

# Measurement of the Apparent Dissociation Constants of Hydrofluoric Acid in Concentrated Electrolyte Environments and their Relationship to the Thermodynamic Value

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(Received 30th September, 1994, revised 3rd April, 1995)

**Summary:** The notable presence of fluoride in African rift valley salt lakes has important hydrochemical and mineralogical implications. We have studied the fluoride equilibria to determine apparent  $K_a$  values for HF by the method of Vanderborgh over an extended range of ionic strengths covering the lake-like electrolyte environments of interest in a target lake. The apparent  $pK_a$  values of 2.990, 2.929, 2.820 and 2.739 were obtained for ionic strengths of 0.266, 0.584, 1.024 and 1.419 respectively. When extrapolated to infinite dilution (zero ionic strength), these yield the thermodynamic  $K_a$  value of  $7.07 \times 10^{-4}$  which is in good agreement with other literature values.

## Introduction

The measurement of fluoride ion concentration in aqueous HF or fluoride salts is complicated by various factors. When a glass electrode is used as an indicating electrode in potentiometric work, errors at lower pH ranges arise from presence of molecular HF which attacks silica and glass [1] according to:



finally, yielding  $\text{H}_2\text{SiF}_6$  in aqueous media.

Moreover, molecular HIF is not sensed by the electrode [2]. In higher pH ranges, the isoelectronic  $\text{OH}^-$  ion interferes leading to "alkaline" errors [3]. In addition, the number of species reported in aqueous fluoride solutions include  $\text{F}^-$ ,  $\text{HF}$  and  $\text{HF}_2^-$  as the most well known [3] whilst the polynuclear species  $\text{H}(\text{HF}_3)^+$ , a dimer  $(\text{HF})_2$  and hexamer  $(\text{HF})_6$  have also been postulated [1,4-6].

The use of the Fluoride Selective Electrode (FSE) or other indicating electrodes for fluoride

measurement in aqueous media and subsequent evaluation of the HF dissociation constants has been examined by several workers, among them Bauman [7], Vanderborgh [3] and Broene *et al.*, [8] who reported  $K_a$  values of  $6.85 \times 10^{-4}$ ,  $6.46 \times 10^{-4}$  and  $6.71 \times 10^{-4}$  respectively. We have employed the Vanderborgh method for the determination of  $K_a$  for hydrofluoric acid extending over a wide range of lake-like ionic strengths. A major objective was to examine the fluoride system in the high electrolyte environments which occur in African salt lake brines. Fluoride is a major constituent of the lake electrolytes and has important hydrochemical and mineralogical consequences.

### Theory

Anthony and Hudleston [9] have shown how total fluoride is distributed among various species according to:

$$[F_T] = [F^-] + [HF] + 2[HF_2^-]$$

$$HF = H^+ + F^-; K_a = \frac{[H^+][F^-]}{[HF]}$$

$$HF + F^- = HF_2^-; \text{Formation constant } K_t = \frac{[HF_2^-]}{[HF][F^-]}$$

When appropriately substituted:

$$[F_T] = [F^-] + \frac{[H^+][F^-]}{K_a} + \frac{2K_t[H^+][F^-]^2}{K_a}$$

Subtracting  $[F^-]$  and factorising yields.

$$[F_T] - [F^-] = \frac{[F^-][H^+]}{K_a} (1 + 2K_t[F^-])$$

$K_t = 4$  (approximately) [8] and  $[F^-] = 10^{-3}M$ .

Thus  $1 + 2K_t[F^-] \approx 1$

$$\text{Then: } \frac{[F_T] - [F^-]}{[F^-]} = \frac{[H^+]}{K_a}$$

Taking logarithms and assuming  $[F^-] \leq 10^{-3}M$  [3]

$$\log [F_T] - \log [F^-] = \log [H^+] - \log K_a \quad (1)$$

Changing signs and taking  $pH = -\log (H^+)$  then:

$$\log [F^-] - \log [F_T] = pH + \log K_a$$

The Nernstian relationship for the electrode is given:  $E_F = E^0 - \frac{RT}{F} \ln F$

Thus the fluoride concentration at given ionic strength as a function of the electrode potential gives the response:

$$E_F = E^0 - S \log [F^-]$$

$S$  = slope; defines the response at that ionic strength

$E^0$  = a formal potential.

Substituting into equation (1) gives

$$\frac{\Delta E_F}{S} = \frac{E_{F_T} - E_{F^-}}{S} = pH + \log K_a$$

$E_{F_T}$  = potential in absence of any added  $H^+$  ions

$E_F$  = potential measured as a function of pH.

### Results and Discussion

For the  $E$  versus  $\log [F^-]$  plots, the slope ( $S$ -term) values obtained were 58.39, 58.21, 56.87 and 56.38 for ionic strengths of 0.266, 0.584, 1.024 and 1.419 respectively. The precision limit of the mV measurements was  $\pm 1.0mV$ . The electrode response is linear within the concentration ranges and the slope is within 4% of the Nernstian value and the correlation coefficient equals unity.

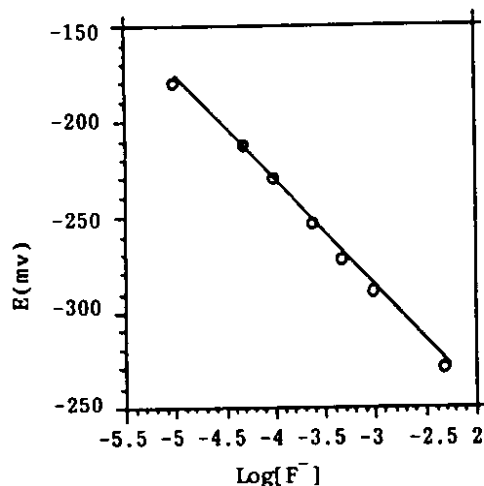
The intercept of the linear plot of  $E_{F_T} - E_F/S$  versus pH gives the value of  $\log K_a$ . The  $K_a$  results for the ionic strengths of interest in this work together with those reported in the literature for zero ionic strength (thermodynamic values) are shown in the table below:

Table-1: Apparent and thermodynamic  $K_a$  values for HF

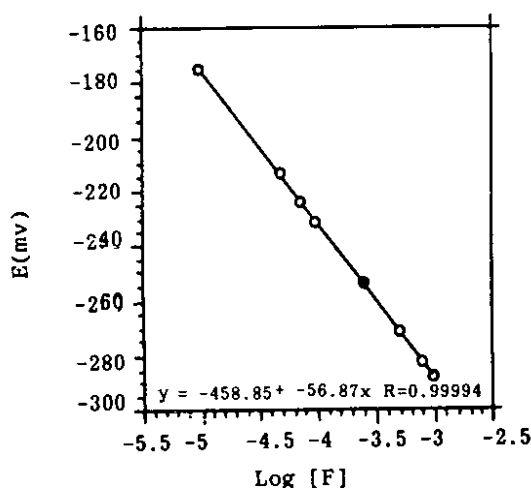
$I^* = 0.5 \sum C_i Z_i^2$	$K_a$	Reference
0.266	$1.096 \times 10^{-3}$	This work
0.584	$1.177 \times 10^{-3}$	"
1.024	$1.513 \times 10^{-3}$	"
1.419	$1.823 \times 10^{-3}$	"
0	$7.07 \times 10^{-4}$	"
0	$6.850 \times 10^{-4}$	ref.7
0	$6.460 \times 10^{-4}$	ref.3
0	$5.850 \times 10^{-4}$	ref.10
0	$6.710 \times 10^{-4}$	ref.8

\*Extrapolation to  $I = 0$  yields the thermodynamic  $pK_a$  value.

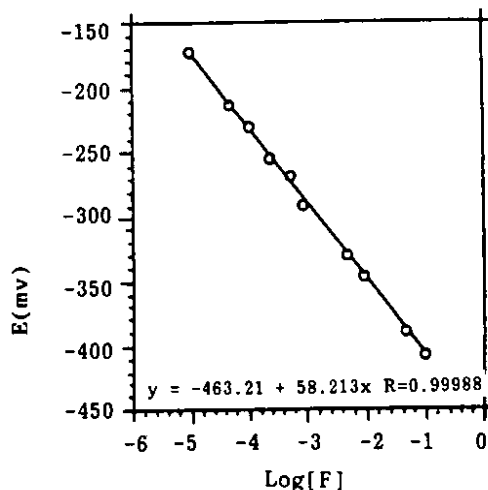
(a) Ionic strength = 1.42



(b) Ionic strength = 1.02



(c) Ionic strength = 0.58



(d) Ionic strength = 0.26

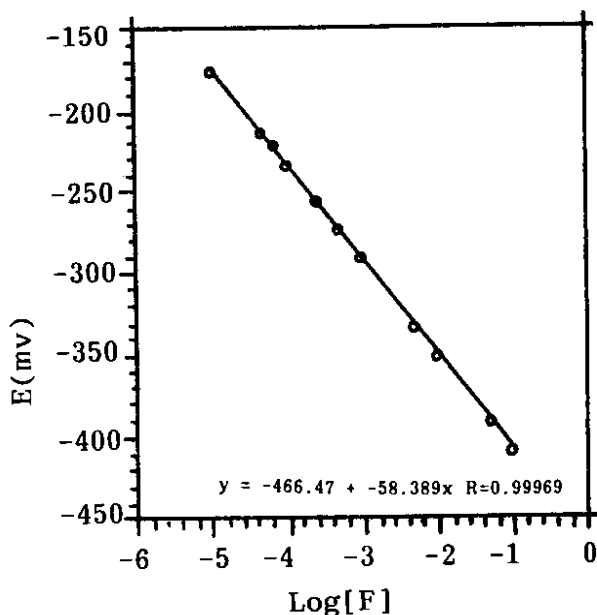


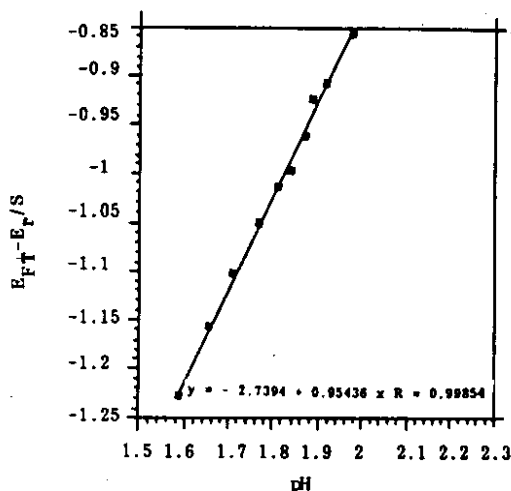
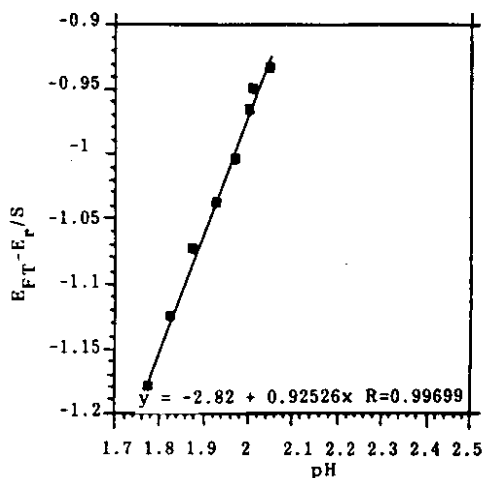
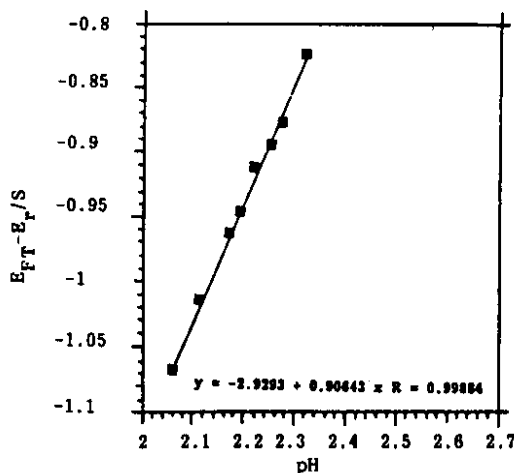
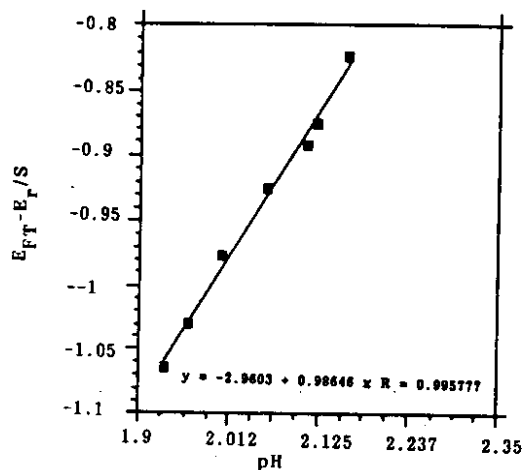
Fig. 1 (a), (b), (c) and (d): Calibration curves for Fluoride Selective Electrode.

The thermodynamic  $K_a$  values for HF have been obtained by plotting  $\log K_a$  values versus  $1$  from the preceding data at finite ionic strengths. When extrapolated to the zero ionic strength value, the thermodynamic  $K_a$  value of  $7.07 \times 10^{-4}$  is obtained. This linear plot is shown in Fig. 3 as a least square fit of the data.

### Experimental

Ionic strengths of 1.419, 1.024, 0.584 and 0.266 emerged as important representative lake-like aquatic environments occurring in Lake Manyara, the target lake in northern Tanzania (chemical constitution is location dependent). These were established from analysis of major cations and anions. Each ionic strength value was investigated independently. Sodium fluoride was pre-dried at  $120^\circ\text{C}$  for 24 hours. A standard concentrated stock was prepared using volumetric glassware, and lower concentrations obtained by appropriate dilution. Hydrofluoric acid standard stock was similarly prepared and lower concentrations obtained in the same manner.

Although the preparation of standard stock solutions of HF and NaCl needed volumetric

(a) Ionic strength  $I = 1.42$ (b) Ionic strength  $I = 1.02$ (c) Ionic strength  $I = 0.58$ (d) Ionic strength  $I = 0.266$ Fig. 2: (a), (b), (c) and (d): Plot of  $E_{FT} - E_r/S$  versus pH

glassware, prompt transferring to plastic storage bottles was necessary. Teflon beakers were used and stirring of solutions was by use of a plastic protected magnet. A WTW model F500 fluoride selective electrode was used for the fluoride measurements while pH was monitored by a glass electrode. Potentials were measured versus a WTW model R501 reference electrode. A digital WTW91 pH-mV meter was used to record potentials. Measurements were made to  $\pm 1.0$  mV at  $25^\circ\text{C}$ .

#### Calibration of the FSE and evaluation of the $S$ term

Several similar ionic strength solutions (with  $\text{NaNO}_3$  as supplementary electrolyte) were made up to include various  $\text{NaF}$  molarities ( $10^{-5}$  to  $10^{-2}\text{M}$  range). The potential as a function of  $[\text{F}^-]$  was recorded as linear plots in Figures 1 (a) to (d). The  $S$  term in the expression  $E_F = E^0 - S \log [\text{F}^-]$  at each ionic strength is the slope of the corresponding linear plot.

$$\text{Evaluation of the } \left[ \frac{E_{FT} - E_F}{S} \right] \text{ term}$$

A series of solutions at various acidities (with respect of  $\text{HNO}_3$ ) ranging from  $6 \times 10^{-3}$  to  $3.8 \times 10^{-2}\text{M}$   $\text{HNO}_3$  at a selected ionic strength were prepared to include fluoride ( $5 \times 10^{-4}\text{M}$  with respect of  $\text{NaF}$ ). Both the potential of the fluoride selective

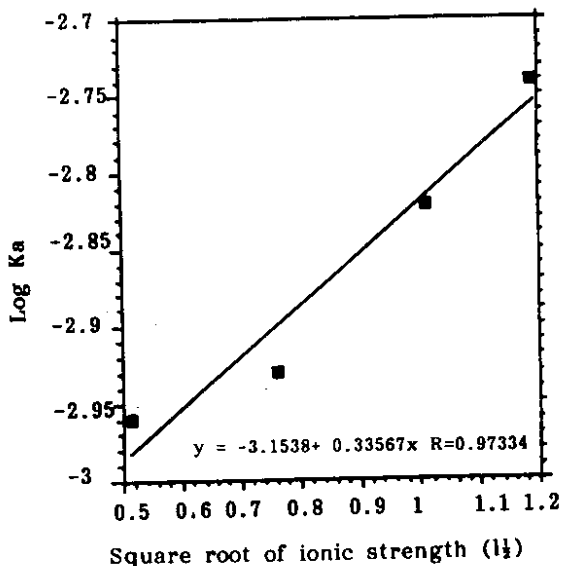


Fig.3: Variation of equilibrium constants with ionic strength.

electrode and the pH were recorded over the series of acidities. It has been shown by Warren [1] that pH measurement employing a glass electrode under the conditions of pH and NaF molarities given above has negligible effect on the electrode. The E value without added  $\text{HNO}_3$  (zero acidity) was assigned as  $E_{\text{F}_T}^0$ .

The results are shown as linear plots of ( $E_{\text{F}_T}^0 - E_{\text{F}}/S$ ) versus pH (Figure 2(a), (b), (c) and (d))

whose intercept yields the value of  $K_a$ . We have found it necessary to exclude points in higher pH ranges as these show significant inconsistencies, presumably due to the postulated polynuclear species such as  $\text{H}(\text{HF}_3)^+$ ,  $\text{H}(\text{HF})_2$  and  $(\text{HF})_6$  mentioned earlier. High acidities suppress HF dissociation and may favour formation of these species.

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