decreases down the halide group and as the water content of the solvent decreases.

### 6.2 Enthalpies and entropies

The relatively featureless variations of  $\Delta_t G(F^-)_{H_2O-H_2O+S}$  with solvent composition (Fig. 5) mask complex and dramatic changes which are clearly revealed in the enthalpy and entropy changes (ref. 11), in the few systems which have been studied (ref. 9). Enthalpy data for water-alcohol systems (ref. 9,12) are plotted in Fig. 6. Although there are significant differences, all three alcohols show an initial increase in  $\Delta_t H(F^-)$  at low alcohol levels followed by a decrease and then a steady rise to strongly positive (unfavourable) values. These complex variations arise from a subtle interplay of ion-solvent and solvent-solvent interactions (ref. 11,30).

It is generally thought, from volumetric and other measurements, that the addition of small amounts of alcohol to an aqueous electrolyte solution results in re-enforcement of the water structure with most of the organic molecules accommodated within the voids (ref. 1,30). Since  $F^-$  is preferentially solvated by the water molecules which are now less available,  $\Delta_t H(F^-)_{H_2O-H_2O+ROH}$  becomes more positive. As the alcohol concentration increases, the organic molecules eventually can no longer be fitted into the water structure which then begins to break down. Water molecules are thus more available for interaction with  $F^-$ , resulting in a (favourable) decrease;  $\Delta_t H(F^-)_{H_2O-H_2O+ROH}$  thus passes through a maximum. The composition at which this occurs depends

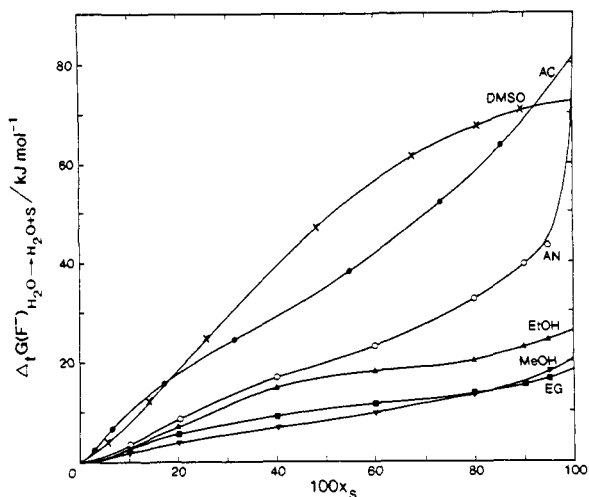


Fig. 4. Gibbs energies of transfer of fluoride in aqueous mixed solvents at 298K as a function of solvent composition. Mixtures of  $H_2O$  with: EG (■); MeOH (▼); EtOH (▲); AN (○); DMSO (×); AC (●). Data from (ref. 9,13).

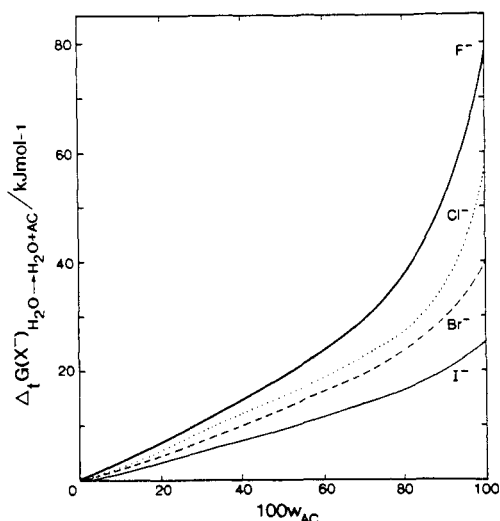


Fig. 5. Gibbs energies of transfer of the halides in acetone/water mixtures at 298K as a function of solvent composition. Data from (ref. 13,32).

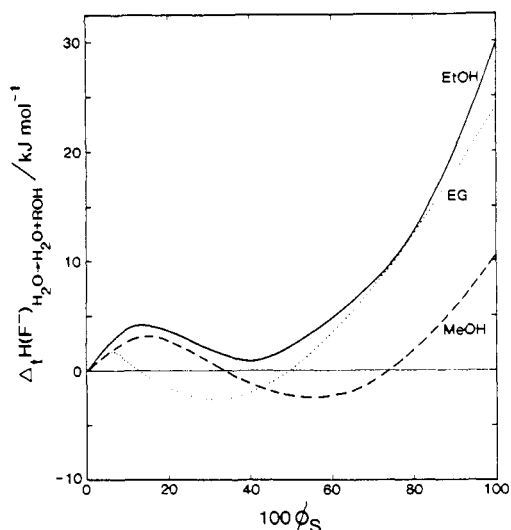


Fig. 6. Enthalpies of transfer of fluoride in alcohol/water mixtures at 298K as a function of solvent composition. Data from (ref. 11,12).

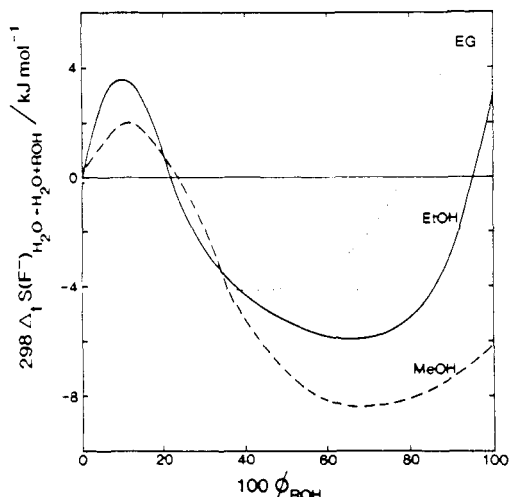
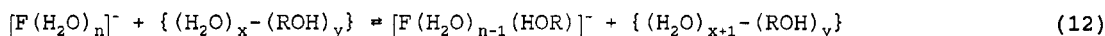


Fig. 7. Entropies of transfer of fluoride in alcohol/water mixtures at 298K as a function of solvent composition. Data from (ref. 11,12).

on the ability of the alcohol to fit into the water structure. As this decreases with the increasing size of the alcohol molecule it would be expected that the maximum in  $\Delta_t H(F^-)_{H_2O-H_2O+ROH}$  would shift to lower  $x_{ROH}$  in going from MeOH to EtOH to EG and this is indeed found (Fig. 6). It may also be noteworthy that the size of the maximum in  $\Delta_t H(F^-)$  is much smaller in EG/ $H_2O$  mixtures (Fig. 6), given that the **relative** preference of  $F^-$  for water is probably weakest amongst these three alcohols (EG has, for example, been postulated to chelate  $F^-$  (ref. 33)).

As the alcohol concentration is further increased, a point will be reached when it begins to compete with water in the  $F^-$  solvation sphere. Since alcohols are weaker acceptors than water (ref. 1) their ability to coordinate with  $F^-$  is weaker and thus  $\Delta_t H(F^-)$  becomes more positive. The location of the minimum in  $\Delta_t H(F^-)_{H_2O-H_2O+ROH}$  will depend on the relative attraction of the ROH and  $H_2O$  molecules for the solvent and the  $F^-$  coordination sites. The

situation may be encapsulated by the following (simplistic) equilibrium



where  $\{(H_2O)_x-(ROH)_y\}$  represents the (largely destructured) solvent mixture ( $x, y \gg n$ ). Under these circumstances the location of the minimum in  $\Delta_t H(F^-)_{H_2O-H_2O+ROH}$  shows no simple dependence on, e.g., ROH acceptor properties. However, it does correlate with the alcohol size, reflecting their ability to disrupt the 3-D water structure (ref. 1,30).

The dependence of  $\Delta_t S(F^-)_{H_2O-H_2O+ROH}$  on solvent composition (Fig. 7) is almost a mirror image of the enthalpies (Fig. 6) and may be explained with analogous arguments.

The behaviour of  $F^-$  in these mixtures, although complex, is by no means unique. Similar plots for  $\Delta_t H(\text{ion})$  and  $\Delta_t S(\text{ion})$  have been observed in  $CH_3OH/H_2O$  mixtures (ref. 11) for both the halide ions and, in an opposite manner, the alkali metal cations.

### 6.3 Enthalpies and entropies in acetonitrile-water mixtures

Only one study has been made of fluoride enthalpies and entropies of transfer in dipolar aprotic/aqueous mixture: AN/ $H_2O$  (ref. 12). Figures 8 and 9 plot these quantities in AN/ $H_2O$  and, for comparison,  $CH_3OH/H_2O$ . Again the almost monotonic variation of  $\Delta_t G(F^-)_{H_2O-H_2O+AN}$  with solvent composition (Fig. 4) is seen to result from the cancellation of complex changes in  $\Delta_t H$  and  $\Delta_t S$ . However, what is more remarkable is that, apart from the additional complexity of an extra extremum, the data in AN/ $H_2O$  are almost a mirror image of those in  $CH_3OH/H_2O$  (Fig. 8 and 9).

It is not easy to explain these observations but consider the following. At low co-solvent concentrations ( $100\phi_s < 10$ ), the voids in the 3-D water structure are partially filled with more or less monomeric  $H_2O$  molecules. Small amounts of AN, as with  $CH_3OH$ , would be expected to fit into these voids. However, in contrast to the hydrophilic  $CH_3OH$ , AN is somewhat hydrophobic (for example, binary AN/ $H_2O$  mixtures show an upper critical solution temperature at ca 275 K (ref. 34)). Thus, it may be that the monomeric  $H_2O$  is not only salted out of the voids onto the water structure but also onto the  $F^-$  ions resulting in a favourable  $\Delta_t H(F^-)$  (this may be a second coordination sphere effect). Since a limited amount of  $H_2O$  can be accommodated in the coordination shells of  $F^-$ , a further increase in the AN concentration results in reinforcement of the water structure corresponding to a less favourable  $\Delta_t H(F^-)$ . As for  $CH_3OH$ , but at much higher mole fractions, the water structure breaks down, increasing the number of water molecules available for solvation of the fluoride, resulting in a decrease in  $\Delta_t H(F^-)$ . Because the interaction of  $F^-$  and AN is so unfavourable this pattern persists up to a very high  $x_{AN}$ . Eventually  $H_2O$  must be replaced by AN in the  $F^-$  coordination sphere resulting in a very sharp rise in  $\Delta_t H$ . (Fig. 8.) The slope of the curve at high  $x_{AN}$  is possibly heightened by a decrease in coordination number of  $F^-$  which has been inferred from NMR measurements (ref. 12).

These arguments are not fully convincing but the reality of at least some of these effects is hard to doubt (always accepting, of course, the validity of the extra-thermodynamic assumption on which they are based). That the solvent-solvent interactions in AN/ $H_2O$  are substantially different from those in  $CH_3OH/H_2O$  is supported by the excess enthalpies of mixing of the binary mixtures which are also very different (ref. 35,36).

A possible alternative explanation for the delay in the breakdown of the water structure (corresponding to the major decrease in  $\Delta_t H(F^-)$ ) is the possibility of microphase separation. This phenomenon has been implicated in heat capacity studies of electrolytes in AN/ $H_2O$  (ref. 15) and in other work (ref. 34).

The variation of  $\Delta_t S(F^-)$  can be explained in terms similar to those for the enthalpies. Thus at low  $x_{AN}$   $\Delta_t S(F^-)$  is unfavourable because the AN in the voids reinforces the water structure about  $F^-$ . As  $x_{AN}$  increases, these water molecules are forced onto the (partially weakened) water structure. Eventually as the water structure breaks down the  $H_2O$  molecules can be more strongly orientated by the  $F^-$  and  $\Delta_t S(F^-)$  decreases. There is some



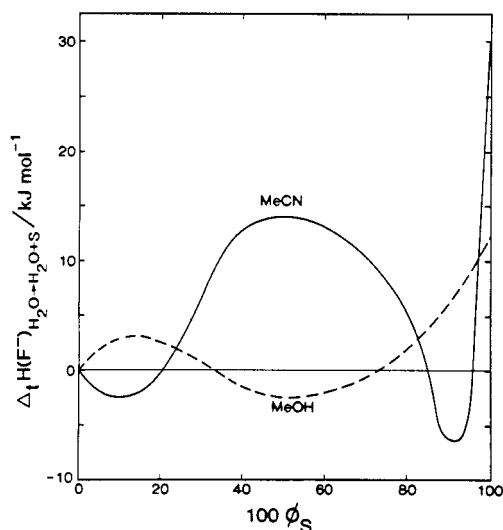


Fig. 8. Enthalpies of transfer of fluoride in AN/H<sub>2</sub>O and MeOH mixtures at 298K as a function of solvent composition. Data from (ref. 11,12).

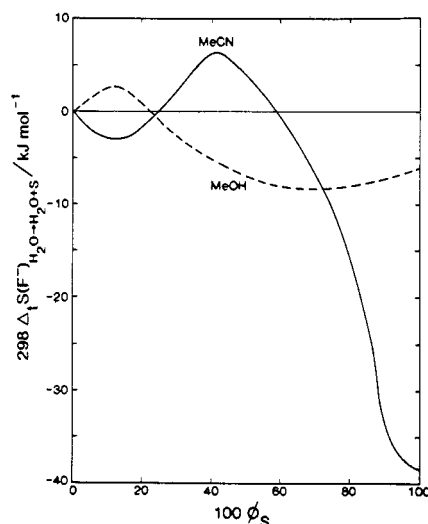


Fig. 9. Entropies of transfer of fluoride in AN/H<sub>2</sub>O and MeOH mixtures at 298K as a function of solvent composition. Data from (ref. 11,12).

uncertainty about the magnitude of  $\Delta_t S(F^-)$ , calculated from  $\Delta_t S = (\Delta_t H - \Delta_t G)/T$ , at very high  $x_{AN}$  because of the uncertainties in  $\Delta_t G$  (ref. 9). However, it would seem that unlike  $\Delta_t H$  it does not show a sharp reversal in sign at high  $x_{AN}$ .

## 7. COMPARISONS WITH THE HYDROXIDE ION

Fluoride is isoelectronic with  $OH^-$  and similar in size (136 and 140 pm respectively), so not surprisingly these two ions show considerable similarities in their properties. For example,  $F^-$  can substitute for  $OH^-$  in many of its compounds (ref. 5), the best known instance being the conversion of apatite to fluoroapatite in human tooth enamel. In aqueous solution there is a remarkable similarity between the equilibrium constants of fluoro- and hydroxo-complexes of metal ions (ref. 7,37). It is of some interest to see if this similarity persists in nonaqueous solutions.

This paper has referred to fluoride as the "missing ion" but it would seem that this title should truly belong to  $OH^-$ . The only data which could be found for  $OH^-$  in standard compilations were the Gibbs energies of transfer to limited ranges of MeOH and EtOH mixtures. These data are plotted in Fig. 10 against the corresponding fluoride data (ref. 9) and show a reasonable but not perfect correlation. In the absence of experimental data it is proposed that the solvation behaviour of hydroxide be predicted by the approximation

$$\Delta_t X^\circ(OH^-) \approx \Delta_t X^\circ(F^-)$$

where  $X = G, H, S$ , etc. It will be interesting to see how this prediction stands up to experimental investigation.

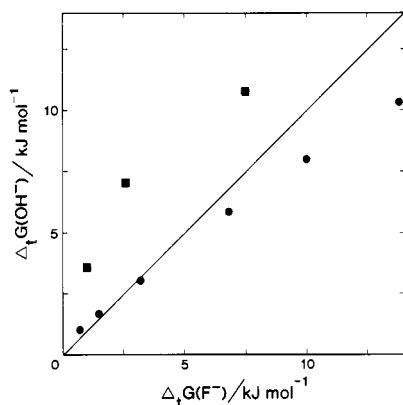


Fig. 10. Correspondence between Gibbs energies of transfer of fluoride and hydroxide in aqueous mixtures of MeOH(●) and EtOH(■). The straight line represents perfect correspondence. Data from (ref. 9,10,31).

## 8. CONCLUSIONS

Although the solvation characteristics of the fluoride ion are beginning to emerge from reliable solubility measurements much remains to be done in both pure and mixed solvents. Fluoride ion solvation is dominated by H-bonding and thus  $\Delta_c G^\circ(F^-)_{H_2O-S}$  is highly positive, especially for dipolar aprotic solvents, and correlates well with acceptor solvent properties.

Few reliable enthalpy and entropy data are available, however, there is tantalizing evidence to suggest that fluoride solvation may be entropy controlled.

$\Delta_c G(F^-)_{H_2O \rightarrow H_2O+S}$  generally increase monotonically due to the cancellation of dramatic, but opposing, changes in  $\Delta_c H$  and  $\Delta_c S$ . The shape of the enthalpy and entropy curves for  $F^-$  and the other halides are complex, reflecting changes in both ion-solvent and solvent-solvent interactions.

## REFERENCES

1. Y. Marcus, Ion Solvation, Wiley, New York (1985).
2. B.G. Cox and W.E. Waghorne, Chem. Soc. Rev. **9**, 381 (1980).
3. B.G. Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Austral. J. Chem. **27**, 477 (1974).
4. G. Gritzner, Pure Appl. Chem. **60**, 1743 (1988).
5. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon, Oxford (1984).
6. A. Bhattacharya, K. Das, A.K. Das and K.K. Kundu, Bull. Chem. Soc. Japan **54**, 2194 (1981).
7. G.T. Heftner, Coord. Chem. Rev. **12**, 221 (1974).
8. See for example, E.J. Corey and A. Venkateswarlu, J. Amer. Chem. Soc. **94**, 6190 (1972).
9. G.T. Heftner, Rev. Inorg. Chem. **10**, 185 (1989).
10. G.T. Heftner and P.J. McLay, J. Solution Chem. **17**, 535 (1988).
11. G.T. Heftner and P.J. McLay, Austral. J. Chem. **41**, 1971 (1988).
12. G.T. Heftner and T.S. Pang, submitted for publication.
13. G.T. Heftner, unpublished observations.
14. G.T. Heftner, J.-P.E. Grolier and A.H. Roux, J. Solution Chem. **18**, 229 (1989).
15. G.T. Heftner, J.-P.E. Grolier, A.H. Roux and G. Roux-Desgranges, J. Solution Chem. **19**, 207 (1990).
16. G.H. Nancollas, Interactions in Electrolyte Solutions, Elsevier, Amsterdam (1966).
17. A.M. Bond and G.T. Heftner, "Critical Survey of Stability Constants and Related Thermodynamics Data of Fluoride Complexes in Aqueous Solution", Pergamon, Oxford (1980).
18. J.W. Bixler, M.E. Cobb, R.J. French, B.E. Morse, T.R. O'Toole, J.A. Schudel, G.A. Yogis and A.M. Bond, Inorg. Chim. Acta **128**, 105 (1987).
19. J.F. Coetzee and M.W. Martin, Anal. Chem. **52**, 2412 (1980).
20. V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York (1978).
21. Y. Marcus, M.J. Kamlet and R.W. Taft, J. Phys. Chem. **92**, 3613 (1988).
22. D.C. Luehrs and K.A. Godbole, J. Solution Chem. **19**, 187 (1990).
23. Y. Marcus, Pure Appl. Chem. **57**, 1103 (1985).
24. A.J. Parker, Electrochim. Acta **21**, 671 (1976).
25. J.P. Gabano, Ed., Lithium Batteries, Academic Press, London (1983).
26. P. Atkins, G.T. Heftner and P. Singh, J. Solution Chem., in press.
27. L.M. Harwood and C.J. Moody, Experimental Organic Chemistry, Blackwell, Oxford (1989).
28. A.J. Parker, Chem. Rev. **69**, 1 (1969).
29. D.M. Muir, Search **15**, 81 (1984).
30. F. Franks and J.E. Desnoyers, Water Sci. Rev. **1**, 171 (1985).
31. Y. Marcus, Pure & Appl. Chem. **62**, 899 (1990).
32. M.J. Blandamer, B. Briggs, J. Burgess, P. Guardado, S. Radulovic and C.D. Hubbard, J. Chem. Soc. Faraday Trans. 1 **84**, 1243 (1988).
33. J.H. Clark, K. Kanippayoor and J.M. Miller, J. Chem. Soc. Dalton Trans. 1152 (1981).
34. R. Diguët, Chemical Reactivity in Liquids, Plenum, New York (1988), p. 105.
35. J.J. Christenson, R.M. Izatt and R.W. Hanks. Handbook of Heats of Mixing, Wiley, New York (1982).
36. C. Trenier, P. Tzias and M. Chemla, J. Chem. Soc. Faraday Trans. 1 **72** 2007 (1976).
37. R.E. Mesmer and C.F. Baes, The Hydrolysis of Cations, Academic Press, New York (1976).