

Direct Potentiometric Determination of Fluoride Species by Using Ion-Selective Fluoride Electrode

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A novel approach and method for potentiometric determination of acid dissociation constant (K_a) of hydrofluoric acid are described. Proposed method is based on using commercial fluoride ISE (FISE) as very inexpensive, simple and reasonably fast method for determination of fluoride species. We are proposing a usage a direct potentiometric method for determination of fluoride species and K_a of hydrofluoric acid in water solutions for $1.01 \leq \text{pH} \leq 7.01$ and $1.0 \times 10^{-1} \leq c_T(\text{F}^-) \leq 1.0 \times 10^{-6} \text{ mol L}^{-1}$. Found acid dissociation constant of hydrofluoric acid ($\text{p}K_a = 3.24 \pm 0.02$, $K_a = 5.75 \times 10^{-4} \text{ L mol}^{-1}$) and formation constant of HF_2^- ($\log \beta = 0.600$, $\beta = 3.98 \text{ L mol}^{-1}$) are in very good agreement with literature ones.

Keywords: fluoride, potentiometric, determination, ion-selective electrode

1. INTRODUCTION

In this paper we tried to find can potentiometric methods be used for determination of fluoride species and how much are potentiometric methods appropriate for teaching in early stage of Analytical Chemistry for understanding problem of dissociation of weak acid in function of pH and analytical (total) concentration of a weak acid and species what dissociation yields too. In the most cases we give an example for dissociation of weak acid ethylenediaminetetraacetic acid (EDTA). EDTA is very complex organic compound with hexaprotic dissociation system. On the other hand, hydrofluoric acid is inorganic compound well known to students through course of Inorganic Chemistry. Fluoride solutions are very interested for analysts because many fluoride species can occur depend of analytical fluoride concentration and pH value.

Back in history, dissociation constant of hydrofluoric acid was determined both potentiometrically and conductometrically [1-5] with reported values for pK_a from 2.82 to 3.33 at 25 °C, but IUPAC suggests $pK_a = 3.164$ while in other handbooks of Analytical Chemistry was established values of $pK_a = 3.19 \pm 0.02$ [6-8]. Wide range of pK_a values can be explained by creating different fluoride species like H_mF_m , $m = 1$ to 2 and H_nF_{n+1} , where $n = 1$ to 4 and F^- [4,5]. Searching the literature we were not able to find a recently made potentiometrically determination values for pK_a using fluoride ion-selective electrode (FISE), but there are numerous papers potentiometrically made determination values for pK_a of different weak organic acids. This fact is interesting because FISE was described in paper of Frant et al. back in 1966 [9]. FISE is one of the earliest designed ion-selective electrode beside glass or pH electrode.

For our needings we calculated $pK_a = 3.24 \pm 0.02$ at 25 °C. Calculated value is in very good agreement with literature ones [6-8], with error of 1.89 %. Values of stability constant (β) of HF_2^- are in wide range, but one value, $\log \beta = 0.600$ is in very good agreement with literature found ones [2,3].

2. EXPERIMENTAL

2.1. Reagents and chemicals

All needed solutions were prepared by solving certain amount of chemicals in suprapure water. Suprapure water (declared conductivity $0.04 \mu S cm^{-1}$) was prepared by Millipore Simplicity (USA).

Following chemicals were used: Sodium nitrate, $NaNO_3$, p.a., Sodium fluoride, NaF , p.a., Sodium acetate, CH_3COONa , p.a., Sodium hydroxide, $NaOH$, p.a., Acetic acid, CH_3COOH , p.a., Nitric acid, HNO_3 , p.a., Kemika (Croatia). NaF was dried at 110 °C for two hours and after cooling was used for solutions preparation.

2.2. Apparatus

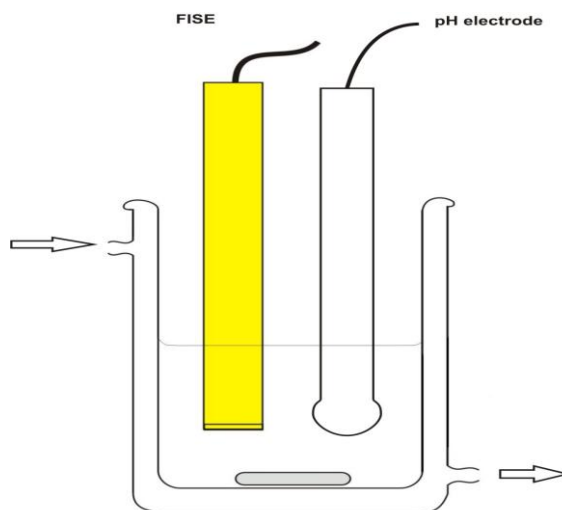


Figure 1. Potentiometric system in thermostated vessel

The indicator electrode was a combined fluoride ion-selective electrode DC219 from Mettler Toledo (Switzerland).

Potentiometric data were recorded at 25 ± 0.01 °C in thermostated polyethylene vessel with a millivoltmeter (Model MA 5740, Iskra, Ljubljana, Slovenia) coupled to a personal computer and recorder, Fig. 1. pH was controlled by Metrohm pH meter 827 with pH electrode.

3. RESULTS AND DISCUSSION

Potentiometric measurements have been done by using previously described FISE. FISE has been tested for response to fluoride concentration for pH values between 1.01 and 7.01. Change of concentration of F^- was performed by standard dilution method. During measurement, solution was stirred and kept at constant temperature of 25 ± 0.01 °C. Results are shown at Figure 2.

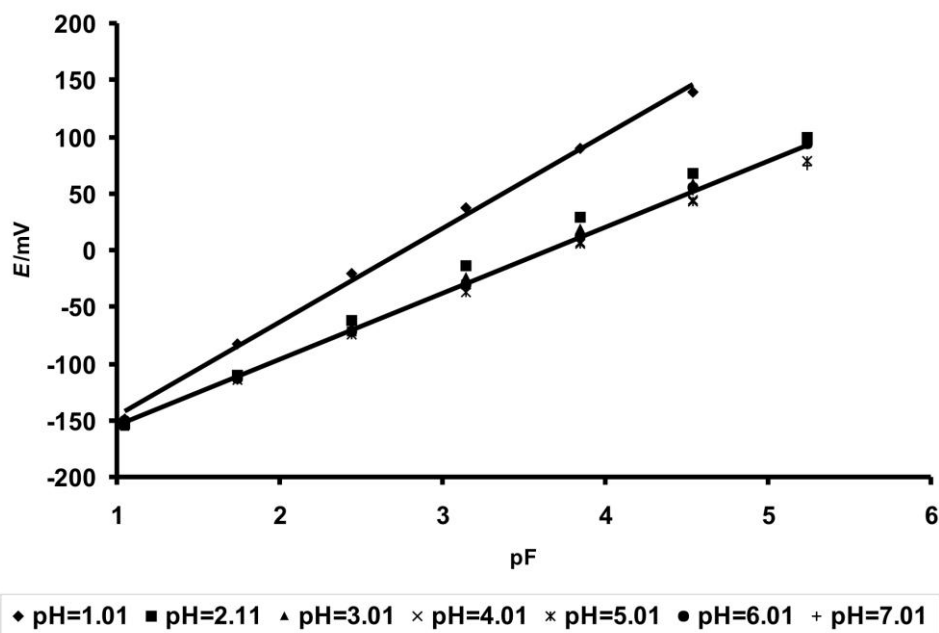


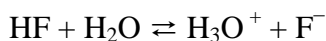
Figure 2. Response of FISE to fluoride ions in pH range from 1.01 to 7.01

Points on the graph represent experimental data and straight line was calculated by using method of linear regression. As it can be seen, FISE linearly follows changing of F^- concentration in wide concentration range. Stable potential was reached in 1 minute. Potential change of 58.10 mV per decade of fluoride concentration change was recorded in solutions pH ranged between 2.11 and 7.01, with correlation coefficient of 0.9986, which is in good agreement with theoretical Nernstian slope for monovalent cations. For solutions with pH = 1.01, we obtained superNernstian slope of 82.49 mV per decade with correlation coefficient of 0.9971 what was expected [10]. In solutions with pH = 1.1, FISE gives shorter linear response range ($2.9 \times 10^{-5} - 9.0 \times 10^{-2}$ mol L⁻¹) than for other pH values ($1.2 \times 10^{-6} -$

$9.0 \times 10^{-2} \text{ mol L}^{-1}$). This effect was expected because in solutions with high H^+ concentration, dominated specie would be HF and by dilution it would be less and less F^- for reaction with active places at FISE membrane. In the other hand, it is very interesting that there is no significant difference in slope of calibration curves for $\text{pH} > 2.11$ in wide concentration range and we can suggest using a same calibration curve for $2.11 \leq \text{pH} \leq 7.01$ (Fig. 2).

3.1. Calculating pK_a

pK_a can be calculated both numerically and graphically. For numerical calculation we used next chemical equation with its equilibrium constant, equation (1):



$$K_a = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{F}^-}}{a_{\text{HF}}} \quad (1)$$

Where a denotes activity of each chemical specie.

For constant ionic strength, activity coefficient of each ion can be easily calculated using equation (2):

$$\log \gamma_{\pm} = -0.51z^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (2)$$

where γ_{\pm} denotes activity coefficient, z ion's charge number and μ ionic strength of solution.

By equation (3) is given relationship between activity and free concentration:

$$a_X = [\text{X}] \cdot \gamma \quad (3)$$

Hence free analytical concentration can be expressed as product of analytical (total) concentration and fraction of each chemical specie, equation (4):

$$[\text{X}] = c_T \cdot \alpha_X \quad (4)$$

where c_T denotes analytical concentration and α denotes fraction of each chemical specie.

We prepared six different fluoride solution by dissolving and/or diluting appropriate amount of NaF in acetic buffer solutions ($\text{pH} = 1.01 - 7.01$) so resulting $c_T(\text{F}^-)$ were 1.0×10^{-1} , 1.0×10^{-2} , 1.0×10^{-3} , 1.0×10^{-4} , 1.0×10^{-5} and $1.0 \times 10^{-6} \text{ mol L}^{-1}$. Prepared solutions were tested by changing pH value by adding sodium hydroxide (for increasing pH value) or nitric acid (for decreasing pH value) and we were measuring and recording potential of FISE in the function of pH changing, Fig. 3.

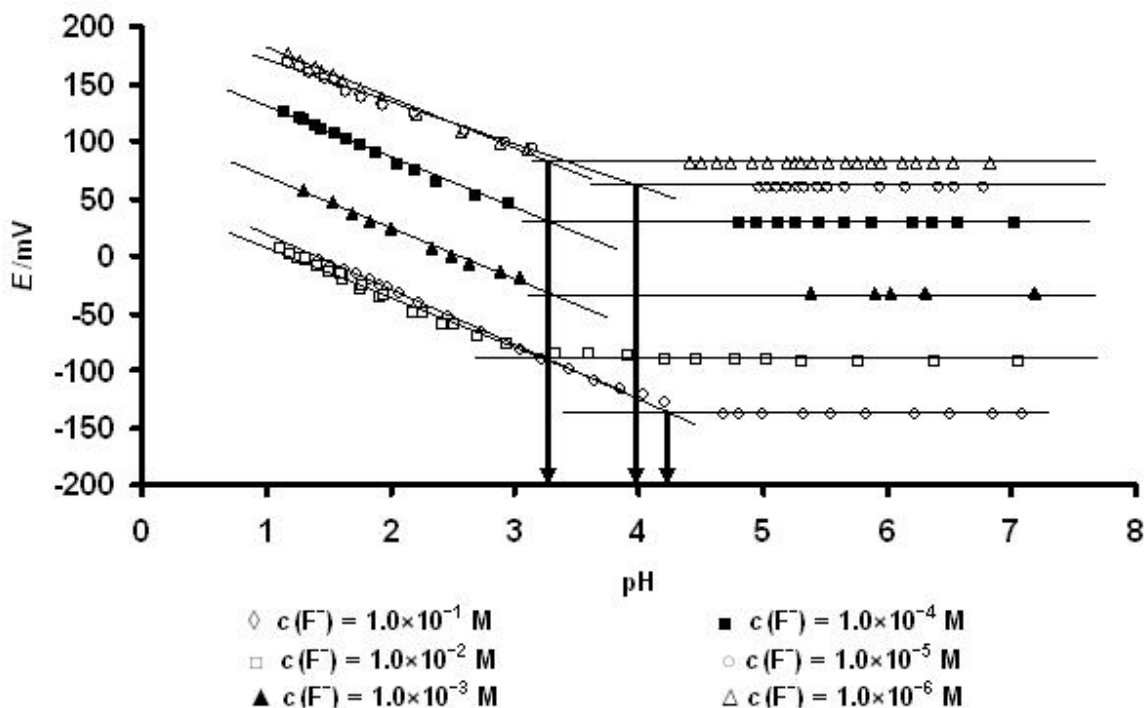


Figure 3. Response of FISE in function of pH changing

Collected experimental data were drawn and by using method of linear regression we added trend lines with calculated equations for each fluoride concentration. When we extrapolate every trend line to intersect with the line on the right side of Fig. 3 for suitable concentration, pK_a values can be calculated as point what suits equations of both lines, a decreasing (on the left side Fig. 3) one and constant (on the right side Fig. 3) one. We gave an example of calculating pK_a value for $c_T(F^-) = 1.0 \times 10^{-2} \text{ mol L}^{-1}$.

$$E_1 = -43,6647pH + 51,4851$$

$$E_2 = -90$$

Hence pK_a is intersection of 2 lines, that point suits both lines' equations :

$$E_1 = E_2$$

$$-43,6647pH + 51,4851 = -90$$

$$pH = \frac{-90 - 51,4851}{-43,6647}$$

$$pH = 3,24$$

$$pH \equiv pK_a$$

Calculated pK_a values are given in Table 1.

Table 1. Found pK_a values

$c_T(F^-)/\text{mol L}^{-1}$	pK_a	
	Calculated values	Graphically found values
1.0×10^{-1}	4.33*	4.34
1.0×10^{-2}	3.24	3.23
1.0×10^{-3}	3.27	3.28
1.0×10^{-4}	3.22	3.25
1.0×10^{-5}	3.24	3.25
1.0×10^{-6}	3.94*	3.94
$\overline{pK_a}$	3.24	3.25
Standard deviation	0.02	0.02

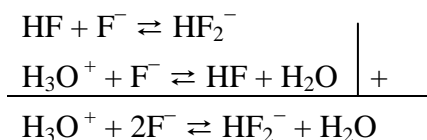
* Values did not taken under consideration

Graphically finding of pK_a values was done by drawing a perpendicular line from intersection of two lines added to experimental data by method of linear regression to the abscissa axis.

From results given in Table 1 can be seen very good agreement between calculated and graphically found results and they are practically same. There are only significant difference for $c_T(F^-) = 1.0 \times 10^{-1} \text{ mol L}^{-1}$ and $c_T(F^-) = 1.0 \times 10^{-6} \text{ mol L}^{-1}$ what can be easily explained. For all weak acids dissociation is turned to reactant's side by increasing analytical concentration [11-14] what happened in our case. In the other hand, for $c_T(F^-) = 1.0 \times 10^{-6} \text{ mol L}^{-1}$ that concentration is on the very end or even below of linear response range and can not be taken without suspicion. We decided to ignore pK_a for $c_T(F^-) = 1.0 \times 10^{-1} \text{ mol L}^{-1}$ and $c_T(F^-) = 1.0 \times 10^{-6} \text{ mol L}^{-1}$ on fact that trend lines on left sides at Fig. 3 are overlapped with ones for $c_T(F^-) = 1.0 \times 10^{-2} \text{ mol L}^{-1}$ and $c_T(F^-) = 1.0 \times 10^{-5} \text{ mol L}^{-1}$, respectively. All other found pK_a values are also in very good agreement with values, $pK_a = 3.19$, the literature ones [6-8].

After we had determined pK_a of hydrofluoric acid, we tried to calculate a stability constant of hydrogendifluoride ion, HF_2^- . HF_2^- is a very interest ion created on strong hydrogen bond between H and F. HF_2^- is dominated specie in solutions with $c_T(F^-) > 1.0 \text{ mol L}^{-1}$ and $\text{pH} \approx 3$ and $\mu = 1.0 \text{ mol L}^{-1}$ [3].

Creation of HF_2^- can be shown with next chemical equations:



With belonging stability constant, β :

$$\beta = \frac{a_{HF_2^-}}{a_{HF} \cdot a_{F^-}} \quad (5)$$

When we substitute a_{HF} in equation (5) with $a_{\text{H}_3\text{O}^+}$ and a_{F^-} shown in equation (1), we would get an equation (6):

$$\beta = \frac{K_a \cdot a_{\text{HF}_2^-}}{a_{\text{H}_3\text{O}^+} \cdot a_{\text{F}^-}^2} \quad (6)$$

While we know accurate $c_{\text{T}}(\text{F}^-)$, we can write equation (7):

$$c_{\text{T}}(\text{F}^-) = [\text{H}_2\text{F}_2] + [\text{HF}] + [\text{HF}_2^-] + [\text{H}_2\text{F}_3^-] + [\text{H}_3\text{F}_4^-] + [\text{H}_4\text{F}_5^-] + [\text{F}^-] \quad (7)$$

In dilute solutions, what is in our case, we can expect reasonable concentrations of only three species, HF, F^- and HF_2^- hence we are able rewrite Eq. (7) in next form using mass balance:

$$c_{\text{T}}(\text{F}^-) = [\text{HF}] + 2[\text{HF}_2^-] + [\text{F}^-] \quad (8)$$

In next step, we can substitute free analytical concentration using Eq. (3):

$$c_{\text{T}}(\text{F}^-) = \frac{a_{\text{HF}}}{\gamma} + 2 \frac{a_{\text{HF}_2^-}}{\gamma} + \frac{a_{\text{F}^-}}{\gamma} \quad (9)$$

Forwarding, we can substitute a_{HF} and $a_{\text{HF}_2^-}$ using equations (1) and (6), and can assume that $\gamma(\text{HF}) = 1$:

$$c_{\text{T}}(\text{F}^-) \cdot \gamma = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{F}^-}}{K_a} \cdot \gamma + 2 \frac{\beta \cdot a_{\text{H}_3\text{O}^+} \cdot a_{\text{F}^-}^2}{K_a} + a_{\text{F}^-} \quad (10)$$

When we rearrange Eq.(10), we would get:

$$\beta = \frac{K_a \cdot c_{\text{T}}(\text{F}^-) \cdot \gamma - a_{\text{F}^-} \cdot a_{\text{H}_3\text{O}^+} \cdot \gamma - K_a \cdot a_{\text{F}^-}}{2 \cdot a_{\text{H}_3\text{O}^+} \cdot a_{\text{F}^-}^2} \quad (11)$$

Results calculated using Eq.(11) are given in Table 2.

Analyzing data are shown in Table 2., we can see that results are very divaricated and pretty much different of results found in literature, $\log\beta = 0.598$ [2,3]. Only result what is close to literature value is $\log\beta = 0.600$, with very good agreement. This awkward situation can be explained that our solutions not contain enough F^- concentration; in fact they are dilute and to acidic. By decreasing pH value and especially decreasing $c_{\text{T}}(\text{F}^-)$, it is obviously that dominate specie becomes HF and statistically is very hard expect that would be enough available F^- to form HF_2^- . On the other hand for

$4 \leq \text{pH} \leq 6$ and $c_T(\text{F}^-) \leq 1.0 \times 10^{-4} \text{ mol L}^{-1}$, we have got high $\log\beta$ values, so it can be assumed that chemical equilibrium is moved to the products and HF_2^- would be dominated specie, but that can not be possible.

Table 2. Calculated $\log\beta$ values

$\text{p}\{c_T(\text{F}^-)\}$	pH						$\log\beta$
	1	2	3	4	5	6	
1	0.600	3.72	3.19	2.71	3.10	3.77	
2	*	*	1.42	2.35	3.59	5.13	
3	*	*	2.37	3.49	4.93	5.39	
4	*	*	2.82	5.23	6.33	6.83	
5	*	*	*	4.85	7.13	8.12	

* β values are negative hence there is no possibility calculate $\log\beta$

We should explain this phenomena very easy if we look up to Eq.(6). High $\log\beta$ values are resulted by decreasing values of $a_{\text{H}_3\text{O}^+}$ and a_{F^-} , and especially that a_{F^-} is put on second power. Most results shown in Table 2 are within range found in work of Warren [15] under similar conditions. We are stressing that divergence of $\log\beta$ values is common in cited literature [2,3,15] and authors often selected one value.

Final part of our investigation was calculating specie's fraction values. This part is very important because from these results can be clearly seen what specie dominated as function of pH and concentration. Calculation was done using Eq.(12) for HF and Eq.(13) for F^- . Fraction of HF_2^- was calculated using Eq.(14). In Table 3. are given calculated fraction values of HF, HF_2^- and F^- .

$$\alpha = \frac{[\text{H}^+]}{[\text{H}^+] + K_a} \tag{12}$$

$$\alpha = \frac{K_a}{[\text{H}^+] + K_a} \tag{13}$$

$$\alpha = \frac{a_{\text{HF}_2^-}}{c_T(\text{F}^-) \cdot \gamma} \tag{14}$$

Results are shown in Table 3. confirm our assumptions earlier said about HF_2^- concentration in dilute fluoride solution are very low and for most cases it can be taken as zero. Same situation is for other H_nF_{n+1} complex, where $n = 1$ to 4 for dilute solutions because they are formed in very acidic and very concentrate fluoride solutions.

Nice way for show calculated and collected data is graphical draw in MS Excell®. Fractions of species are shown at Fig. 4. We prefer drawing results in that way because it is not possible that concentration of any specie is zero, even we are able to use this assumption sometimes.

Table 3. Calculated species' fraction values

pH	p{c _T (F ⁻)}														
	1			2			3			4			5		
	α(HF)	α(HF ₂ ⁻)	α(F ⁻)	α(HF)	α(HF ₂ ⁻)	α(F ⁻)	α(HF)	α(HF ₂ ⁻)	α(F ⁻)	α(HF)	α(HF ₂ ⁻)	α(F ⁻)	α(HF)	α(HF ₂ ⁻)	α(F ⁻)
1	0.986	5×10 ⁻⁴	0.014	0.990	*	0.010	0.990	*	0.010	0.991	*	0.009	0.929	*	0.071
2	0.911	1×10 ⁻⁵	0.089	0.936	*	0.064	0.929	*	0.071	0.921	*	0.079	0.573	*	0.427
3	0.524	6×10 ⁻⁶	0.476	0.576	8×10 ⁻⁵	0.424	0.538	9×10 ⁻⁷	0.462	0.533	4×10 ⁻⁹	0.467	0.105	*	0.895
4	0.101	1×10 ⁻⁷	0.899	0.140	2×10 ⁻⁶	0.860	0.102	1×10 ⁻⁸	0.898	0.096	9×10 ⁻¹³	0.904	0.012	9×10 ⁻¹⁴	0.988
5	0.012	6×10 ⁻⁹	0.988	0.012	1×10 ⁻⁸	0.988	0.013	3×10 ⁻¹¹	0.987	0.010	6×10 ⁻¹⁵	0.990	0.002	1×10 ⁻¹⁷	0.998

* Values were not calculated due β was negative

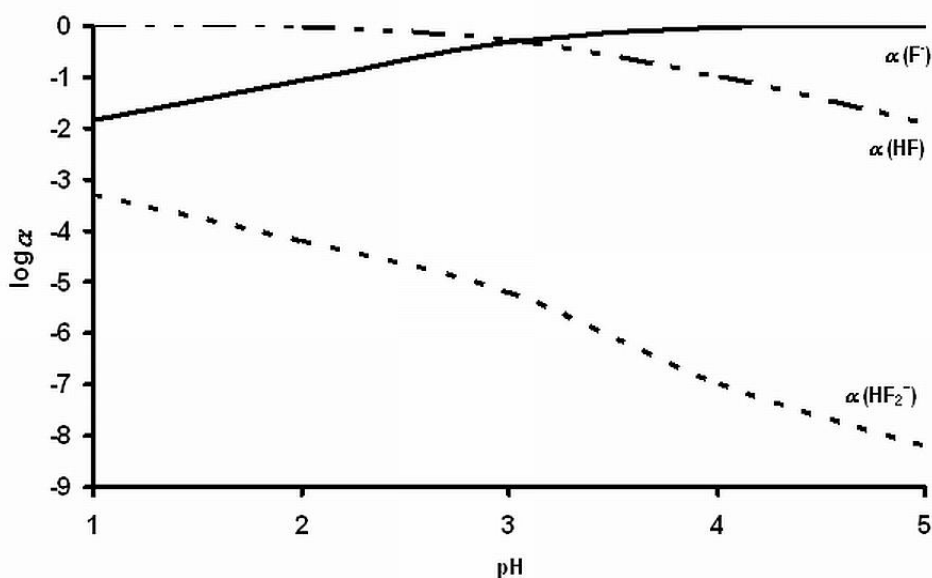


Figure 4. Fraction of fluoride specie in function of pH changing for c_T(F⁻) = 1.0×10⁻¹ mol L⁻¹

4. CONCLUSIONS

All done experiments were helpful for students and students' understanding problem of dissociation of weak acid and forming different species in solutions. During this work we took a few assumptions, choosing a temperature of 25 °C for experiments, using dilute and very dilute solutions (c_T(F⁻) ≤ 1.×10⁻¹ mol L⁻¹) and approximation of concentration of H_nF_{n+1} complex, where n = 1 to 4 are zero for dilute solutions (this was direct consequence of using dilute solutions). Choosing to do all experiments at 25 °C made doing experiments simpler but we can not be sure what situation about species' fraction would be at lower or higher temperature of 25 °C. On the other hand, choosing 25 °C was logically because of most analytical methods are done at 25 °C. Dilute solutions are also interest for students attend elementary grade of Analytical Chemistry because of all experimental teaching is done with dilute concentration. The last, but not less important thing was use of glass electrode for pH

measurements. We can not neglect this fact had some influence to final results. If we remember experiment had a qualitative purpose for teaching students in their very beginning, we neglected this fact, but deeply aware of.

On the other hand, using potentiometric methods as an example of simple analytical technique was an excellent choice. Results were collected by using potentiometric methods gave very accurate values of constant dissociation of hydrofluoric acid ($pK_a = 3.24 \pm 0.02$) compared with results were found ($pK_a = 3.19 \pm 0.02$) or suggested in literature ($2.82 \leq pK_a \leq 3.33$). Situation with stability constant of HF_2^- complex was complicated, but one value ($\log \beta = 0.600$) is in very good agreement with literature ones.

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