Hydrofluoric and Hydrochloric Acid Behaviour in Concentrated Saline Solutions *

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Ion-selective electrode measurements of mean NaF and Cl/F activities in concentrated NaCl media at 25 °C have been used to estimate Pitzer activity coefficient model parameters $\theta_{\mathrm{Cl,F}}$ (0.01), $\psi_{\mathrm{Na,Cl,F}}$ (0.002 33), and $\psi_{\mathrm{K,Cl,F}}$ (−0.003 3). Dissociation constants (K^1) of HF and stability constants (K^*) of MgF^+ were determined in NaCl media at 25 °C up to $I = 5.0$ mol kg^{-1} and are described by: $\log K^1 = -3.165 + 1.81I^{\frac{1}{2}}/(1 + 3.73I^{\frac{1}{2}}) - 0.06I - 0.0136I^2$ and $\log K^* = 1.822 - 0.982I^{\frac{1}{2}}/(1 + 0.328I^{\frac{1}{2}}) + 0.0713I + 0.0169I^2$. Pitzer model parameters $\beta^{(0)}_{\mathrm{MgF}}$ (3.932), $\beta^{(1)}_{\mathrm{MgF}}$ (−25.17), and C^{ϕ}_{MgF} (−5.294) were also derived. A Henry's law expression for the reaction $HX(g) \rightarrow H^+(aq) + X^-(aq)$ (K_H/mol^2 kg^{-2} atm^{-1}) was applied to HCl ($K_H = 2.04 \times 10^6$) and HF ($K_H = 9.61$). Partial pressures and speciation of the acids in acidified NaCl–$MgCl_2$ media were then calculated over a range of concentrations. The results suggest that fluoride (as HF) is expelled preferentially to chloride from naturally acidified marine aerosols.

Fluorine is cycled through the atmosphere in both inorganic and organic forms. The total concentration of gaseous organic fluoride in the troposphere is *ca.* 1 p.p.b., principally as anthropogenic chlorofluorocarbons, which are decomposed in the upper atmosphere to give HF.[1–3] Tropospheric observations of inorganic fluoride gases have been limited to man-made SF_6.[1] The other significant inorganic species is likely to be HF, which has only been measured in polluted areas.[4,5] Volcanic emissions, estimated at 0.4 Tg per annum for HF, are thought to be the major natural source of HF.[6]

Particulate material cycled through the troposphere may also be a source of gaseous fluorine compounds. Approximately 5×10^3 Tg of sea-salt are cycled through the atmosphere annually as aerosol droplets and particles,[7] largely generated as a result of wave action at the sea surface.[8] This implies a fluoride flux of 0.19 Tg per annum. Aerosol droplets accumulate strong acids such as H_2SO_4 (from the oxidation of natural reduced sulphur compounds)[9] and HNO_3 (from NO_x produced at the earth's surface and by lightning).[10] This dissolved acidity causes the degassing of *ca.* 3% of aerosol chloride as HCl,[11] and it has been proposed that fluoride may be similarly displaced as the weak acid HF.[6] However, it is unclear whether this will occur, particularly considering the high Cl^- content of sea-salt and the volatility of HCl.

The sea-salt aerosol exists largely as brine droplets whose concentration is controlled by the ambient relative humidity. The droplets may be saturated with respect to even very soluble constituents, and behave in a highly non-ideal manner. The equilibrium partial pressures of strong acids such as HCl over concentrated salt solutions can be calculated from the activities of the ions in solution and an appropriate Henry's law constant.[12] Weak acids require a more complex treatment, and the thermodynamic data needed to estimate the solubility of HF in concentrated saline solutions are largely unavailable.

We have made new measurements with ion-selective electrodes of mean NaF and HF activity, and Cl^- and F^- activities in concentrated NaCl media. Using existing solubility data for HF and HCl, together with Pitzer's electrolyte theory,[13] we estimate the solubility and dissolved speciation of these acids in concentrated saline media resembling the marine sea-salt aerosol.

Theory

The equilibrium of an acid, HX, between aqueous and gas phases is represented by equation (1). The thermodynamic Henry's law constant, K_H (mol^2 kg^{-2} atm^{-1}), is given by equation (2), where the prefix '*m*' represents molality, γ_{HX} is the mean activity coefficient of H^+ and X^- ions in solution, and p(HX) the equilibrium partial pessure of HX. The theoretical justification for this approach has been discussed by Denbigh[14] and Clegg and Brimblecombe.[12] The Henry's law constants for HCl and HF at 25 °C are 2.04×10^6 and 9.61 mol^2 kg^{-2} atm^{-1} respectively.[15,16]

$$HX(g) \rightleftharpoons H^+(aq) + X^-(aq) \qquad (1)$$

$$K_H = m(H^+) \cdot m(X^-) \gamma_{HX}{}^2 / p(HX) \qquad (2)$$

The Henry's law equation has been expressed so that partial pressures may be calculated using stoicheiometric ion concentrations and activity coefficients, or free ion concentrations and free ion activity coefficients. Under the formalism we have adopted, all strong electrolytes are treated as completely dissociated.[12] Since HF is a weak electrolyte it might be argued that a Henry's law constant expressed in terms of the associated species HF^0 would be appropriate. However, HF^0 concentrations have not been measured directly even in solutions of the pure acid, although the thermodynamic association constants of HF are known.[17] Until further data become available it is convenient to express the Henry's law constant in terms of measurable quantities, *i.e.* the activities of the free ions.

Activity coefficients are required to calculate partial pressures using equation (2). For strong electrolytes such as HCl these can be modelled using the Pitzer system of equations.[13,18–20] The model, which treats all deviations from ideal solution behaviour as interactions between free ions, is based on an expression for the Gibbs excess free energy as a virial expansion of terms in solute concentration.[21] Equations for osmotic and activity coefficients are derived from this, and the virial coefficients grouped into terms which can be evaluated from empirical data. In a multicomponent solution the following parameters are required for the model. For interactions between pairs of ions of opposite sign four parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} are used. These are obtained by fitting the equations to single electrolyte osmotic or activity coefficient data. For all solutes except 2:2

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* *Non-S.I. unit employed:* atm = 101 325 Pa.

metal sulphates the $\beta^{(2)}$ parameter is set to zero. For interactions between pairs of ions of like sign and triplets of ions (two of like and one of opposite sign) two parameters are used, θ_{ij} and ψ_{ijk}. These are obtained from activity coefficient measurements made on three-ion systems.[22,23]

The model treats conventional strong electrolytes as completely dissociated. However, this approach is not possible for weak electrolytes such as HF. Fluoride associates with H^+ in solution to form HF^0 and HF_2^- and also complexes with the bivalent metal cations present in sea water, particularly Mg^{2+}. In sea water at a normal ionic strength of 0.73 mol kg^{-1} the speciation of fluoride is free F^- (49), MgF^+ (49), and CaF^+ (*ca.* 2%) (ref. 24). Strong ion association such as this cannot in general be parameterised within the Pitzer model. Following the approach of Whitfield[25] and Millero[24,26] these reactions are therefore treated explicitly and replace the H^+–F^- and Mg^{2+}–F^- interactions in the model. Thus the concentrations of free H^+ and F^- in any mixture are first calculated using the appropriate stability constants, and then the activity coefficients of the ions are estimated using the Pitzer equations.

We treat sea-salt aerosols as a mixture of Na^+–Mg^{2+}–Cl^-–F^-. Although major components of sea-salt such as K^+, Ca^{2+}, and $[SO_4]^{2-}$ are ignored, the most important ions interacting with F^- are retained. This simplified approach allows these interactions to be determined individually, which is necessary for model parameterisation and to retain comparability with existing thermodynamic measurements. The activity coefficients of both H^+ and Cl^- in the mixture can be readily calculated using published parameters. However, the activity of F^- has not been measured in concentrated saline media and the stability constants of CaF^+, MgF^+, and HF^0 in a NaCl medium are only available up to an ionic strength of *ca.* 1.0 mol kg^{-1} (refs. 27 and 28).

Experimental

Activity measurements were made using a solid-state fluoride electrode (Orion 9409) paired with either solid-state chloride (Orion 9417), glass pH (Orion 9101), or glass sodium (Orion 9711) electrodes, connected to an Orion model 901 meter. This approach avoids the problem of variable liquid-junction potentials that would be encountered using conventional reference electrodes, and has been used successfully by several other workers to measure mean HF, NaF, and NaCl activities in concentrated solutions.[29–32]

Test solutions were prepared from BDH AnalaR grade chemicals, with the exception of NaCl and HF stock solutions where Aristar grades were used. All crystalline solids were kept in a dry atmosphere at 80 °C for at least 1 d before use, and deionised water was used in the preparation of all solutions. The experiments were carried out in two polyethylene cells fully immersed in a water-bath maintained at 25 ± 0.1 °C. One cell contained the magnetically stirred test solution (*ca.* 40 cm^3), and the other a similar volume of activity standard. The electrode pair was alternated between the cells to maintain a check on electrode stability with time. The electrode slopes (*S*), obtained from measurements of activity standards, deviated from the theoretical value *RT*/*F* by approximately 1% but were highly reproducible over a period of days. Each measurement took approximately 10—15 min to attain stability in electromotive force (e.m.f.). Drift in e.m.f. was $\leqslant$ 0.1 mV per 2—3 min, and was least with the chloride–fluoride electrode pair. Measurements made many hours apart agreed to within ±0.7 mV. Drift in e.m.f. was only cumulative for measurements using a hydrogen–fluoride electrode pair in acidic fluoride solutions, where the glass surface of the electrode was probably degraded.[32]

Results

Activity Coefficient of F^- *in* NaCl *Media.*—A series of measurements of mean NaF activity were made in NaCl–NaF mixtures at $I = 1.0$ mol kg^{-1} using a Na(glass)–F(LaF_3) electrode pair. This was done so that the solutions could be used as standards in later experiments, and as a test of precision and accuracy relative to previous work, particularly that of Butler and Huston.[29] Sodium fluoride standard solutions were used before every set of experimental measurements, to determine both the standard potential (E°) of the electrode pair and the slope of the response according to equation (3).

$$E = E^\circ - S\ln[\gamma_{NaF}^2\cdot m(Na^+)\cdot m(F^-)] \qquad (3)$$

The results are shown in Figure 1, where it can be seen that Harned's rule[33] is obeyed, to within the precision of the measurements, which have a standard error of 0.007 in γ_{NaF} (about 1.2%). The best-fit straight line agrees closely (to 0.001 in γ_{NaF}) with that calculated from the Pitzer equation with the unknown higher interaction terms $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$ set to zero. The slope of the line (0.0267) is close to the value of 0.027 determined by Butler and Huston.[29]

Further measurements were then made up to an ionic strength of 6.0 mol kg^{-1}. The results at all concentrations are listed in Table 1 as the mean activity coefficient of NaF (γ_{NaF}) in the test solutions, calculated using equation (3). The mean activity coefficient of NaF estimated using the Pitzer equations with higher parameters $\theta_{F,Cl}$ and $\psi_{Na,Cl,F}$ set to zero is also given. It can be seen that the experimental and calculated values differ significantly at high ionic strengths, suggesting that $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$ have non-zero values. To confirm these results a second set of experiments were performed using a Cl(AgCl)–F(LaF_3) electrode pair in NaCl solutions containing trace amounts of NaF at total ionic strengths 1.5—5.0 mol kg^{-1}. The electrode pair was calibrated in seven Na^+–Cl^-–F^- solutions at a total ionic strength of 1.0 mol kg^{-1}, and was found to be significantly more stable than the Na(glass)–F(LaF_3) electrode pair. The electrodes measure the quotient of Cl^- and F^- activities according to equation (4).

$$E = E^\circ + S\ln\{m(Cl^-)\cdot\gamma_{Cl}/[m(F^-)\cdot\gamma_F]\} \qquad (4)$$

In the test solutions the concentration of F^- (0.005 mol kg^{-1}) was so low that the activities of Na^+ and Cl^- were essentially unaffected. Thus the Cl^- electrode acted as a 'reference' in these experiments, since γ_{Cl} may be inferred from published NaCl

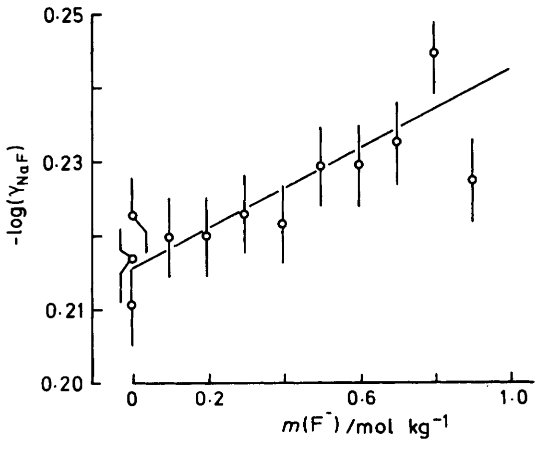

Figure 1. Experimental values of γ_{NaF} plotted against F^- concentration in a NaCl–NaF mixture at ionic strength 1.0 mol kg^{-1}. Results are listed in Table 1

Table 1. Measurements of the activity of NaF in NaF–NaCl solutions at I = 1.0—6.0 mol kg^{-1}. The results are used to determine γ_{NaF}. Values of γ_{NaF} calculated using the Pitzer model [γ_{NaF}(P)] are also listed for I > 1.0 mol kg^{-1}. The different values of E° were determined by recalibration in an activity standard (NaF) between measurements. Electrode slope was assumed to remain constant; I/mol kg^{-1}, m/mol kg^{-1}, E and E°/mV

I	$m(F^-)$	$-E$	S	$-E^{\circ}$	γ_{NaF}	γ_{NaF}(P)
1.00	0.0008	267.5	0.026 04	478.4	0.616	
1.00	0.002	291.1		478.8	0.608	
1.00	0.005	314.3		479.0	0.599	
1.00	0.10	392.4		478.7	0.603	
1.00	0.20	410.4		478.6	0.603	
1.00	0.30	420.5		478.5	0.599	
1.00	0.40	428.0		478.4	0.601	
1.00	0.50	432.8		478.3	0.590	
1.00	0.60	437.4		478.2	0.590	
1.00	0.70	441.0		478.1	0.586	
1.00	0.80	442.9		478.0	0.570	
1.00	0.85	446.5	0.026 09	477.9	0.593	
2.00	0.100	410.5		479.0	0.602	0.579
2.00	0.400	446.6		478.9	0.602	0.569
3.00	0.100	422.7		478.9	0.622	0.583
3.00	0.300	449.3		479.0	0.597	0.576
4.00	0.050	414.2		479.1	0.645	0.603
4.00	0.010	431.9		479.2	0.639	0.601
4.00	0.020	449.7		479.4	0.633	0.597
5.00	0.050	423.8		479.4	0.689	0.633
5.00	0.090	438.9		479.3	0.687	0.632
5.00	0.130	447.7		479.0	0.681	0.630
6.00	0.010	391.6		479.2	0.762	0.675
6.00	0.030	418.0		478.8	0.735	0.674
6.00	0.050	432.0		479.4	0.736	0.673

Table 2. The determination of the trace activity coefficient of F$^-$(γ_F) in NaCl media over a range of ionic strengths. Electrode slope, S, was equal to 0.025 54, and standard potential E° was −0.1566 V. Values γ_F(1) are measured values and γ_F(2) were calculated using the Pitzer model with parameters $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$ set to zero; m/mol kg^{-1}, E/mV

$m(Na^+)$	$m(Cl^-)$	$m(F^-)$	E	γ_{Cl}	γ_F(1)	γ_F(2)
1.50	1.495	0.0050	−6.3	0.655	0.544	0.533
2.00	1.995	0.0050	2.2	0.669	0.529	0.510
2.50	2.495	0.0050	9.0	0.686	0.522	0.494
3.00	2.995	0.0050	15.0	0.712	0.514	0.483
3.50	3.495	0.0050	20.1	0.744	0.514	0.474
4.00	3.995	0.0050	24.7	0.781	0.515	0.469
4.50	4.495	0.0050	28.9	0.824	0.518	0.465
5.00	4.995	0.0050	32.6	0.872	0.527	0.463

activity coefficient data. The results of the experiments are presented in Table 2, which lists values of the activity coefficients of the Cl$^-$ ion (γ_{Cl}) in the test solutions, and experimental values of γ_F, and values estimated using the Pitzer equation. Note that these single ion activity coefficients are conventional values based on the assumption that in pure NaCl solutions γ_{Na} is equal to γ_{Cl} at all ionic strengths, and are consistent with others calculated within the Pitzer formalism. These measurements, showing γ_F to be greater than predicted, are in agreement with those made using the Na(glass)–F(LaF$_3$) electrode pair.

Both series of measurements were then used to determine $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$. First, the measured values of γ_F (Cl–F electrode pair) were combined with γ_{Na} values for pure NaCl solutions to yield γ_{NaF}. The quantity $\delta\ln(\gamma_{NaF})/m(Cl^-)$ was then plotted against 0.5[$m(Na^+) + m(F^-)$], where $\delta\ln(\gamma_{NaF})$ is the difference between the logarithm of the measured activity coefficient and that calculated by the model with $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$ set to zero. This is shown in Figure 2, the best-fit straight line through the points has intecept $\theta_{Cl,F}$ and slope $\psi_{Na,Cl,F}$.[22] The large errors at low ionic strengths reflect the fact that the influence of $\theta_{Cl,F}$ and $\psi_{Na,Cl,F}$ is very small for these solutions, consequently points for I < 1 mol kg^{-1} were not used in the fitting. The non-zero values of the parameters imply a small error in the calibration of the Cl–F experiments. This has been corrected and is within the error bars shown in Figure 2. The fitted line gives $\theta_{Cl,F}$ (0.01) and $\psi_{Na,Cl,F}$ (0.0023). The parameter $\theta_{Cl,F}$ should take the same value in other solutions containing Cl$^-$ and F$^-$ ions. Bagg and Rechnitz[34] have measured the activity coefficient of trace F$^-$ in KCl media to high ionic strength. Their results, and the observation that within the limits of experimental error the activity coefficient has the same value as γ_F in a pure KF solution at the same ionic strength, are consistent with $\theta_{Cl,F}$ equal to 0.01. In addition they suggest that $\psi_{K,Cl,F}$ is approximately equal to −0.0033. Solubility data for KCl in KF solutions,[35] which should also yield $\theta_{Cl,F}$, are discordant at low ionic strengths. However, calculations using the Pitzer model suggest solubilities intermediate between the two available data sets.

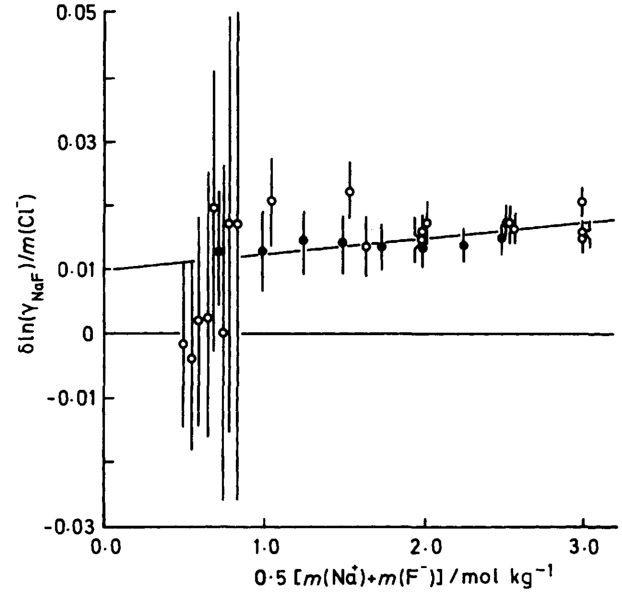

Figure 2. Determination of $\theta_{Cl,F}$ (intercept) and $\psi_{Na,Cl,F}$ (slope) from experimental values of γ_{NaF} (○), and γ_F (●) in NaCl–NaF mixtures up to I = 6.0 mol kg^{-1} (The values of γ_F were combined with γ_{Na} to yield γ_{NaF}, see text.)

Stability Constant of MgF$^+$ *in* NaCl *Media.*—Test solutions consisted of 0.002 or 0.0008 mol kg^{-1} of F$^-$, and 0.0—0.06 mol kg^{-1} of Mg^{2+} in a NaCl medium at total ionic strengths of 1.0, 3.0, and 5.0 mol kg^{-1}. The activity of NaF was measured in each solution following the methods described above, the results are listed in Table 3. The concentration of added Mg^{2+} is low and has only a small effect on the activity of Na$^+$ thus the observed decrease in NaF activity is due to a change in F$^-$ activity in the solutions. This is caused by the formation of the complex MgF$^+$, whose stability constant, K^*, is defined by equation (5). The stability constant of MgF$^+$ is small enough for

$$K^* = m(MgF^+)/[m(Mg^{2+})\cdot m(F^-)] \qquad (5)$$

there to be two alternative approaches to treatment of the experimental results. (*i*) To assume that the activity coefficients of the free F$^-$ and Mg^{2+} are unaffected by each others presence

Table 3. Measurements of the activity of NaF in Na^+-F^--Cl^--Mg^{2+} solutions at I = 1.0, 3.0, and 5.0 mol kg^{-1}. Results were used to determine γ_{NaF}; I/mol kg^{-1}, m/mol kg^{-1}, E and E°/mV

I	$m(F^-)$	$m(Mg^{2+})$	$-E$	S	$-E^{\circ}$	γ_{NaF}
1.00	0.002 00	0.0000	291.1	0.026 04	478.8	0.608
1.00	0.002 00	0.0010	290.1		478.3	0.604
1.00	0.002 00	0.0035	289.7		478.3	0.601
1.00	0.002 00	0.0055	288.3		478.2	0.588
1.00	0.002 00	0.0080	287.4		478.4	0.578
1.00	0.000 80	0.0000	267.5		478.3	0.616
1.00	0.000 80	0.010	264.1		478.9	0.581
1.00	0.000 80	0.020	258.7		479.0	0.531
1.00	0.000 80	0.030	255.1		479.0	0.503
1.00	0.000 80	0.040	251.2		478.7	0.478
1.00	0.000 80	0.045	250.4	0.026 09	478.9	0.475
1.00	0.000 80	0.050	248.3	0.026 04	478.7	0.460
1.00	0.000 80	0.055	247.2	0.026 09	478.7	0.454
1.00	0.000 80	0.060	245.2	0.026 09	478.7	0.444
3.00	0.000 80	0.000	296.3	0.026 03	477.6	0.627
3.00	0.000 80	0.010	292.7		477.6	0.588
3.00	0.000 80	0.020	288.1		477.6	0.541
3.00	0.000 80	0.030	285.4		477.6	0.516
3.00	0.000 80	0.040	281.6		477.6	0.483
3.00	0.000 80	0.050	279.5		477.6	0.466
5.00	0.000 80	0.000	314.5		477.6	0.689
5.00	0.000 80	0.010	309.2		477.6	0.624
5.00	0.000 80	0.020	305.1		477.6	0.579
5.00	0.000 80	0.030	300.6		477.6	0.532
5.00	0.000 80	0.040	297.2		477.6	0.500
5.00	0.000 80	0.050	293.6		477.6	0.468

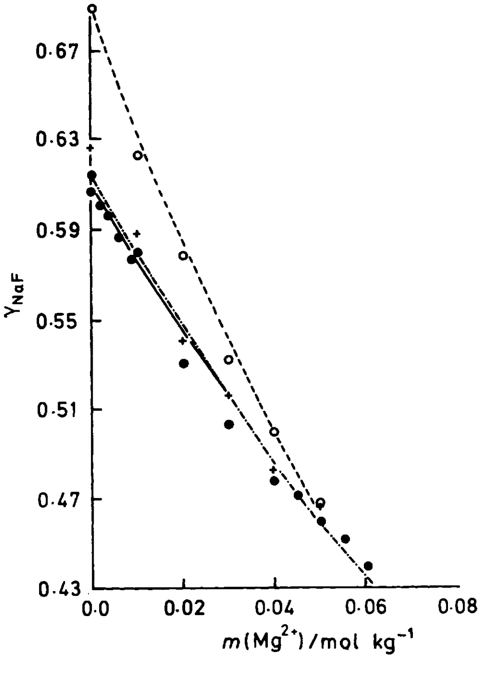

Figure 3. Experimental values of γ_{NaF} in Na^+-F^--Cl^--Mg^{2+} mixtures at ionic strengths (I) 1.0 (●), 3.0 (+), and 5.0 mol kg^{-1} (○). The curves were calculated using the Pitzer model with the parameters obtained by fitting equation (7) to the data

in the solution and that the ion complex MgF^+ is formed. (*ii*) To assume no ion complex is formed and that the reduction in measured fluoride activity is caused by a strong interaction between free Mg^{2+} and F^-.

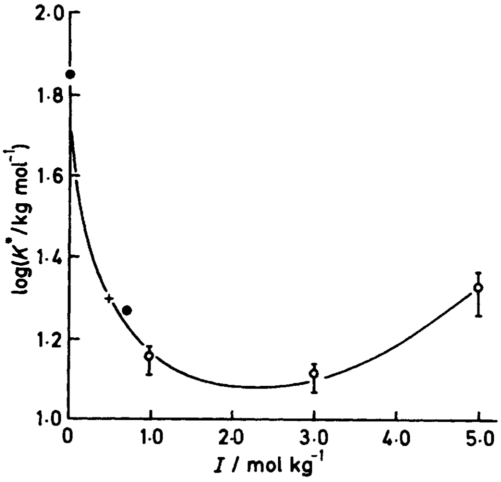

Figure 4. The variation of the stability constant of MgF^+ (K^*) with ionic strength in a NaCl medium. This study (○), values reported by Elgquist and Wedborg (●),[27] value for $NaClO_4$ medium (+).[28] Equation of curve is given in the text

Adopting (*i*), the results in Table 3 were used to calculate a value for K^* at each ionic strength using the following equation (6), relating free fluoride to total fluoride, where $m(F_T)$ is the

$$m(F^-) = m(F_T)\cdot\gamma_{NaF}^{\,2}/(\gamma'_{NaF})^2 \qquad (6)$$

stoicheiometric F^- concentration, γ_{NaF} is the experimentally determined activity coefficient, and γ'_{NaF} is that determined at the same ionic strength but with no Mg^{2+} present, or calculated using the Pitzer equations with Mg^{2+}-F^- parameters set to zero. Both approaches yield similar results. The following values of K^* were estimated: 14.4 ± 1.0 (I = 1.0), 13.1 ± 0.64 (I = 3.0), and 21.1 ± 0.85 kg mol^{-1} (I = 5.0 mol kg^{-1}).

The activity coefficient data from the present experiments at all ionic strengths are shown in Figure 3 as (stoicheiometric) γ_{NaF} against total Mg^{2+} concentration. Taking the approach (*ii*) above, these values of γ_{NaF} were used to determine the $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} parameters for the Mg^{2+}-F^- interaction, valid at ionic strengths up to 5.0 mol kg^{-1}, by least squares fitting of equation

$$\ln(\gamma_{NaF}) = m(Mg^{2+})\{\beta^{(0)} + g(2I^{\frac{1}{2}})\beta^{(1)} + C[Z/2 + m(F^-)]\} + \ln(\gamma'_{NaF}) \qquad (7)$$

(7). This is derived from the Pitzer-model equations in a similar way to that for the θ_{ij} and ψ_{ijk} parameters [see Pitzer and Kim[22] for expressions of the functions $g(x)$ and Z, and the relationship between C and C^{φ}]. The parameters take the following values: $\beta^{(0)}$, 3.932; $\beta^{(1)}$, −25.17; C^{φ}, −5.294. The poor fit at 5.0 mol kg^{-1} and high Mg^{2+} concentrations may be due to the $Mg^{2+}-F^-$ interaction being too great to be described without explicit recognition of the complex species MgF^+.

This parameterisation of the Mg^{2+}-F^- interaction is compact and convenient, and should be valid at all ionic strengths up to 5 mol kg^{-1} and Mg^{2+} concentrations of *ca.* 0.05 mol kg^{-1}. The equations may also be used to estimate K^* over a range of ionic strengths by calculating values of γ_{NaF} both with and without the Mg^{2+}-F^- parameters for model solutions and using equations (5) and (6) to calculate K^*. Results are shown in Figure 4 together with other available data points with which there is reasonable agreement. The variation of K^* is given by the equation: $\log K^* = 1.822 - 0.982I^{\frac{1}{2}}/(1 + 0.328I^{\frac{1}{2}}) + 0.0713I + 0.0169I^2$.

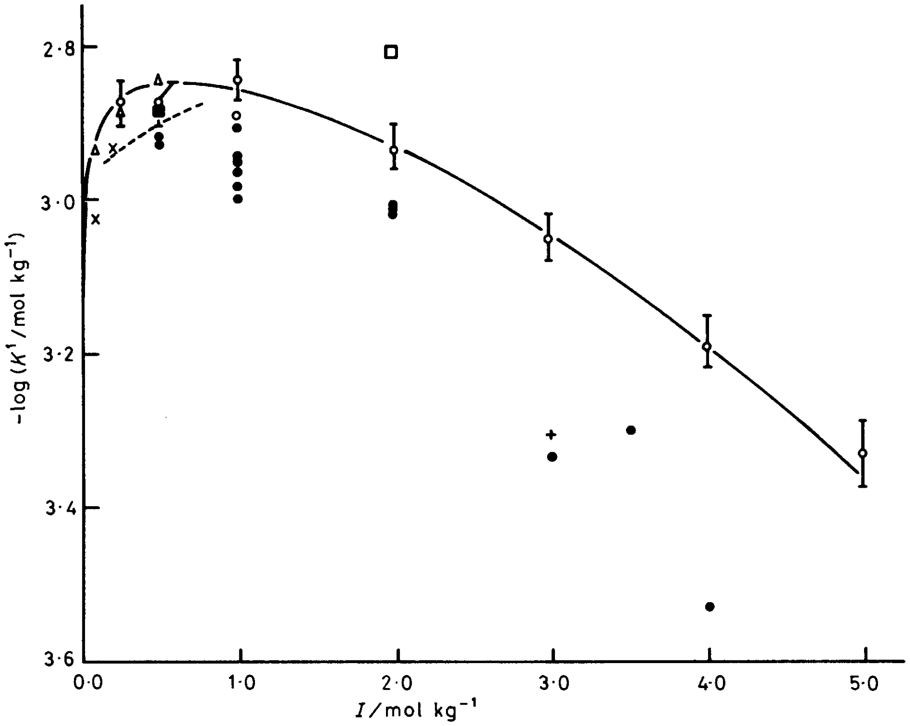

Figure 5. The stoicheiometric dissociation constant of HF (K^1) in different media. This study: NaCl (○), other data compiled by Hogfeldt:[28] (●) $NaClO_4$, (+) KCl, (△) NH_4NO_3, (×) KNO_3, (□) $HClO_4$, (■) $NaNO_3$. The dotted line represents values for a sea-water medium, corrected for MgF^+ formation, obtained by Perez and Fraga.[36] Equation of the best-fit curve is given in the text

Table 4. The stoicheiometric mean activity coefficient of HF (γ_{HF}) in NaCl media determined from experiments using a H(glass)–F(LaF_3) electrode pair; I/mol kg^{-1}, m/mol kg^{-1}, E/mV. Electrode slope, S, was equal to 0.027 15, and standard potential E° was −0.5709 V. Both measured e.m.f.s (E) and values corrected for drift [E(corr.)] are given

I	m(HCl)	m(NaCl)	m(NaF)	E	E(corr.)	γ_{HF}	K^1/mol kg^{-1}
0.25	0.0010	0.248	0.000 75	150.0	150.8	0.505	13.4×10^{-4}
0.50	0.0010	0.498	0.000 75	149.6	148.8	0.487	13.4×10^{-4}
1.00	0.0010	0.998	0.000 75	150.7	149.9	0.497	14.3×10^{-4}
2.00	0.0010	1.998	0.000 75	153.6	153.0	0.526	11.7×10^{-4}
3.00	0.0010	2.998	0.000 75	157.5	157.0	0.566	8.8×10^{-4}
4.00	0.0010	3.998	0.000 75	161.4	161.0	0.609	6.3×10^{-4}
5.00	0.0010	4.998	0.000 75	165.6	165.2	0.658	4.5×10^{-4}

Dissociation Constant of HF^0 *in* NaCl *Media.*—The mean activity of HF was measured directly using a H(glass)–F(LaF_3) electrode pair and the results used to determine the stoicheiometric dissociation constant of HF^0, given by equation (8). The

$$K^1 = m(H^+) \cdot m(F^-)/m(HF^0) \qquad (8)$$

H(glass)–F(LaF_3) electrode pair was calibrated in dilute solutions of HF (0.000 25—0.001 75 mol kg^{-1}) for which mean activity coefficients are known over most of the concentration range.[17] Seven test solutions at ionic strengths of 0.25—5.0 mol kg^{-1} were used, each containing 0.001 mol kg^{-1} of H^+ and 0.000 75 mol kg^{-1} of F^- in a NaCl medium. While the F^- concentration used here is unrealistically high for the sea-salt aerosol, it is still sufficiently low for the formation of HF_2^- to be negligible. During the experimental measurements the test solutions were alternated with a single standard to check for drift due to attack on the glass bulb of the H^+ electrode by HF. A drift of about 1.5 mV was noted over a period of 3 h and the experimental results were corrected for this, Table 4.

Values of K^1 were derived from the results in the following way. First the activity coefficients of free H^+ and F^- in the test solutions were calculated using the Pitzer model (note that the H^+–F^- interaction is set to zero as this is assumed to be entirely accounted for by the formation of HF^0). The activity of HF in the test solutions may be expressed as the stoicheiometric concentration multiplied by the square of the stoicheiometric mean activity coefficient (Table 4), or as free ion concentrations multiplied by the free ion activity coefficients (calculated from the Pitzer model). The following equation (9) was obtained by

$$m(H_T) \cdot m(F_T) \cdot \gamma_T^2 = m(H^+) \cdot m(F^-) \cdot \gamma_H \cdot \gamma_F \qquad (9)$$

equating the two, where subscript T indicates stoicheiometric values, and other values are for free ions. This equation was solved for the concentrations of the free ions in each solution and then K^1 calculated from equation (8). Note that K^1 is sensitive to small errors in the calculated activity coefficients, where a 2% error leads to an 8% error in K^1. Values are listed in Table 4, and are shown in Figure 5 with values for other saline media including sea water[36] (corrected for the formation of MgF^+). Comparison of the constants with the thermodynamic values showed the activity coefficient of HF^0 to be very close to unity at all ionic strengths. The variation of K^1 was therefore estimated from the thermodynamic value and calculated trace H^+ and F^- activity coefficients. The curve in Figure 5 was fitted to these values and is described by the equation: $\log K^1 = -3.165 + 1.81I^{\frac{1}{2}}/(1 + 3.73I^{\frac{1}{2}}) - 0.06I - 0.0136I^2$. There is reasonable agreement with the single existing value for 1.0 mol kg^{-1} NaCl.

Discussion

The activity coefficient model parameters and stability constants determined above describe the major interactions of

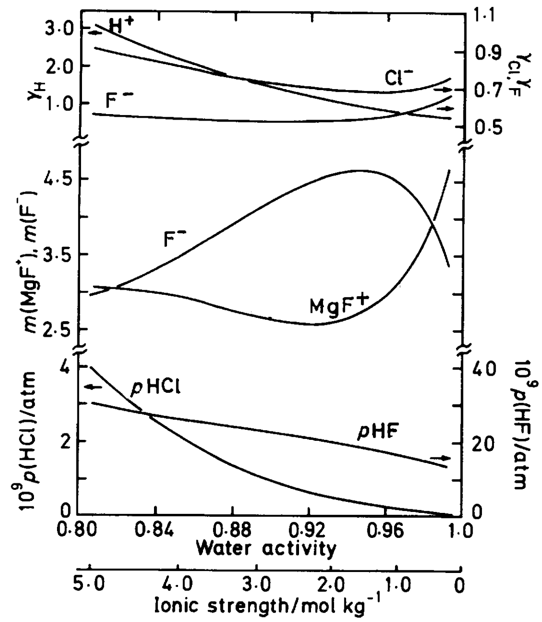

Figure 6. Speciation, partial pressure and activity coefficients in NaCl media containing 0.05 total Mg^{2+}, 0.001 total H^+, and 0.001 mol kg^{-1} total F^-. Activity coefficients were calculated using the Pitzer model, and partial pressures using equation (2)

H^+ and F^- in saline solutions such as the sea-salt aerosol. The importance of non-ideal effects in concentrated solutions is apparent from the ionic strength dependence of the activity coefficients and stability constants measured in this work.

The very different behaviour of HCl and HF in saline media is shown in Figure 6 where the activities and concentrations of the solute species are shown for NaCl media containing 0.001 mol kg^{-1} of H^+, 0.05 mol kg^{-1} of Mg^{2+}, and 0.001 mol kg^{-1} of F^-. The concentrations of free Mg^{2+}, H^+, and F^- were first calculated by solving iteratively a set of equations relating free ion to total ion concentrations. The Pitzer model was then used to estimate the mean (free ion) activity coefficients of HCl and HF in the solutions. Partial pressures of HCl and HF were calculated using these values, the free ion concentrations and Henry's law constants listed above. The osmotic coefficient and water activity were also calculated, this is important for problems involving aerosol systems where aqueous concentrations are controlled by the ambient relative humidity.

Hydrofluoric acid and HCl degassing from sea water were estimated using similar model solutions to those above, but with ions present in sea-salt ratios and including $[SO_4]^{2-}$ (ref. 15). Calculated partial pressures of HF varied from a maximum of seven times that of HCl at ionic strength 1 mol kg^{-1} to approximately equal values at ionic strength 5 mol kg^{-1}. Thus HF will be degassed preferentially to HCl, particularly from low ionic strength solutions (corresponding to high relative humidities in the atmosphere). This result suggests that the sea-salt aerosol must be considered as a source of HF in the marine atmosphere.

Previous comparisons of measured HCl and HNO_3 partial pressures with predicted values[18,19] have demonstrated the robustness of the simple treatment of volatile strong electrolyte behaviour used here. This work has shown how the treatment may be extended to include weak electrolytes, where sufficient thermodynamic data are available.

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