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Studies on Aqueous HF System

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The thermodynamic properties of equilibria $H^+ + F^- = HF$ and $HF + F^- = HF_2^-$ were evaluated at 15°, 25°, and 35°C in water. $NaNO_3$ was used to maintain a constant ionic strength of 0.5000*m*. No evidence was found to indicate the presence of complexes higher than HF_2^- or of polynuclear complexes.

This paper is concerned with the complex equilibria of fluoride ions in acidic aqueous solution. There are two predominant equilibria in this system represented by the three relationships

$$H^+ + F^- = HF \qquad (K_1 \text{ or } \beta_1) \qquad (1)$$

$$HF + F^- = HF_2^- \qquad (K_2) \qquad (2)$$

$$H^+ + 2F^- = HF_2^- \qquad (\beta_2) \qquad (3)$$

The values in parentheses denote either a stability constant (β) or an equilibrium constant (K). These equilibria have received considerable attention for almost 80 years (e.g., *1–10*), and values for K_1 and K_2 appear to be fairly consistent (Table I). Broene and DeVries (*6*) were the only investigators to study these reactions as a function of temperature, and their work is the most widely quoted one today. There are, however, two problems associated with their results. First is the fact that their measurements included liquid junction potentials which had to be approximated. Second is the fact that their results for K_2 at 15° and 25°C were, within experimental error, identical.

With the development of the solid state LaF_3 electrode, it became possible to make measurements on the HF system in a constant ionic strength medium where the liquid junction potential effectively cancels out. This was first demonstrated by Srinivasan and Rechnitz (*10*) and later by Neumann and Sillén (*9*). In the present work, the solid state LaF_3 electrode has been employed in the study of the HF system at three temperatures.

Experimental

The salts NaF and $NaNO_3$ (reagent grade) were air dried at 125°C for 24 hr and stored in a desiccator over P_2O_5 before use. Reagent grade HNO_3 was used to prepare a 4.402*m* stock solution. Stock solutions of 0.5000*m* NaF and $NaNO_3$ were prepared at 25.0°C. Mixtures of these three solutions were made by titrating aliquots into polypropylene bottles in proportions such that the total ionic strength was maintained at 0.5000*m*. Water jacketed burets maintained at 25.0°C were used throughout these preparations. All densities (except that of 0.5000*m* NaF) were obtained from standard tables (*12*). The density of 0.5000*m* NaF was determined pycnometrically to be equal to 1.0184 g/ml at 25.00°C. All solutions were stored in polypropylene bottles until used. Three solutions were stored in 125-ml Pyrex vessels but had to be discarded for the following reasons: In two flasks of high fluoride concentration (0.1 and 0.2*m*), some precipitation occurred upon cooling. In a third flask for $[F^-] = 0.003m$ and $[H^+] = 0.001m$, one experimental point was obtained at 35°C before inconsistent behavior occurred, presumably due to adsorption of F^- on the Pyrex. The experimental points for this solution at 15° and 25°C were discarded.

All measurements were carried out in a temperature bath at 14.95 ± 0.05, 25.00 ± 0.01, and 35.00 ± 0.02°C. The electrochemical cell was a polypropylene vessel of ~125-ml capacity. The reference electrode was a saturated (25°C) calomel sealed in a 7/20 standard taper Pyrex joint. The entire joint was immersed into the study solution, and the liquid junction was formed around the ground joint sleeve. An Orion Model 94-09A solid state fluoride electrode was used as the indicator electrode and an Orion Model 801 pH meter was used for the emf measurements. This instrument has an accuracy of ±0.1 mV. All emf measurements were recorded after at least 10 min, the minimum time required to obtain steady values in these unstirred solutions.

Results

The potential of the fluoride electrode vs. the calomel is given by

$$E = E_0' - \frac{2.3\,RT}{F}\log[F^-] \qquad (4)$$

In Equation 4, E_0' is a formal potential which includes activity coefficient effects and a liquid junction potential, both of which are invariant in the present work because

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Table I. Values of K_1 and K_2 in Water at 25°C[a]

Log K_1	Log K_2	Ionic medium	Year
3.14	0.74	HF ($M \rightarrow 0$)	1885 (*1*)
3.14	0.74	HF ($M \rightarrow 0$)	1912 (*2*)
3.13	0.67	HF ($M \rightarrow 0$)	1924 (*3*)
3.62	1.52	HF ($M \rightarrow 0$)	1939 (*4*)
2.82	0.59	0.53*M* NH_4NO_3	1942 (*5*)
3.17	0.59	HF ($m \rightarrow 0$)	1947 (*6*)
2.91	...	0.5*M* $NaClO_4$	1956 (*7*)
2.89	...	1.0*m* NaCl	1968 (*8*)
3.31	0.72	3.0*M* KCl	1969 (*9*)
2.90	0.77	1.0*M* $NaNO_3$	1968 (*10*)
2.88	0.40	0.5*m* $NaNO_3$	Present

[a] *M* denotes molarity and *m* denotes molality. A more detailed version of this table can be found in ref. *11*.

Table II. Experimental Data[a]

		E, mV		
C_H	C_F	15°C	25°C	35°C
0.0100	0.0030	32.7	36.0	38.3
0.0100	0.0050	13.8	14.9	15.8
0.1000	0.0050	72.7	78.7	84.1
0.2000	0.0050	87.9	95.0	101.1
0.0050	0.0100	−30.9	−33.9	−36.4
0.1000	0.0100	54.5	59.6	64.7
0.0400	0.0300	−14.6	−14.1	−12.8
0.0600	0.0600	−38.3	−40.3	−41.0
0.0100	0.2000	−119.0	−124.6	−130.4
0.1250	0.2500	−105.0	−109.0	−114.3
0.2500	0.2500	−55.0	−55.1	−57.0
0.0010	0.0030			−13.0

[a] C_H and C_F are in mol kg^{-1}; E is the observed emf.

Table III. Equilibrium Constants for Equations 1-3

°C	log β_1	log β_2	log K_2
15	2.80 ± 0.02	3.15 ± 0.09	0.35 ± 0.09
25	2.88 ± 0.01	3.28 ± 0.06	0.40 ± 0.06
35	2.96 ± 0.01	3.39 ± 0.04	0.43 ± 0.05

Table IV. Thermodynamic Quantities for Reactions 1-3[a]

Reaction	ΔG, 25°C	ΔH	ΔS
1	−3.93 ± 0.02	3.15 ± 0.35	23.7 ± 1.4
2	−0.54 ± 0.09	1.51 ± 1.93	6.9 ± 6.4
3	−4.47 ± 0.08	4.66 ± 1.90	30.6 ± 6.2

[a] All values refer to molal units: ΔG and ΔH are in kcal mol^{-1} and ΔS is in equivalent units.

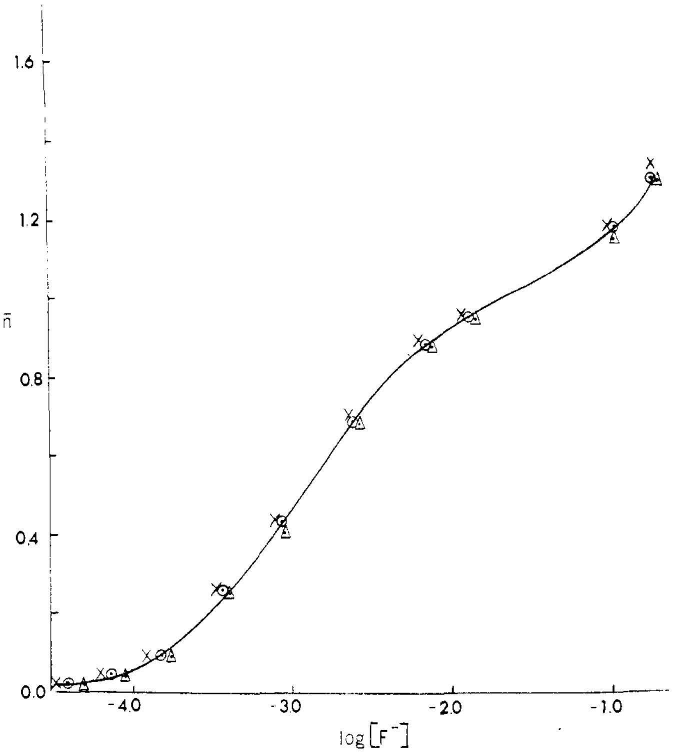

Figure 1. Bjerrum plot of ligand number as function of [F^-]
△ 15°C
○ 25°C
× 35°C

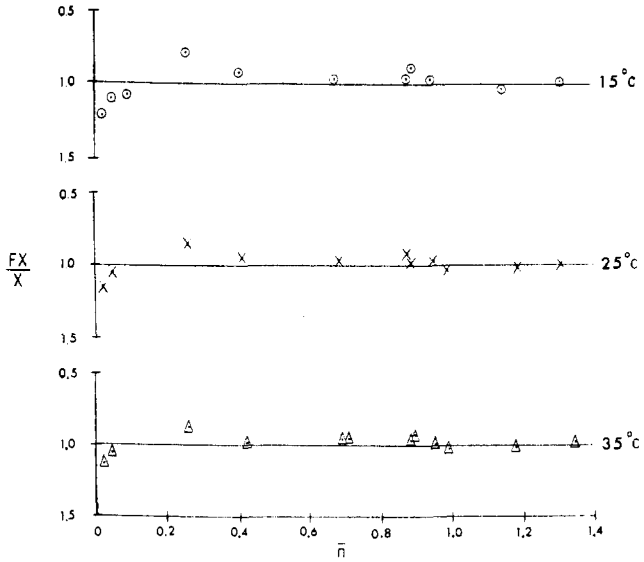

Figure 2. Deviation of experimental points from theoretical value

of the constancy of the ionic strength. The values of E_0' were obtained from standard NaF solutions in $NaNO_3$ using six solutions ranging from $[F^-] = 2.61 \cdot 10^{-4} m$ to 0.3000*m*. The results are summarized below:

$$\begin{aligned} &14.95°C \quad E = (-161.0 \pm 0.8) - (57.7 \pm 0.4) \log[F^-] \\ &25.00°C \quad E = (-168.0 \pm 0.6) - (59.6 \pm 0.2) \log[F^-] \qquad (5) \\ &35.00°C \quad E = (-175.2 \pm 0.6) - (61.5 \pm 0.2) \log[F^-] \end{aligned}$$

The relationships in Equation 5 were obtained by a least squares fit and the values are shown with the standard deviations of the intercepts and slopes. Previous works have shown that Equation 5 is valid in the presence of HF and HF_2^- (*8–10*). No observable changes in the values of Equation 5 could be detected during the course of the emf measurements. The results of the measurements on the study solutions are given in Table II. In this table, the observed E, in mV, is given for each temperature studied, C_H is the total hydrogen molality (from HNO_3), and C_F is the total fluoride molality (from NaF). The existence of HF and HF_2^- was again confirmed by plotting the average ligand number, $\bar{n}$, against log [F^-]. This is shown in Figure 1. The average ligand number as defined by Bjerrum (*13*) is given by

$$\bar{n} = \frac{C_F - [F^-]}{C_H} \qquad (6)$$

The fact that all points in Figure 1 fall on the single line confirms the absence of complexes higher than HF_2^- and of polynuclear species.

The stability constants were evaluated using a least squares technique based on the following mass-balance relationships:

$$C_H = [H^+]\{1 + \beta_1[F^-] + \beta_2[F^-]^2\} \qquad (7)$$

$$C_F = [F^-] + [H^+]\{\beta_1[F^-] + 2\beta_2[F^-]^2\} \qquad (8)$$

The equilibrium constant K_2 is obtained from

$$K_2 = \beta_2/\beta_1 \qquad (9)$$

For each experimental point, $[F^-]$ is obtained from the observed E; β_1 and β_2 are chosen intuitively; and $[H^+]$ values are calculated from Equation 7. A new set of β's is obtained from Equation 8 by minimizing the function

$$\sum_1^k \{1 - FX_k/X_k\}^2 \qquad (10)$$

where

$$FX_k = \beta_1[F^-]_k + 2\beta_2[F^-]_k^2 \qquad (11)$$

and

$$X_k = \{(C_F)_k - [F^-]_k\}/[H^+]_k \qquad (12)$$

The process is repeated using the new β's to generate new $[H^+]$ values, and the β's are further refined until convergence is achieved. The resulting β's along with their standard deviations are given in Table III. The standard deviations of log β_1 and log β_2 were obtained by the pit-mapping method of Sillén (*14*). The variance in log K_2 is taken as the sum of the variances of log β_1 and log β_2.

Figure 2 is a plot of the deviation of FX/X from the theoretical value. Although there is some scatter at low $\bar{n}$ (high C_H/C_F) values, there is no systematic deviation that would indicate the presence of species other than HF and HF_2^-.

The enthalpies and entropies for Equations 1 and 3 were obtained by conventional methods, and the results are given in Table IV.

Conclusions

The above results once again confirm the existence of HF and HF_2^- and the absence of other complexes. The temperature coefficients of the equilibrium constants appear to be more accurate than previous estimates (*6*). The entropy change for Equation 1 of 23.8 equiv. units (molal units) is in good agreement with the value of 22.0 equiv. units (molar units) quoted in ref. 7 for 0.5*M* $NaClO_4$ solutions. The major disagreement between all the works listed in Table I appears to be associated with β_2 and hence K_2.

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Isothermal Vapor-Liquid Equilibrium Data of DMSO Solutions by Total Pressure Method. DMSO-Acetone, DMSO-Tetrahydrofuran, and DMSO-Ethyl Acetate Systems

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Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for the binary mixtures of dimethyl sulfoxide (DMSO) with acetone, tetrahydrofuran, or ethyl acetate at 25°, 35°, and 45°C. These data were reduced to obtain excess Gibbs free energies.

The extensive applications of dimethyl sulfoxide (DMSO) as solvent and reaction medium have been markedly increased in recent years (*8*). In spite of the increased use of DMSO, few phase equilibrium data for the systems containing DMSO have been studied.

As DMSO has a strong polarity, it is highly self-associated and has the ability to make molecular complexes with other compounds. For the fundamental understanding of the effects of the strong molecular interactions on the thermodynamic excess properties, systematic studies of vapor-liquid equilibria for DMSO mixtures have been projected. This paper reports vapor-liquid equilibrium data for the DMSO-acetone, DMSO-tetrahydrofuran, and DMSO-ethyl acetate systems at 25°, 35°, and 45°C.

Experimental

Total vapor pressures for the three systems studied were measured as a function of composition at constant temperature. A schematic diagram of the apparatus described here (Figure 1) was taken from the studies of

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