

## The Influence of Ionic Strength on Apparent and Thermodynamic Parameters (Ka, pKa's) for HF and Phosphate Buffer Capacities

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### ABSTRACT

The apparent and thermodynamic parameters (pKa, pKb, Ka, Kb) are among the most common used physical parameters and their determinations are of interest to a broad range of research. It is apparent that hypersaline hydrochemical environment in concentrated salt lake brines has a profound modifying influence on parameters such as Ka, pKa's and buffer capacities. This study presents chemical parameters (Ka, pKa and buffer capacities) at typical high ionic strength salt lake brines, which were evaluated at 25 °C and have revealed both pKa<sub>1</sub> and pKa<sub>2</sub> to decrease as ionic strength of the solution increases. The apparent dissociation constant Ka for HF is increasing as the ionic strength increases and thermodynamic Ka = 7.46 × 10<sup>-4</sup> found is in good agreement with the values reported in the literature. The phosphate buffer capacity in the target Rift Valley Salt Lake systems is observed to exceed that of pure water by a factor of 36 to 1000.

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### Introduction

The acid dissociation constant is among an important physicochemical parameter of a substance, and knowledge of it is of paramount in a wide range of applications and research areas. To be more specific acid dissociation constant (pKa) is recognized as being among the most commonly used parameter in modern-days chemistry [1, 2]. A good example is that the constant is a prerequisite in the studies of phosphate uptake during bio-uptake, metabolic pathways in plants, animals, drug design and optimization [3, 4, 5, 6, 7]. For the case of the pKa of a drug, this influences lipophilicity, solubility, permeability, metabolism and excretion [8, 9, 10]. In physicochemical studies, pKas values can provide information on the ionic interactions of phosphate in both sea and hypersaline lake brines [11]. The pKa values themselves represent useful piece of physicochemical information, but in isolation they have limited value.

There have been a number of methods employed for Ka, and pKa measurements based on solubility and potentiometric titration [12, 13]. When pKa is measured as a function of pH the characteristic sigmoid curve from which the pKa will be determined by locating the inflection point. It is true that pKa is universally referred as constant, but it is not truly constant because it depends on temperature, ionic strength (I), and solvent dielectric constant (ε) [14, 15, 16].

The study of the relationship between apparent dissociation constants of phosphoric acid with ionic strength of solution is one of the most neglected physical factors which influence biochemical processes [17]. In addition, ionic strength of solution can affect the equilibrium states of weak acids in solution, which is of great importance in chemical analysis [18, 19]. An aqueous solution consisting a mixture of a weak acid and its conjugate base or vice-versa is called buffer solution (pH buffer, hydrogen ion buffer). Its pH changes very little when a small or moderate amount of

strong acid or base is added to it, is used to prevent changes in the pH of the solution.

Buffer capacity ( $\beta$ ), is a quantitative measure of the resistance of buffer solution to pH change or addition of hydroxide ion. In other words, buffer capacity depends on the amounts of substance of weak acid and its conjugate base in the buffer. It is in fact, directly related to the first derivative of the buffer titration curve or refers to the slope of the titration curve. Buffer capacity can be defined as:

$$\beta = \frac{dn}{d(p[H^+])}$$

where  $dn$  is infinitesimal amount of added base and  $d(p[H^+])$  is the resulting infinitesimal change in the co-logarithm of the hydrogen ion concentration. Thus, controlling the pH value within the optimal pH range is one of the most important task in ensuring buffer capacity [20, 21]. Having such definition in mind the buffer capacity of a weak acid with dissociation constant Ka can as well be expressed as:

$$\frac{dn}{d(p[H^+])} = 2.303 \left( \frac{C_A K_a [H^+]}{K_a + (H^+)^2} \right)$$

where  $C_A$  is the analytical concentration of the acid [22, 23]. The pH is defined as  $-\log [H_3O^+]$ . The buffer capacity of a buffering agent is at a local maximum when  $p[H^+] = pKa$ . It can go up to 33% of the maximum value at  $p[H^+] = pKa \pm 1$  and to 10% at  $p[H^+] = pKa \pm 1.5$ . This is the reason why the useful range is approximately  $pKa \pm 1$ . Buffer capacity, therefore is proportional to the concentration of the buffering agent,  $C_A$ , so dilutions have little buffer capacity.

It is well established that hydrofluoric acid in aqueous media is a weak acid; this aspect in dilute solution is due to the existing high H-F bond strength, which combines with the high dissociation enthalpy of HF of which outweigh the more negative of hydration of the fluoride ion [24].

It is true that numerous  $K_a$  values of HF have been reported in the past, [25] however, values of its equilibrium constant at a total ionic strength above 1.0 over the temperature range 25-55 °C are not available. The inadequacy of such information (apparent and thermodynamic constants for phosphate and HF) at high ionic strength as well as phosphate buffer capacities acted as a driving force in the present study given the importance of these parameters.

### Materials and Methods

#### A pH scale Suitable for Reporting pH in High Electrolyte Media

In ordinary procedures, the pH-meter electrode was first calibrated against a buffer supplied by the manufacturer, and then the meter reading obtained with the target solution is the pH of that sample. This simple technique was applied to either actual brines or synthetically re-constituted lake-like equivalents (using usually NaOH or NaNO<sub>3</sub> or a recipe to attain the required ionic strength of the test brine) as a check/comparison.

**The Artificial Reconstituted** lake brines at various ionic strengths were made up by diluting calculated volumes of standardized electrolyte solutions (NaOH and NaNO<sub>3</sub>) with CO<sub>2</sub>-free distilled water in a 250 mL volumetric flask. The following stock solutions were made. Sodium nitrate stock solution of 6.00 M was prepared by dissolving 255 g of analytical grade sodium nitrate in 500 mL volumetric flask using distilled water and then made up to the mark with distilled water. Similarly, NaOH stock solution 0.10 M was prepared by dissolving 2.00 g analytical grade NaOH in 500 mL volumetric flask and made up to the mark with distilled water. This was standardized against standard 0.10 M HCl using phenolphthalein as indicator. The concentrations of standard sodium hydroxide (10<sup>-2</sup>, 10<sup>-3</sup>, 10<sup>-4</sup>, and 10<sup>-5</sup> M) were obtained from appropriate dilution of the stock solution.

The ionic strength for brine was evaluated by analysis of all cations and anions. The target lakes were alkaline (pH ≥ 10 due to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>). The pH scale for each I value (I = 0.5 ∑ C<sub>i</sub> Z<sub>i</sub><sup>2</sup>) was developed by re-constituting a synthetic brine (as explained above) which included of [NaOH] = (i) 10<sup>-1</sup> M (pH = 13); (ii) 10<sup>-2</sup> M (pH = 12); (iii) 10<sup>-3</sup> M (pH = 11) and (iv) 10<sup>-4</sup> M (pH = 10). For a given brine, a linear plot of pH vs log [NaOH] was obtained for pH measurement for test samples of that ionic strength.

#### Phosphate Buffer Capacities Evaluation

From basic definition buffer capacity is the number of moles of a strong base for example NaOH that must be added to one litre of the solution to raise its pH by one unit [ 26], then this parameter was evaluated directly from the potentiometric curves. This was carried out from the potentiometric curve for synthetic brines at different ionic strengths. The curve of each graph was subdivided into three portions as it will be seen in the results part (Figure 1.0). Each point located on the curve was joined to its adjacent points (two) at the lower and the upper part to obtain a new curve. Each curve obtained had its respective general equation  $y = mx + c$  the slope was noted and substituted into phosphate buffer capacity general equation below:

$$\text{Phosphate buffer capacity } \beta = \frac{1}{\text{slope}} \times \frac{1}{V}$$

where V stands for volume at point of inflection

These buffering capacities were plotted against ionic strength giving the trend of which will be seen later.

#### Measurement of pKa's for Phosphate

Phosphoric acid is a triprotic acid which can undergo three stepwise dissociations [27, 28], but the third ionization constant pKa<sub>3</sub> is not discernible in water due to its closeness to pK<sub>w</sub> (ionic product for water) while a minimum separation requirement of 10<sup>5</sup> to 10<sup>6</sup> between equivalence points is the conditionality for identification.

Thus,

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

For the hydrolysis of PO<sub>4</sub><sup>3-</sup> :

$$K_{hy} = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]}$$

multiplying by  $\frac{[H_3O^+]}{[H_3O^+]} = 1$  :

$$K_{hy} = \frac{[HPO_4^{2-}][OH^-][H_3O^+]}{[PO_4^{3-}][H_3O^+]} = \frac{K_w}{K_{a3}}$$

Thus: pK<sub>hy</sub> + pKa<sub>3</sub> = pK<sub>w</sub> = 14.

Since pK<sub>hy</sub> = 1.33 at 25 °C [29], then pKa<sub>3</sub> = 12.67. This is relatively close enough to pK<sub>w</sub> = 14 and alternative techniques (e.g. use of alternative non-aqueous solvents or thermodynamic derivations) for its evaluation are needed [27].

A model of the phosphate equilibria was re-constituted in the laboratory at the same ionic strength as the actual concentrated Salt Lake brine of the target lake. This was intending to minimize the influence of chemical (ammonium salts, dissolved gases and organic matter or suspension) effects which may be out of control and produce reproducible information for brines of such high ionic strength [30, 31]. The experimental details for synthetic brine: Due to the fact that the target Rift Valley Lake Eyasi found in Tanzania East Africa has a maximum of I = 11.32 this was not possible to be reconstituted in the laboratory only solutions with up to I = 7.5 were reconstituted. The latter was obtained by mixing up NaCl and NaNO<sub>3</sub> salts at different ratios, which depend on the required ionic strength. The synthetic solutions were prepared using ionic strength equation hereunder [32]:

$$I = 0.5 \sum C_i Z_i^2$$

where C<sub>i</sub> stands for molar concentration of the ion in mole. dm<sup>-3</sup>.

Z<sub>i</sub> stands for charge on the ion.

I stand for ionic strength of solution and it is a dimensionless quantity.

The summation (∑) extends over the ions in the solution.

A worked example of I = 6 represents how the rest (6.5, 6.8, 7.3 and 7.5) ionic strengths were prepared.

#### Salt Lake electrolyte at 0.101 M H<sub>3</sub>PO<sub>4</sub> phosphoric acid

A volume of 50 mL of standardized 1.010 M phosphoric acid was transferred into a 500 mL volumetric flask (0.101 M H<sub>3</sub>PO<sub>4</sub>). Weights of 127.50 g of sodium nitrate (3.00 M NaNO<sub>3</sub>) and 69.99 g of NaCl (2.39 M NaCl) were added into the flask. The volume was made up to about 450 mL with distilled water and shaken well to allow the solid to dissolve. Then the volume was made up to the mark with distilled water and tightly closed with a stopper. The ionic strength was computed as follows:

$$I = 0.5 \sum C_i Z_i^2$$

where: I, C<sub>i</sub> and Z<sub>i</sub> carry usual meaning as above

$$C(H_3PO_4) = 0.101 \text{ M}; Z(H^+) = 1 \text{ and } Z(PO_4^{3-}) = 3$$

$C(\text{NaNO}_3) = 3.00 \text{ M}$ ;  $Z(\text{Na}^+) = 1$  and  $Z(\text{NO}_3^-) = 1$

$C(\text{NaCl}) = 2.39 \text{ M}$ ;  $Z(\text{Na}^+) = 1$  and  $Z(\text{Cl}^-) = 1$

$$I = 0.5 \sum \{(0.101 \times 1^2 \times 3) + (0.101 \times 3^2) + (3 \times 1^2) + (3 \times 1^2) + (2.39 \times 1^2) + (2.39 \times 1^2)\}$$

$$I = 0.5 \sum \{1.21 + 6 + 4.78\}$$

$$I = 6.00$$

The compound ionic strength of this electrolyte is 6.0 and molarity of phosphoric acid is 0.101 M. Also Salt Lake electrolyte at 0.101 M sodium hydroxide was as well prepared in the same way as phosphoric acid.

### Experimental Procedure

A 50 mL of synthetic 0.101 M phosphoric acid solution at a given ionic strength was transferred into a 400 mL beaker provisioned with a Teflon protected stirring magnet. The electrode of the calibrated pH meter was immersed into the solution. The solution was stirred for about twenty minutes and the pH reading was noted. This solution was titrated with synthetic 0.101 M sodium hydroxide of the same ionic strength and molarity from the burette. Both the burette and pH readings were recorded after each addition of sodium hydroxide solution. The titration continued just above pH 11 though it was difficult to go up to pH 12 because  $K_{a3}$  of phosphoric acid is very close to  $K_w$  of water. A titration curve of pH against volume of NaOH was then constructed.

### Evaluation of $K_a$ for Hydrofluoric Acid

The dissociation constant of hydrofluoric acid is determined through direct measurements of concentrations of free fluoride ions by lanthanum fluoride membrane electrode which is permeable only to fluoride ions [33, 34].

Through measurement of fluoride electrode potential and  $[\text{H}^+]$ , the  $K_a$  of hydrofluoric acid is calculated at different ionic strengths and extrapolation of the linear curve is made up to infinite dilution when ( $I = 0$ ). Thus, the thermodynamic dissociation constant for HF at room temperature is obtained. The determination was done in aqueous solutions of varying ionic strengths (6.0, 6.5, 6.8, 7.3 and 7.5) with sodium nitrate as a supplementary electrolyte. In this case Vanderborgh method was used to measure  $K_a$  of HF as a function of ionic strength [33, 34]. This was obtained from the following general equation;

$$\frac{E_{FT} - E_F}{S} = \log Ka + pH$$

where:  $E_{FT}$  stands for measured potential in absence of  $[\text{H}^+]$ ,  $E_F$  stands for measured potential as a function of pH

$\frac{E_{FT} - E_F}{S}$  against pH should yield a linear relationship of slope = 1.00 with intercept  $\log Ka$ .

### Experimental Procedure

The stock solution of 1.01 M NaF was prepared by weighing reagent grade NaF after drying at 120 °C for 24 hours. A 10 mL volume of NaF stock solution was transferred by pipette into a 100 mL volumetric flask, then topped to the mark with distilled water, this contains  $10^{-1}$  M NaF. From this solution 10 mL was pipette and transferred into another 100 mL volumetric flask, and then topped up with distilled water to the mark, this contains  $10^{-2}$  M NaF. The rest of the standard HF concentrations were prepared in this sequence up to  $10^{-5}$  M NaF.

Hereunder there is an example of how a mixture of sodium nitrate and nitric acid for a specified ionic strength was prepared.

### How to prepare a mixture of $I = 7.5$

From the stock solutions of sodium nitrate 7.80 M and 1.00 M  $\text{HNO}_3$ , a mixture of  $I = 7.5$  of varying  $\text{NaNO}_3$  and  $\text{HNO}_3$  was prepared and then topped up to the mark with

distilled water. *Dilution law* was used to obtain the volume of  $\text{NaNO}_3$  which was required to prepare  $I = 7.5$  in 100 mL volumetric flask.

$$M_1 V_1 = M_2 V_2$$

where:  $M_1$  stands for molarity of stock solution  $\text{NaNO}_3$

$V_1$  stands for volume of  $\text{NaNO}_3$  stock solution to be used

$M_2$  stands for molarity of  $\text{NaNO}_3$  to be prepared which is 7.5

$V_2$  stands for volume of flask to be used which is 100 mL

$$\frac{M_2 V_2}{M_1} = V_1$$

$$\frac{7.5 \times 100}{7.80} = V_1$$

$$V_1 = 96.15 \text{ mL}$$

The volume of 96.15 mL  $\text{NaNO}_3$  was required to prepare a solution of  $I = 7.5$  from stock solution of 7.80 M in 100 mL volumetric flask.

### Preparation of 0.01 M $\text{HNO}_3$

A 1 mL of 1.00 M  $\text{HNO}_3$  was transferred into a 100 mL volumetric flask. In terms of ionic strength  $\text{HNO}_3$  has contributed  $I = 0.01$ . The difference is  $7.5 - 0.01 = 7.49$  which is contributed by  $\text{NaNO}_3$ . Since  $V_1 = 96.15$  mL of  $\text{NaNO}_3$  is required to prepare  $I = 7.5$  then, this difference requires;

$$\frac{96.15 \times 7.49}{7.50} = \text{Volume}$$

$$\text{Volume} = 96.02 \text{ mL NaNO}_3$$

Hence 96.02 mL of 7.80 M  $\text{NaNO}_3$  and 1 mL of 1.00 M  $\text{HNO}_3$  were transferred into 100 mL volumetric flask. This was made up to the mark with distilled water. The ionic strength of this solution is 7.5 and the rest ionic strengths were prepared following same procedure.

### Experimental Procedures

#### Procedure 1

A calibration curve for standard fluoride solution to check the Nernstian response of the electrode was run as follows:

From a stock solution of fluoride, different fluoride concentrations, ranging between  $10^{-1}$  and  $10^{-5}$  M at the ionic strengths 6.0, 6.5, 6.8, 7.3 and 7.5 each ionic strength was prepared in 100 mL volumetric flasks. A 50 mL of the test solution was pipette and transferred into a 100 mL plastic beaker fitted with a Teflon protected stirrer. The electrodes were immersed into the solution i.e., fluoride and reference electrode. The solution was then stirred for fifteen minutes and the potential in mV noted. A plot of  $E_F$  against  $\log [F]$  was made and linear plot was obtained at a given ionic strength. This was done for five samples and a slope  $S$  established at a given ionic strength which was used in the next stage.

#### Procedure 2

From the mixture of  $\text{HNO}_3$  and  $\text{NaNO}_3$ , potential measurements were made in the series of solutions. Each series was of constant ionic strength mixtures of sodium nitrate and nitric acid. A 20 mL of each test solution was mixed with 20 mL of 0.001 M NaF into a 100 mL plastic beaker fitted with a Teflon protected stirrer. The electrodes were immersed into the whole mixture and stirred for about fifteen minutes. When a steady state was reached the pH, potential  $E_F$  and room temperature were noted. From this general equation

$$\frac{E_{FT} - E_F}{S} = \log Ka + pH$$

a plot of  $(E_{FT} - E_F)/S$  against pH was constructed. From the latter values of  $-\log Ka$  were

determined at different ionic strength and plotted against the square root of ionic strength ( $\sqrt{I}$ ) and a linear plot was obtained.

**Results and Discussion**

The apparent dissociation constants of phosphoric acid in both sea water and hypersaline lake brines are important for studies of the formation and solubility of apatites and phosphorites [35]. These constants are also necessary for the studies of uptake of phosphate during bio-uptake, metabolic pathways in plants and animals [6, 7, 36]. In physicochemical studies, these constants can provide information on ionic interactions of phosphate in both sea and hypersaline lake brines. The pKa values are used to compare the strength of acids; the higher the pKa of an acid the weaker is the acid. The pKas were evaluated from potentiometric curve for synthetic brines at a selected ionic strength value for example, Figure 1.0. Each point located on the curve was joined to its adjacent points (two) at the lower and the upper part to obtain a new curve Figure 2.0. Each curve obtained had its respective general equation  $y = mx + c$  Figure 3.0 the slope was noted and substituted into phosphate buffer capacity general equation below:

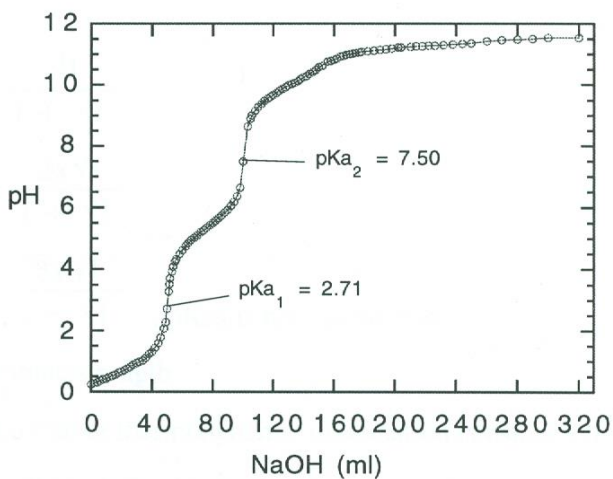
$$\text{Phosphate buffer capacity } \beta = \frac{1}{\text{slope}} \times \frac{1}{V}$$

The examination of apparent dissociation constants for phosphate in the target lake has shown both pKa<sub>1</sub> and pKa<sub>2</sub> to decrease with increasing ionic strength (Table 1.0). In fact similar decrease in apparent dissociation constants has been revealed by the rise in salinity of sea water Table 2.0 [37].

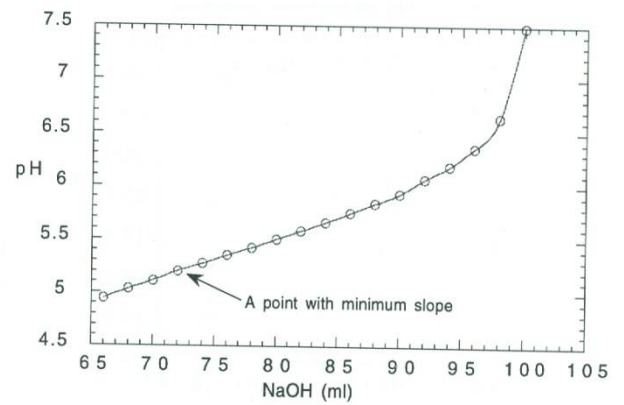
**Table 1.0. Apparent Phosphate Equilibria Parameters Obtained Graphically**

Ionic Strength	6.0	6.5	6.8	7.3	7.5
pKa <sub>1</sub>	3.66	3.49	3.40	3.01	2.71
pKa <sub>2</sub>	8.24	8.15	7.98	7.73	7.50
pKa <sub>3</sub>	n.d	n.d	n.d	n.d	n.d
pKa <sub>1</sub>	3.24 x 10 <sup>-4</sup>	3.24 x 10 <sup>-4</sup>	3.98 x 10 <sup>-4</sup>	9.77 x 10 <sup>-4</sup>	1.95 x 10 <sup>-3</sup>
pKa <sub>2</sub>	5.75 x 10 <sup>-9</sup>	7.08 x 10 <sup>-9</sup>	1.05 x 10 <sup>-8</sup>	1.86 x 10 <sup>-8</sup>	3.16 x 10 <sup>-8</sup>
pKa <sub>3</sub>	n.d	n.d	n.d	n.d	n.d

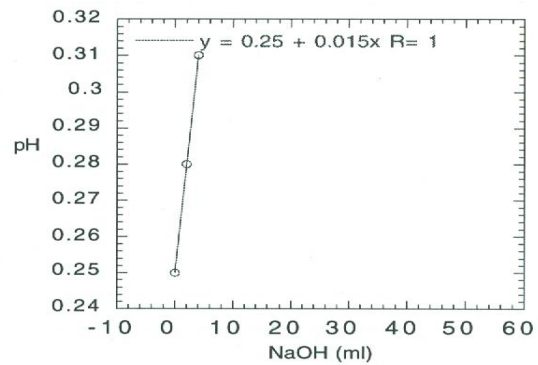
n.d stands for not determined



**Figure 1.0. Potentiometric Curve for Synthetic Lake Brines at Selected Ionic Strength Value Showing Parameters for Evaluation of Phosphate pKa Values for I = 7.5.**



**Figure 2.0. A Plot of pH Against Volume of Synthetic Sodium Hydroxide from a Portion of Figure 1.0 at 2<sup>nd</sup> Inflection Point.**



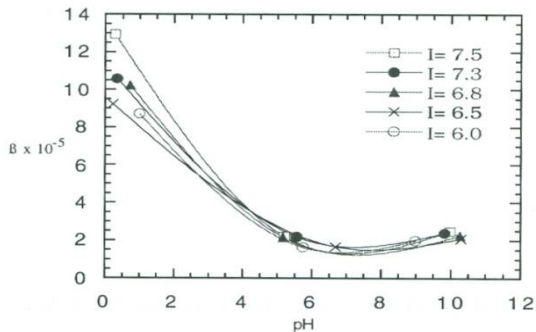
**Figure 3.0. A Plot of pH Against Volume of Synthetic Sodium Hydroxide from a Portion of Figure 1.0 for I = 7.5.**

**Table 2.0. Apparent Dissociation Constants for Phosphoric Acid in Seawater at 25 °C [37].**

Salinity	30%	33%	36%
pKa <sub>1</sub>	1.63	1.60	1.62
pKa <sub>2</sub>	6.13	6.10	6.03
pKa <sub>3</sub>	8.75	8.60	8.55
Ka <sub>1</sub>	2.36 x 10 <sup>-2</sup>	2.52 x 10 <sup>-2</sup>	2.37 x 10 <sup>-2</sup>
Ka <sub>2</sub>	7.40 x 10 <sup>-7</sup>	7.90 x 10 <sup>-7</sup>	9.30 x 10 <sup>-7</sup>
Ka <sub>3</sub>	1.79 x 10 <sup>-9</sup>	2.50 x 10 <sup>-9</sup>	2.80 x 10 <sup>-9</sup>

On the other hand high ionic strength electrolytes have revealed numerically large phosphate buffer capacity values (Table 3.0). This implies that the high ionic strength solution is essentially a good buffer [38]. Thus, there can be no doubt that the composition of high ionic strengths medium influences the buffer capacity of phosphate system since the experimental equilibrium constants (apparent) are observed to alter when the medium changes (Table 1.0). The data on buffer capacities of artificial lake brines suggest that the target lake possesses high phosphate buffer capacity. The phosphate buffer capacity values of an artificially reconstituted lake brine are between 30 and 300 times more than that of water which is 4.6 x 10<sup>-7</sup> mole.dm<sup>-3</sup> [39, 40] and for typical salinities in the Rift Valley Lake Eyasi, the magnitudes exceed this value by about 36-1000 times. Such high buffering capacity which is extremely chemically aggressive aquatic environment and with high pH are critical factors for life forms in the salt lakes, and therefore the capacity of the brine to resist sudden drastic pH alterations maximizes the tolerance of such life forms to this environment. A good buffering capacity is essential in such system so as to sustain processes therein which operate within strict pH tolerances for most of the resident biological life forms.

The buffer capacity  $\beta$  values for each plot (Table 3.0) are maximum at a point just before first inflection, small at a point before the second inflection and a bit large before the third inflection, but not more than the value obtained before the first inflection. The  $\beta$  values are maximum at low pH, decrease gradually as pH raises and at a certain pH value the  $\beta$  values start raising depending on the ionic strength of the solution see Figure 4.0.



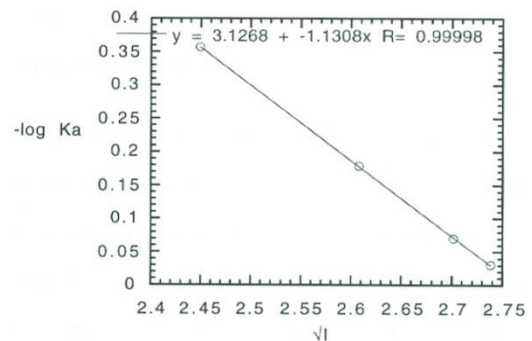
**Figure 4.0. A plot of Buffer Capacity Against pH**

It is well known that hydrofluoric acid in aqueous media is a weak acid [24], this has triggered the study on both apparent and thermodynamic dissociation constants for HF at different ionic strengths of like-like environments. This has revealed the relationship between dissociation constants of HF and ionic strength. In this work the Vanderborgh approach has been expanded to work with high ionic strength concentrations. The apparent dissociation constants obtained at varying ionic strengths facilitate the basis for estimation of the thermodynamic constant  $K_a$  for HF system.

The experimental results presented in Table 4.0 indicate that the apparent dissociation constants increase with the

increasing ionic strength. When a plot of  $\log K_a$  against square root of ionic strength in Figure 5.0 is extrapolated to infinite dilution ( $I = 0$ ) at room temperature, the intercept of the line gives a value of  $-\log K_a = 3.127$ ; this corresponds to the thermodynamic value  $K_a = 7.46 \times 10^{-4} \text{ mol.dm}^{-3}$ . The thermodynamic constants for HF at infinite dilution have been determined by different workers [34, 41, 42, 43].

While Vanderborgh worked in the ionic strength values ranging between 0.05 to 0.50, Qulwi, worked in a range between 0.266 and 1.42 and this work presents the results for ionic strength values between 6.0 and 7.5 at room temperature. The thermodynamic value obtained by this work, however, is in good agreement with those reported by other research groups Table 4.0. The significant variations in both thermodynamic and apparent dissociation constants in Table 4.0 are due to a number of limiting factors which give rise to errors in the measurements.



**Figure 5.0. A plot of  $-\log K_a$  against  $\sqrt{I}$  for Fluoride Equilibria at 25 °C.**

**Table 3.0. Different Values Used for Evaluation of Buffer Capacity at Points of Minimum Gradients**

Ionic Strength	Inflection points	pH at point of inflection	Volume V at point of inflection in mL	Slope at point of inflection	$\beta$ (mole.dm <sup>-3</sup> ) x 10 <sup>-5</sup>
6.0	1 <sup>st</sup>	0.99	8 + 50	0.020	8.106
	2 <sup>nd</sup>	5.74	78 + 50	0.048	1.644
	3 <sup>rd</sup>	8.98	100 + 50	0.032	2.104
6.5	1 <sup>st</sup>	0.23	2 + 50	0.021	9.249
	2 <sup>nd</sup>	6.68	78 + 50	0.047	1.679
	3 <sup>rd</sup>	10.29	100 + 50	0.032	2.104
6.8	1 <sup>st</sup>	0.72	8 + 50	0.017	10.243
	2 <sup>nd</sup>	5.16	66 + 50	0.040	2.177
	3 <sup>rd</sup>	10.26	136 + 50	0.024	2.262
7.3	1 <sup>st</sup>	0.34	3 + 50	0.018	10.587
	2 <sup>nd</sup>	5.56	82 + 50	0.035	2.186
	3 <sup>rd</sup>	9.82	126 + 50	0.024	2.391
7.5	1 <sup>st</sup>	0.28	2 + 50	0.015	12.949
	2 <sup>nd</sup>	5.20	72 + 50	0.038	2.208
	3 <sup>rd</sup>	9.98	130 + 50	0.023	2.494

**Table 4.0. Apparent and Thermodynamic (pKa and Ka) of HF Values**

	Ionic strength	pKa	Ka	References
<b>Apparent</b>	0.226	3.96	$1.10 \times 10^{-3}$	41
"	1.02	2.82	$1.15 \times 10^{-3}$	"
"	1.49	2.74	$1.82 \times 10^{-3}$	"
"	6.00	0.36	0.44	This work
"	6.50	0.22	0.60	"
"	6.80	0.18	0.66	"
"	7.30	0.07	0.85	"
"	7.50	0.03	0.93	"
<b>Thermodynamic</b>	0.00	3.13	$7.46 \times 10^{-4}$	"
	0.00	3.15	$7.07 \times 10^{-4}$	41
	0.00	3.19	$6.46 \times 10^{-4}$	34
	0.00	3.16	$6.85 \times 10^{-4}$	42
	0.00	3.17	$6.71 \times 10^{-4}$	44
	0.00	3.13	$7.40 \times 10^{-4}$	43

## Conclusions

The study of apparent dissociation constants for phosphate in the target lake brines has shown that both  $pK_{a1}$  and  $pK_{a2}$  decrease as ionic strength of the solution increases. This has been also revealed by the rise in salinity of sea water [37]. The phosphate buffer capacity rises proportionally with ionic strength of the lake brines. Therefore, the target lake being highly concentrated system should possess high buffer capacity. This was revealed by an example of phosphate buffer capacity at  $I = 7.5$  which is up to 300 times that of pure water ( $4.6 \times 10^{-7}$  mol.dm<sup>-3</sup>). For typical salinities in the Rift Valley Lake Eyasi Salt Lake, the magnitudes of buffer capacity exceed this value by about 36-1000 times.

A good buffering capacity is essential in such systems so as to sustain processes therein which operate within strict pH tolerances particularly for most biological forms. It is important to be aware that extreme hypersaline aqueous environment harboring limited phylogenetic diversity provide tractable model ecosystems to confront both physical and biological challenges faced by living organisms and entire communities [45,46, 47]. The thermodynamic dissociation constant ( $K_a$ ) for HF =  $7.46 \times 10^{-4}$  mole.dm<sup>-3</sup> obtained in this study is in good agreement with the value of  $K_a = 3.55 \times 10^{-4}$  mole.dm<sup>-3</sup> reported in the literature together with those values obtained by other research groups in Table 4.0. The observed variation in the thermodynamics constants  $K_a$  for HF value obtained in this work ( $7.07 \times 10^{-4}$ ) compared to the value obtained by other workers, may be due to higher ionic strength of the solution used in evaluation of apparent  $K_a$  values.

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## References

- [1]. H.Li, F. Liu, L. Kang, and M. Zheng, Study on Buffer Capacity of Wort, *Journal of the Institute of Brewing*, Vol. 122 no.1, pp138-142, 2016.
- [2]. L.Reijenga, A. Vanitoof, A. Van Loon, and B. Teunissen, "Development of Methods for the Determination of  $pK_a$  Values," *Anal. Chem. Insight*, Vol. 8, pp 53-71, 2013.
- [3]. S. Babic, M. J. Alka, and K. M. Macan, Determination of  $pK_a$  Values of Active Pharmaceutical Ingredients, Vol. 26, pp 1043-1061, 2007.
- [4]. J Ho, Predicting  $pK_a$  Implicit Solvents: Current Status and Future Direction, *Australia Journal of Chemistry*, Vol. 67, no.10, pp 1441-1460, 2014.
- [5]. J.Ho, M. L. Coote,  $pK_a$  Calculation of Some Biological Important Carbon Acid-An-Assessment of Contemporary Theoretical Procedure, *J. Chem. Theory and Computation*, 5 no. 2, pp 295-306, 2009.
- [6]. R.C. I. Holford, Soil Phosphorus: Its Measurement and its Uptake by Plant. *Aust. J. Soil. Res.*, Vol. 35, 227-239, 1997.
- [7]. A.Kuhl, *Inorganic Phosphate Uptake and Metabolism*, Academic Press New York, 1962.
- [8]. H.E. Kerns, L. Di, *Physicochemical Profiling: Overview of the Screens. Drug Discov Today: Technologies*, 1, pp 343-348, 2004.
- [9]. H.Wan, and J. Ulander, High-throuput  $pK_a$  Screening and Prediction Amenable for ADME Profiling. *Expert Opinion. Drug Metab. Toxicol.*, 2, pp 139-155, 2006.

- [10]. C.Zhou, Y. Jin, J.R. Kenseth, and K.R. Wehmeyer, Rapid  $pK_a$  Estimation Using Vacuum-assisted Multiplexed Capillary Electrophoresis (VMCE) with Ultraviolet Detection, 94, 576-589, 2005.
- [11]. S.Podell, J B. Emerson, G.M. Jones, J.A. Ugalde, S. Welch, K. B. Heidelberg, J. F. Banfield, and E. E. Allen, Seasonal Fluctuations in Ionic Concentrations Drive Microbial Succession in a Hypersaline Lake Community, *Multidisciplinary Journal of Microbial Ecology*, 8, pp 979-990, 2014.
- [12]. A. Albert, and P.E. Sarjeant, *The Determination of Ionization Constants* 3<sup>rd</sup> ed. Chapman and Hall, New York, 1984.
- [13]. A. Avdeef, A E J. Corner, and J.S. Thomson, pH Metric log P. 3. "Glass Electrode Calibration in Methanol-Water, Applied  $pK_a$  Determination of Water Insoluble Substances." *Anal. Chem.*, Vol. 65, 42-49, 1993.
- [14]. M.F. Everaerts, L.J. Beckers, and M. E P. T. Verheggen, *Isotacophores, Theory, Instrumentation and Applications*. Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [15]. B. K. Monzy, and L. A. Crumbliss, "Acid Dissociation Constants ( $K_a$ ) and Their Temperature Dependencies ( $\Delta H_a$ ,  $\Delta S_a$ ) for a Series of Carbon and Nitrogen Substituted Hydroxamic Acids in Aqueous Solution," *J. Org. Chem.*, Vol. 45, pp 4670-4675, 1980.
- [16]. K.Sarmini, and E.Kennler, Capillary Zone Electrophoresis in Mixed Aqueous- Organic Media: Effect of Organic Solvent on Actual Ionic Mobility Acidity Constants and Separation Selectivity of Substituted Aromatic Acids . I. Methanol, *J. Chromatogr. A*. Vol. 805, pp 325-335, 1998.
- [17]. S.J.Khouri, Titrimetric Study of The Solubility and Dissociation of Benzoic acid in Water: Effect of Ionic Strength and Temperature, *Am. J. Anal. Chem.* Vol. 6, pp 429-436, 2015.
- [18]. J.A. Smetana, and I. A. Popov, On the Influence of Ionic Strength on Equilibrium Constant of Ion-Molecule Reaction, *Journal of Chemical Thermodynamics*, Vol. 11, pp 1145-1149, 1979.
- [19]. M. K. Tawarah, and J. S. Khouri, Determination of the Stability and Stoichiometry of p-Methyl Red Inclusion Complexes with  $\gamma$ -Cyclodextrin Dyes and Pigments, Vol. 45, p 229-233, 2000.
- [20]. E.D. Briggs, A.P. Brookes, R. Stevens, A.C. Boulton, *Brewing Science and Practice*, Elsevier London, 2004.
- [21]. G.D. Taylor, The importance of pH Control During Brewing, *Tech. Q. Master. Brew. ASSC. Am.*, Vol. 27, pp 131-136, 1990.
- [22]. N. J. Butler, *Ionic Equilibrium: A Mathematical Approach*, Addison-Wesley, 1964.
- [23]. R. Scorpio, *Fundamentals of Acids, Bases, Buffers and Their Application to Biochemical Systems*, Kendall Hunt Publishing Co., 2000.
- [24]. C.E.Housecroft, and A.G.Sharpe, "Inorganic Chemistry." Pearson Prentice Hall, 2<sup>nd</sup> ed, 2005.
- [25]. C.E. Connick, and M.S.Tsao, "Complexing of Magnesium Ion by Fluoride Ion," *J. Am. Chem. Soc.*, Vol. 76, pp 5311-5314, 1954.
- [26]. I. M. Kolthoff, *Treatise on Analytical Chemistry*, Vol. 1, John Wiley and Sons, Inc., New York, 1965.
- [27]. D. Cooper, and C. Doran, "Classical Methods," John Wiley and Sons, New York, 1987.
- [28]. P.A. Kreshkov, and A.A. Yaroslavtsev, "Course of Analytical Chemistry," Vol. 2, Mir Publishers, Russia, 1977.

- [29]. A.Freiser, and Q.Fernando, *Ionic Equilibria in Analytical Chemistry*; Wiley-Interscience, 1963.
- [30]. J. Barbara, *Hypersaline Environment*, Springer-Verlag, New York, 1989.
- [31]. P. . Curtis, and H. E. Adams, "Dissolved Organic Matter Quantity and Quality from Freshwater and Salt Lakes in East-Central Alberta," *Biogeochemistry*, Vol. 30, pp 59-76, 1995.
- [32]. W.P.Atkins, "Physical Chemistry 3<sup>rd</sup>," Oxford University, Oxford, 1986.
- [33]. J.J. Lingane, "A Study of the Lanthanum Fluoride Membrane Electrode for End Point Detection in Titration of Fluoride with Thorium, Lanthanum, and Calcium," *J. Anal. Chem.*, Vol. 39, pp 881-889, 1967.
- [34]. N.E. Vanderborgh, Evaluation of the Lanthanum Fluoride Membrane Electrode Response in Acidic Solutions. *Talanta*, Vol. 15, pp 1009-1013, 1986.
- [35]. S.R. Dietz, K. O. Emery, and F. P. Shepard, Phosphate Deposits on the Sea Flow off Southern California," *Bull. Geol. Soc.*, Vol. 53, pp 815-847, 1942.
- [36]. M.Shiruan, H. Shariatmadavi, and M. Kalbasi, Phosphorus Buffering Capacity Indices as Related to Soil Properties and Plant Uptake, Vol. 28, pp 537-550, 2007.
- [37]. R.D. Kester, Thesis; In Horne, R. A. "Marine Chemistry," Wiley-Interscience, New York, 1969.
- [38]. L. Such, "Solution Equilibria in Analytical Chemistry," Van Nosrand Reinhold Co., London, 1972.
- [39]. R.Weast, *CRC Handbook of Chemistry and Physics*. 52<sup>nd</sup> ed., CRC Press, (1978/79).
- [40]. W.M. Haynes, *CRC Handbook of Chemistry and Physics* 92<sup>nd</sup> ed., CRC Press, 2011.
- [41]. Q. Qulwi, A Study of the Hydrochemistry of Brines and Associated Inflows of Lake Manyara Tanzania M.Sc. Thesis, University of Dar es salaam, 1995.
- [42]. E.Baumann, Determination of Stability Constants of Hydrogen and Aluminium Fluorides with a Fluoride-selective Electrode. *Journal of Inorganic and Nuclear Chemistry*, Vol. 31, pp 3155-3162, 1969.
- [43]. J.Anthony and J. Hudleston, "The Freezing Points of Hydrofluoric Acid," *J. Chem. Soc.* Vol. 127, 1122-1128, 1925.
- [44]. H.H. Broene and T. De Vries, The Thermodynamics of Aqueous Hydrofluoric Acid Solutions. *Journal of the American Chemical Society*, Vol. 69, pp 1644-1646, 1947.
- [45]. C.Demergasso, L.Escudero, O. L. Casmayor, G. Chong, V. Balague, C. Pedrós-Alió, Novelty and Spatio-temporal Heterogeneity in the Bacterial Diversity of Hypersaline Lake Tebenquiche (Solar de Atacama) *Extremophiles*, Vol. 12, pp 491-504, 2008.
- [46].I.Bodaker, I.Sharon, T.M. Suzuki, R.Feingersch, M. Shmoish, E.Andreishchev, Comparative Community Genomics in the Dead Sea: An Increasingly Extreme Environment, *Isme, J.*, Vol.4, pp 399-407, 2009.
- [47]. A.Oren, Life of High Salt Concentrations in Rosenberg E(ed). *The Prokaryotes-Prokaryotic Communities and Ecophysiology* 4<sup>th</sup> ed., Springer Varlag: Berlin Heidelberg, 2013.