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ENTHALPIES OF TRANSFER OF IONS FROM WATER INTO AQUEOUS HYDROGEN FLUORIDE

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SUMMARY

Enthalpies of solution of a variety of inorganic salts, including several alkali metal halides and potassium hexafluoroelementates(IV), have been measured in 0, 12, 24, and 48% w/w aqueous hydrogen fluoride. From these results, and appropriate extrathermodynamic assumptions, we have estimated enthalpies of transfer of constituent ions from water into aqueous hydrogen fluoride. They are also compared with enthalpies of transfer of ions from water into aqueous methanol, aqueous acetonitrile, and aqueous dimethyl sulphoxide. These estimates are compared with those from Born calculations.

INTRODUCTION

There are rather few data available on solubilities and enthalpies of solution of salts in aqueous hydrogen fluoride. Solubilities have been measured for a selection of binary and ternary fluorides in liquid hydrogen fluoride [1] and for sodium hexafluorosilicate(IV) in aqueous hydrogen fluoride [2]. Enthalpies of solution of sodium and ammonium hydrogen fluorides have been measured in liquid hydrogen fluoride [3], and of three alkali metal fluorides in a range of aqueous hydrogen fluoride solvent mixtures [4]. In the present paper we report enthalpies of solution for a variety of salts in aqueous hydrogen fluoride containing up to 48% by weight of hydrogen fluoride.

Single ion enthalpies of transfer have been estimated for a variety of cations and of anions between various solvents and solvent mixtures [5]; many values have been published for transfer from water into binary aqueous solvent mixtures containing organic cosolvents. Here we report estimates for single ion enthalpies of transfer for a selection of simple and complex ions from water into aqueous hydrogen fluoride, derived from our direct calorimetric determination of enthalpies of solution of appropriate salts in such mixtures.

EXPERIMENTAL

Reagents

Most materials were commercial products; AnalaR grade materials were used as such, the others were recrystallised from distilled water. Potassium hexafluoromanganate(IV) [6], potassium hexafluororhenate(IV) [7], and potassium hexachlororhenate(IV) [8] were prepared by published methods, and were recrystallised from 48% hydrofluoric acid, distilled water, and dilute hydrochloric acid respectively. Aqueous hydrofluoric acid (48% HF by weight; AnalaR) was obtained from B.D.H.

Apparatus

The calorimeter consisted of a 250 cm^3 polythene beaker surrounded by a block of expanded polystyrene to ensure thermal isolation. The beaker was equipped with a 150 ohm thermistor inserted in a paraffin-filled F.E.P. plastic well, with brass at the bottom of the well to ensure good thermal contact with the solution in the calorimeter, a sheathed 100 ohm wire-wound calibration heater, and an F.E.P. sample entry port, all mounted through a tightly fitting rubber bung which had been waxed to prevent corrosion. The contents of the calorimeter were stirred at constant speed (ca. 100 r.p.m.) by a Teflon stirrer driven by a constant torque motor. The calorimeter was connected to the monitoring circuits and apparatus described elsewhere [9]. Between 40 and 100 mg dried solid and about 150 cm^3 solvent were used in each determination. The calorimeter was operated at 295 $\pm$ 1K; it was calibrated against the enthalpy of solution of potassium chloride in water [10].

RESULTS

Measured values for enthalpies of solution of salts in hydrogen fluoride-water mixtures, and appropriate published enthalpies of solution in water, are given in Table 1.

DISCUSSION

Enthalpies of solution of the fluorides of lithium, sodium, and potassium in various mixtures of hydrogen fluoride and water, up to the practicable composition limit of about 48% hydrogen fluoride dictated by volatility considerations, have been reported recently [4]. Our more limited set of enthalpy of solution determinations for sodium fluoride and potassium fluoride agree satisfactorily with these values; agreement is not so good for lithium fluoride. The disagreement over values for lithium fluoride may be due to dissolution difficulties in one or other of the calorimeters used. Lithium fluoride is only sparingly soluble in water and in low concentrations of hydrogen fluoride; efficient agitation (not normally beneficial for precise calorimetry) may be needed to effect complete solution within a reasonable period.

TABLE 1

Enthalpies of solution (kJ mol^{-1}) of electrolytes in water and in aqueous hydrogen fluoride.[i]

	water[a]	12%HF	24%HF	48%HF
LiF	+4.6			-11
NaF	+0.4			-23
KF	-17.6	-19	-30	-52
KCl	+17.3			-6
KBr	+19.9			-4
Bu^n_4NBr	-8.6[b]			+22
Ph_4AsF	+12.5[c]			-6
K(m-toluate)	0[c]			-60[d]
$KSbF_6$	+38.5[c]	+30	+20	+12
Na_2SiF_6[e]	+30.8[c]			-2
K_2SiF_6	+73.0[c]	+31	+22	+6
K_2MnF_6	+61.1[c]	+26	+13	-6[f]
K_2ReF_6	+63.0[g]			-6
K_2ReCl_6	+43.5[h]			+12

[a] Enthalpies of solution in water from NBS Circular 500 unless indicated otherwise.

[b] T. S. Sarma and J. C. Ahluwalia, J. Phys. Chem., 74, 3547 (1970); Trans. Faraday Soc., 67, 2528 (1971); C. de Visser and G. Somsen, J. Chem. Thermodynamics, 5, 147 (1973).

[c] This work.

[d] The enthalpy of solution of m-toluic acid in 48%HF is -4 kJ mol^{-1}.

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Enthalpies of solution of salts seem generally to be positive in water, negative in 48% hydrofluoric acid. Enthalpies of transfer from water to aqueous hydrofluoric acid are nearly always negative. The exceptions are tetra-n-butylammonium bromide (cf. Table 1), and the alkali metal fluorides from water into low concentrations of hydrogen fluoride [4]. Enthalpies of transfer from water into 48% hydrogen fluoride appear to be smallest when both ions are small or both are large; values for 1:1 electrolytes are smaller than for 1:2 electrolytes.

We are currently interested in thermodynamic properties pertaining to ion solvation, and have recently estimated single ion hydration enthalpies for, e.g., the hexafluoro-anions RuF_6^{2-}, SiF_6^{2-}, and ReF_6^{2-} [11]. In order to obtain such single ion values it is necessary to have good estimates of lattice energies of appropriate salts. This is often difficult, especially for salts of complex ions [12]. Ion solvation in various solvent media can be compared in terms of thermodynamic parameters for transfer between solvents. Here values are independent of lattice energies, but this advantage is balanced by the need to make assumptions in order to obtain single ion values from the appropriate transfer parameters for whole salts. Much effort has been expended on

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TABLE 1 (cont.)

[e] Enthalpies of solution calculated by the van't Hoff method from the published temperature dependence of solubilities (ref. [2]) are +46, +29, +20, +20, and +16 kJ mol^{-1} in 0, 5.5, 15.5, 21.0, and 26.5%HF respectively.

[f] The solubility of K_2MnF_6 in 48%HF at 298.2K is 71g dm^{-3}.

[g] J. Burgess, N. Morton, and R. D. Peacock, J. Fluorine Chem., 11, 197 (1978)

[h] R. H. Busey, H. H. Dearman and R. B. Bevan, J. Phys. Chem., 66, 82 (1962).

[i] 90% confidence limits are generally 2% or less, though these rise to 4% for some of the smallest enthalpies measured.

efforts to establish an acceptable method for carrying out the separation into individual ion values; a consensus has yet to be reached. The numerous methods proposed fall into two categories, those ultimately based on calculations derived from the Born model for ion solvation and those based on empirical but intuitively more or less acceptable assumptions about solvation of particular ions. The former may be illustrated by the methods of Wells [13] and of de Ligny and colleagues [14]. The latter approaches include the currently popular assumption of equal solvation changes for the large, lightly solvated, cation and anion Ph_4As^+ and Ph_4B^- [5,15], or the assumption of zero solvation change for transfer of a large ion, e.g. Me_4N^+ [16]. As will be seen, there are certain limitations in approaches which can be used for transfer to aqueous hydrogen fluoride.

The simplest way of obtaining single ion transfer parameters to aqueous hydrogen fluoride is to use the classical assumption of equal values for equal size cation and anion. Usually $K^+ \equiv Cl^-$ has been assumed (though radii are 1.38 and 1.81 Å respectively [17]); we can use this with our values for solution enthalpies for potassium chloride. The assumption $Na^+ \equiv F^-$ can also be used, with the French workers' data on enthalpies of solution of sodium fluoride. Certain features of their results and ours suggest that the use of the F^- anion may be unwise, in particular in view of the stability of the HF_2^- anion. We therefore prefer $K^+ \equiv Cl^-$, and in Table 2 report values for single ion enthalpies of transfer thus derived from our Table 1 results and the earlier results [4] for the alkali metal fluorides (appropriately interpolated). These single ion values are presented in graphical form in Fig. 1. Single ion values based on the $Na^+ \equiv F^-$ assumption are given in Table 3. That these values are less attractive than the $K^+ \equiv Cl^-$ set is suggested by the variation of ΔH_{tr} with solvent composition for some ions, for

TABLE 2

Single ion enthalpies of transfer (kJ mol^{-1}) from water into aqueous hydrogen fluoride, based on the assumption $\Delta H_{tr}(K^+) = \Delta H_{tr}(Cl^-)$ and Table 1 enthalpies.

	12%HF	24%HF	48%HF
Li^+			+6
Na^+			-1^a
K^+	-4.2	-7.7	-11.9
Ph_4As^+			+3
$Bu^n_4N^+$			+42
F^-	+3	-4	-22
Cl^-	-4.2	-7.7	-11.9
Br^-			-12
m.toluate$^-$			+8
SbF_6^-	-5	-11	-15
SiF_6^{2-}	-34	-36	-43^b
MnF_6^{2-}	-27	-33	-43
ReF_6^{2-}			-45
$ReCl_6^{2-}$			-7

[a] Ref. [4] enthalpies give +7 kJ mol^{-1}.

[b] Value from K_2SiF_6, $\Delta H_{tr}(SiF_6^{2-})$ ex Na_2SiF_6 is -47 kJ mol^{-1}.

example Cl^-, SbF_6^-, and SiF_6^{2-}. Regardless of the assumptions used, differences between ΔH_{tr} values for anions, and differences between ΔH_{tr} values for cations, are correct for ions of the same charge and transfer to a given solvent medium. Thus the endothermicity orders

$$\text{m-toluate} < Cl^- < SbF_6^- < F^-$$

$$Bu_4N^+ < Na^+ < Ph_4As^+ < K^+$$

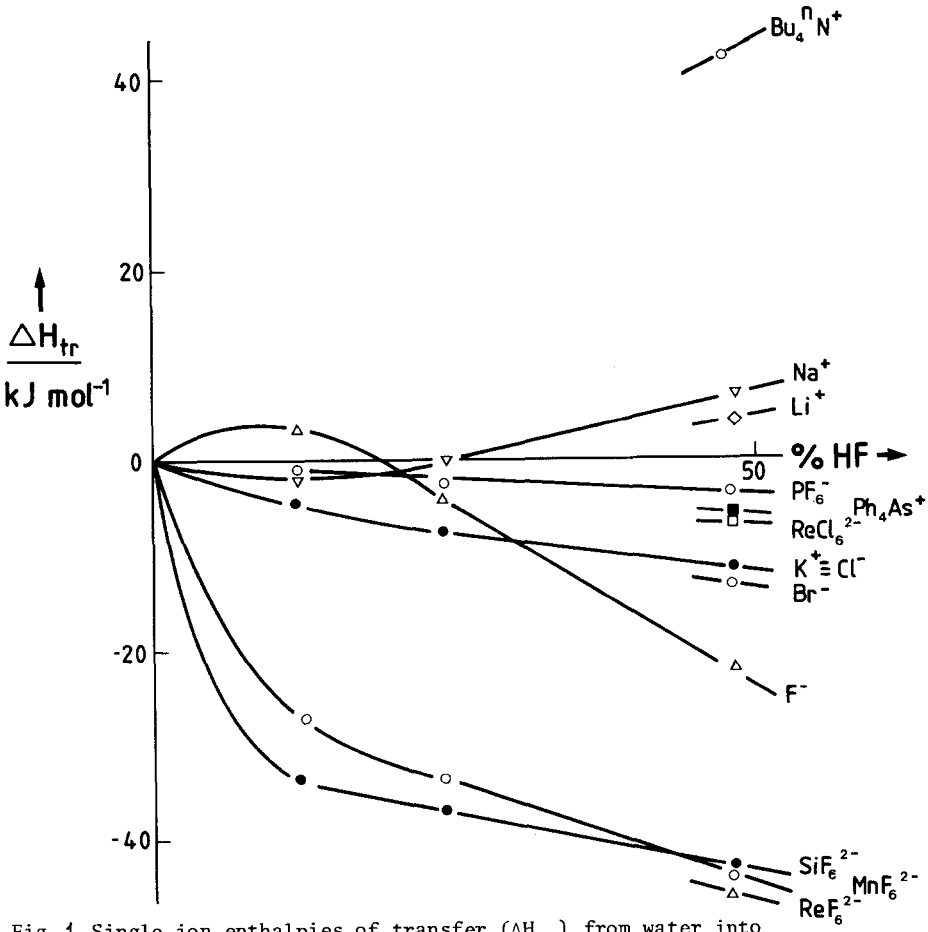

Fig. 1. Single ion enthalpies of transfer (ΔH_{tr}) from water into aqueous hydrogen fluoride, based on the $K^+ \equiv Cl^-$ assumption.

are independent of single ion splitting assumption used. It is interesting that large and small ions are intermingled in these series - simple electrostatics cannot determine such orders. Of course hydrogen bonding will be of great importance both in water and in the aqueous hydrogen fluoride media, affecting both inter- and intra-solvent interactions and solvent-solute interactions, especially for F^- and the hexafluoroanions. The stability of the HF_2^- anion is particularly relevant here, and may well be responsible for features of ΔH_{tr} variation with solvent composition at low % HF.

TABLE 3

Single ion enthalpies of transfer (kJ mol^{-1}) from water into aqueous hydrogen fluoride, based on the assumption $\Delta H_{tr}(Na^+) = \Delta H_{tr}(F^-)$.

	12%HF	24%HF	48%HF
Li^+			-8
Na^+	$+0.6^a$	-2.0^a	-7.3^a
K^+	-1	-9	-23
Ph_4As^+			-12
$Bu^n_4N^+$			+32
F^-	+0.6	-2.0	-7.3
Cl^-	-7	-6	-1
Br^-			-1
_m_-toluate$^-$			+19
PF_6^-	-9	-10	-4
SiF_6^{2-}	-39	-33	-21^b
MnF_6^{2-}	-32	-30	-21
ReF_6^{2-}			-23
$ReCl_6^{2-}$			+15

[a] From ref. [4] enthalpies of solution of NaF.

[b] Value from K_2SiF_6, $\Delta H_{tr}(SiF_6^{2-})$ ex Na_2SiF_6 is -18 kJ mol^{-1}.

Despite the comments in the preceding paragraph, it is interesting to compare some ΔH_{tr}(ion) values from Tables 2 and 3 with theoretical values estimated from the standard Born equations [18]. We restrict these comparisons to the simple monatomic ions. Equations (1) and (2)

$$\Delta G_{solv} = \frac{-695.9z^2}{r_{eff}}\left(1 - \frac{1}{D}\right) \qquad (1)$$

$$\Delta S_{solv} = \frac{695.9z^2}{D\, r_{eff}}\left(\frac{\partial \ln D}{\partial T}\right)\Big|_P \qquad (2)$$

TABLE 4

Born-derived Gibbs free energies (ΔG), entropy terms (TΔS), and enthalpies (ΔH) of solvation (kJ mol^{-1}; 298.2K) for alkali metal and fluoride ions in aqueous hydrofluoric acid.

	H_2O			6% HF			12% HF			24% HF			48% HF		
	ΔG	TΔS	ΔH	ΔG	TΔS	ΔH	ΔG	TΔS	ΔH	ΔG	TΔS	ΔH	ΔG	TΔS	ΔH
Li^+ CN=4	-434.8	-8.2	-443.0	-438.8	-8.7	-443.5	-434.7	-9.3	-444.0	-434.6	-10.5	-445.1	-434.3	-13.0	-447.3
Li^+ CN=6	-397.1	-7.5	-404.6	-397.1	-8.0	-405.1	-397.0	-8.5	-405.5	-396.9	-9.6	-406.5	-396.7	-11.9	-408.6
Na^+	-341.4	-6.4	-348.2	-341.7	-6.9	-348.6	-341.7	-7.3	-349.0	-341.6	-8.3	-349.9	-341.4	-10.2	-351.7
K^+	-289.9	-5.5	-295.4	-289.8	-5.8	-295.6	-289.8	-6.2	-296.0	-289.7	-7.0	-296.7	-289.5	-8.7	-298.2
F^-	-480.4	-9.0	-489.4	-480.3	-9.7	-490.0	-480.3	-10.3	-490.6	-480.1	-11.6	-491.7	-497.7	-14.4	-494.3

give values in kJ mol^{-1} and JK mol^{-1} respectively. We have used Shannon and Prewitt's crystal radii [17] plus 0.85Å for the effective ionic radii, r_{eff} [19]. The dielectric constants of water and of liquid hydrogen fluoride and their temperature dependences are known [20]. In the absence of such data for aqueous hydrogen fluoride we have perforce had to interpolate value for D and $\partial(\ln D)/\partial T|_p$ for 48% hydrogen fluoride from the values for the pure solvents assuming a linear dependence on solvent composition. Values of Gibbs free energies, enthalpies, and entropies of solvation are listed in Table 4, while in Table 5 are given values for the enthalpies of transfer of the alkali metal cations from water in aqueous hydrogen fluoride. We estimate enthalpies of solution for Na^+ and F^- respectively to be -603 and -573 kJ mol^{-1} in water, -610 and -580 kJ mol^{-1} in 48% HF. Thus the Born treatment leads to values of -7 kJ mol^{-1} for $\Delta H_{tr}(Na^+)$ and $\Delta H_{tr}(F^-)$, from water into 48% HF (the positive value for ΔG_{tr} is more than balanced by the unusually large negative $T\Delta S_{tr}$ arising from the strong dependence of dielectric constant of HF on temperature). coincidentally this value is very close to that (-7.3 kJ mol^{-1}) for the $Na^+ \equiv F^-$ assumption (Table 3) for 48% HF; agreement is less satisfactory at lower HF concentrations. Although there is gratifying agreement between these Born-derived values and others discussed in this paper, the limits of the

TABLE 5

Enthalpies of transfer (kJ mol^{-1}) of ions from water into aqueous hydrogen fluoride, calculated by the Born equation.

Ion	6%HF	12%HF	24%HF	48%HF
Li^+	-0.5	-1.0	-2.1	-4.3
Na^+	-0.4	-0.8	-1.7	-3.5
K^+	-0.2	-0.6	-1.3	-2.8
F^-	-0.6	-1.2	-2.3	-4.9

Born approach should be borne in mind [21]. In particular, equations (1) and (2) make no allowance for hydrogen-bonding interactions between halide ions, especially fluoride, and hydrogen fluoride in the mixed solvents.

Unfortunately it is impossible to compare the results of our $K^+ \equiv Cl^-$ single ion split with the rather different $Ph_4As^+ \equiv BPh_4^-$ method (cf. above); consistency between these two would have increased our confidence. We have measured enthalpies of solution of Ph_4AsCl in water and in 48% HF (Table 1) and thus estimated $\Delta H_{tr}(Ph_4As^+)$ (Tables 2 and 3). The problem arises with the BPh_4^- anion. This is known to be unstable in acid media [22] and indeed is known to decompose quickly, with a half-life of a matter of minutes at room temperature [23]. The $BPh_3(CN)^-$ anion is somewhat more resistant to acid [24], but we found from experiments on its sodium salt that it too rapidly decomposes in aqueous hydrogen fluoride We have been unable to find an alternative large uninegative cation that does not hydrogen-bond and which is stable in aqueous acid. Table 2 shows that ΔH_{tr} (m-toluate) and $\Delta H_{tr}(PF_6^-)$ are not too dissimilar from ΔH_{tr} (Ph_4As^+). Certainly the $K^+ \equiv Cl^-$ is to be preferred to the $Na^+ \equiv F^-$ split on arguments of this type (cf. Tables 2 and 3). Here, as in several earlier investigations and discussions, the thermodynamics of the $Bu^n_4N^+$ cation are unexpected in magnitude and difficult to explain.

In Table 6 we compare ΔH_{tr}(ion) values for water to aqueous hydrogen fluoride transfer with values for transfer to aqueous methanol, DMSO, and acetonitrile. The values for the $K^+ \equiv Cl^-$ reference cation and anion show the greatest sensitivity to medium variation for the aqueous hydrogen fluoride series. These ions appear to be (enthalpically) destabilised on transfer to the 'typically aqueous' [25,26] methanol + water mixtures, but stabilised on transfer to 'typically non-aqueous positive' acetonitrile + water mixtures. KCl is marginally stabilised on transfer from water into water-rich aqueous dimethylsulphoxide ('typically non-

TABLE 6

Single ion enthalpies of transfer[f] for K^+,Cl^- from water into aqueous hydrogen fluoride, methanol, acetonitrile, and dimethyl sulphoxide, in all cases based on the assumption $\Delta H_{tr}(K^+) = \Delta H_{tr}(Cl^-)$.

Cosolvent	Mixture type	12%[a]	24%[a]	48%[a]
Methanol[b]	TA	+0.7	+1.0	+0.5
Acetonitrile[c]	TNAP	-1.4	-2.7	-4.9
Dimethyl sulphoxide[d]	TNAN	-0.1	-0.2	-0.4
Hydrogen fluoride	TNAN	-4.2	-7.7	-11.9

a Cosolvent per cent by weight.

b Interpolated from the results of C. M. Slansky, J. Am. Chem. Soc., 62, 2430 (1940).

c Interpolated from the results of B. G. Cox, R. Natarajan and W. E. Waghorne, J. Chem. Soc. Faraday Trans. I, 75, 86 (1979).

d Interpolated from ref. [27] results.

e Mixed solvent classification by excess thermodynamic parameters [25,26]: for TA mixtures G^E is positive and $|TS^E|>|H^E|$, for TNA mixtures $|H^E|>|TS^E|$, with G^E positive for TNAP and negative for TNAN mixtures.

f kJ mol^{-1}; 298.2K.

aqueous negative'); here favourable interaction with the K^+ is balanced by progressive desolvation and destabilisation of the Cl^- [27]. Inspection of excess Gibbs free energies, enthalpies, and entropies of mixing [28] shows that the water + hydrogen fluoride solvent system is, like water + dimethyl sulphoxide, 'typically non-aqueous negative.' However comparisons of transfer parameters for ions, particularly halide ions, are dominated by anion-hydrogen fluoride interactions (especially, of course, for fluoride) rather than by the inter-solvent interactions which are the basis of the 'typical aqueous etc.' classification.

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