International Journal of Research in Chemistry and Environment

Available online at: www.ijrce.org

IJRCE

ISSN 2248-9649

Research Paper

Determination of Base Dissociation Constants (Pk$_b$) of Mono- and Polyamines by pH Metric Method

Mamshad Ahmad[1*], Asha Masohan[2], S.S. Sawhney[1]

[1]Department of chemistry, Uttaranchal College of Science & Technology and Uttarakhand Technical University, Dehradun, INDIA

[2]Department of gas separation, Indian Institute of Petroleum, Dehradun, INDIA

(Received 07th July 2019, Accepted 30th July 2019)

Abstract: *Dissociation constants of acids and bases (pK_a and pK_b) are very important criteria to define the strength of acids or bases. In organic chemistry acids generally the compounds that contain –COOH group and bases are amines and their derivatives. This paper presents the study of pK_b of about 20 organic amines. pK_b determination is done pH metrically which is a very simple method for this type of study. pK_b of some of the reported amines are already determined by various researcher by using different methods. Most of the amines reported in this paper are studied fist time for pK_b study. It is found that those amines which are studied for pK_b value and available in the literature, give almost same result with presented corresponding values. Some of the amines (bases) are common but most of the amines are uncommon and they are used for a very specific purpose. pK_a value is used in many cases to solve connecting problems. These pK_b values can be used for research and other purposes. This paper presents the pK_a/pK_b determination of mono-(one amino group), di-(two amino group), tri-(three amino group) and tetra (four amino groups) amines, which will be a very good work for others for research purposes.*

Keywords: Organic bases, Amines, pK_a, pK_b, pK_a determination, pH metric method.

Introduction

An acid dissociation constant, K_a, is a measure of the strength of an acid in solution quantitatively. It is the equilibrium constant for a reaction of acid with a base. For this chemical reaction, this constant is known as dissociation constant. The larger the K_a value, the more dissociation of the acid in solution. This clarifies the strength of the acid.

The equilibrium of acid dissociation can be written as:

$$HA \rightleftharpoons H^+ + A^-$$

Where HA is treated as an acid which dissociates in proton H^+ and conjugate base of acid A^-. The dissociation constant (equilibrium constant) can be written as:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The logarithmic constant, pK_a, which is equal to $-\log_{10} K_a$, is sometimes also (but incorrectly) referred to as an acid dissociation constant:

$$pK_a = -\log_{10} K_a$$

The larger the value of pK_a, the smaller the extent of dissociation at any given pH and the weaker the acid. A weak acid has a pK_a value in the approximate range −2 to 12 in water. Acids with a pK_a value of less than about −2 are said to be strong acids, a strong acid is almost completely dissociated in aqueous solution, to the extent that the concentration of the undissociated acid becomes undetectable.

The equilibrium constant K_b for a base has been defined as the association constant for protonation of the base, say B, to form the conjugate acid, HB^+.

$$B + H_2O \rightleftharpoons HB^+ + OH^-$$

Using similar reasoning to that used before for acids

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Like pK_a, pK_b is the equal to $-\log_{10}K_b$. K_b is related to K_a for the conjugate acid. In water, the concentration of the hydroxide ion, $[OH^-]$, is related to the concentration of the hydrogen ion by $K_w = [H^+]\,[OH^-]$, therefore

$$[OH^-] = \frac{K_w}{[H^+]}$$

Substitution of the expression for $[OH^-]$ into the expression for K_b gives

$$K_b = \frac{[HB^+]K_w}{[B][H^+]} = \frac{K_w}{K_a}$$

When K_a, K_b and K_w are determined under the same conditions of temperature and ionic strength, pK_b can be written as

$$pK_b \approx 14 - pK_a$$

The above expression is written when K_w is 13.995. The value of K_w changes with temperature and thus the value of pK_b is varied with temperature[1]. In practice there is no need to define pK_b separately from pK_a, but it is done here as often only pK_b values can be found in the older literature.

A lot of work is done on pK_a determination. Different types of method are invented for pK_a determination[2]. Most of the techniques are of economical cost. pH-metry is a cost effective technique and easily applied in the laboratory and also gives satisfactory reproducible results. A method was proposed by Manderscheid et. al. based on liquid charomatography[3]. Rob et. al. determined base dissociation constants of some alkanolamines by potentiometry[4].

The dissociation of inorganic base into a cation and hydroxide ion plays important role in determination of pK_b. Those bases which are not dissociated completely, the degree of dissociation tells us the real picture of the pK_b. In case of amines, they don't give hydroxide ions into aqueous solution. Amines have basic amine groups which have lone pair of electron due which they are basic. They accept protons; therefore association of amine with proton will be counted for base dissociation. Degree of association of amine gives us pK_b. There are many methods which can be applied for the determination of base dissociation constant such as potentiometry, conductometry, voltametry, calorimetry, nuclear magnetic resonance, HPLC, polarimetry[5] and electrophoresis[6].

Organic acid behaves as strong acids but the strength of organic acids (carboxylic acids) is lesser than inorganic acid. Likewise organic bases (amines) are less basic than inorganic bases. The pK_a of some organic acids were determined by Serjeant et. al[7]. pK_b of some organic simple amine were estimated by Perrin et. al[8]. pK_a and pK_b are very important determined value. On the bases of pK_a and pK_b at a particular concentration give the identification of organic acids or organic bases[9]. The structure of organic bases plays important role to decide the pK_a of amines because the structure of amino group in amine facilitates the protonation of amino group[10].

Needs for the study

Alkanolamines are important organic amines as well as bases. They are used at many places such as carbon capture technologies for the separation of carbon dioxide. Except this, they are used in chemical industry and drug industry for the preparation of drugs, and other supporting compounds. In laboratory these are used as chemicals. In all the studies pK_b is the important criterion for the determination of dissociation, doing titration against acids, strength of amines etc. Therefore the present study is based on the determination of pK_b of some industrial and laboratory important alkanolamines.

Material and Methods

Our method for the determination of pK_b is pH-metry. Some standard solutions along with amine solutions are prepared. The reagents and chemicals which are used in the present study include potassium carbonate (inorganic basic salt), and alkanolaminens which are organic bases. Other supporting chemicals and reagents used are sulphuric acid, sodium carbonate etc. The chemicals used in this method and their manufacturer are given in the Table 1.

A specially designed reactor is taken for these studies on laboratory scale. The reactor is a jacketed vessel and is provided a pocket for thermometer for temperature measurement of the solution during the study. Temperature inside the reactor is maintained by circulation of water through the jacket with the help of a circulatory water bath. The reactor temperature is maintained at 25ºC during the pH measurement process.

First of all a solution of amine is prepared by dissolving 3 gm of amine in 40 ml of water. A standard solution of H_2SO_4 (0.25N) is also prepared for the titration with amines. To standardize sulphuric acid, a primary standard solution (0.25N) of sodium carbonate is also prepared. 40 ml of amine solution is taken into the reactor and maintained it at 25ºC with the help of circulating water bath. An electrode of pH meter is dipped into the amine solution. Now standard H_2SO_4 is added drop by drop. After adding few drops of H_2SO_4, reading of pH meter is noted.

Table 1: List of Chemicals with Their Manufacturer/Supplier

S. No.	Chemical	Make
1	Potassium carbonate	Fisher Scientific
2	Sulphuric acid	SDFCL
3	Sodium carbonate	CDH
4	Monoethanolamine	Alfa Aesar
5	Diethanolamine	Fisher Scientific
6	Triethanolamine	Fisher Scientific
7	N-Methyldiethanolamine	Merck
8	Diisopropanolamine	Acros
9	2-Amino-2-methyl-1-propanol	Acros
10	2-(Methylamino)ethanol	Alfa Aesar
11	2-(Ethylamino)ethanol	Merck
12	2-(Dimethylamino)ethanol	Merck
13	Tris(hyddroxymethylamino)methane	Merck
14	Piperazine	Merck
15	1-(2-Hydroxyethyl)piperazine	Merck
16	N-Methylpiperazine	Merck
17	1,4-Dimethylpiperazine	Merck
18	Ethylenediamine	Merck
19	(2-Aminoethylamino)ethanol	Merck
20	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine	Merck
21	Diethylenetriamine	Merck
22	Triethylenetetramie	Merck

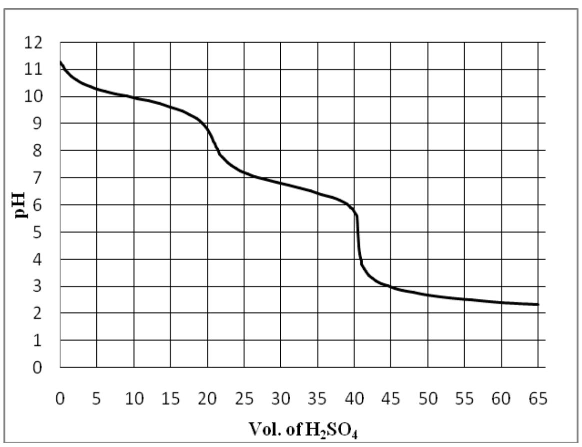


Figure 1: Graph of pH Titration of K_2CO_3 with Standard H_2SO_4

At the end point the pH change is vigorous, therefore H_2SO_4 is added in very small amount at this point and pH is noted. The experiment is over when pH becomes acidic and almost constant. When the experiment is over, a graph between pH and volume of H_2SO_4 added is plotted. A reference graph is shown when K_2CO_3 is titrated with H_2SO_4 (Figure 1).

There are two steep plunges in the plot (Figure 1) which shows that it is a di-acidic base. Each steep plunge gives a pK_b value, therefore for K_2CO_3 there are two pK_bs i.e. pK_b1 and pK_b2. From the plot pK_b is calculated by tangent method. Tangents are drawn on each semi-circular segment of graph. The middle of tangents on the graph will be pK_b value. From the above graph the pK_b1 of K_2CO_3 is 4.00 and pK_b2 is 8.3. These values are almost equal to literature values[11]. The same exercise has been repeated for all the amine reported in this paper.

Result and Discussion

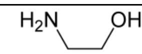
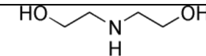
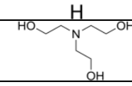
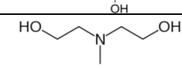
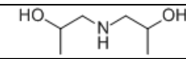
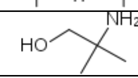
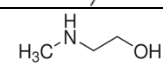
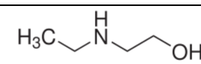
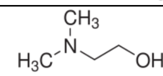
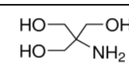
In this paper different types of amines are taken for pK_b measurement which includes mono-amines, di-amines and tri-amines. In all the cases 3 gm of amine is dissolved in 40 ml of water and is titrated with standard 0.25N sulphuric acid. Readings are noted and the graphs are plotted. Results are discussed below.

Mono-amines

Mono-amines contain on Nitrogen atom which connected to carbon atom. Each nitrogen atom provides the site for one proton capture. Therefore mono-amines are monoacidic bases. The mono-amine which are used in present study for pK_b determination are Monoethanolamine, Diethanolamine, Triethanolamine, N-Methyldiethanolamine (MDEA), Diisopropanolamine (DIPA), 2-Amino-2-methyl-1-propanol (AMP), 2-(Methylamino)ethanol (MAE), 2-(Ethylamino)ethanol (EAE), 2-(Dimethylamino)ethanol (DMAE), Tris(hydroxymethylamino)methane (THAM). The structures of mono-amines are given in Table 2. When the structures are analysed it is seen that Monoethanolamine (MEA), 2-Amino-2-methyl-1-propanol (AMP) and

Tris(hydroxymethylamino)methane (THAM) are primary amines. Diethanolamine (DEA), Diisopropanolamine (DIPA), 2-(Methylamino)ethanol (MAE) and 2-(Ethylamino)ethanol (EAE) are secondary amines. Triethanolamine (TEA), N-Methyldiethnaolamine (MDEA) and 2-(Dimethylamino)ethanol (DMAE) are tertiary amines. The tertiary amine comparatively more basic than primary and secondary amines but it is seen that in tertiary amines and secondary amines alkyl groups are attached to nitrogen atoms and thus nitrogen atom becomes bulky. Therefore it shows less interaction towards the proton when dissolved in water.

Table 2: Structures of Mono-amines used for pK_b study

S. No.	Amine	Type of amine	Structure
1	Monoethanolamine (MEA)	Mono-amine	
2	Diethanolamine (DEA)	Mono-amine	
3	Triethanolamine (TEA)	Mono-amine	
4	N-Methyldiethnaolamine (MDEA)	Mono-amine	
5	Diisopropanolamine (DIPA)	Mono-amine	
6	2-Amino-2-methyl-1-propanol (AMP)	Mono-amine	
7	2-(Methylamino)ethanol (MAE)	Mono-amine	
8	2-(Ethylamino)ethanol (EAE)	Mono-amine	
9	2-(Dimethylamino)ethanol (DMAE)	Mono-amine	
10	Tris(hydroxymethylamino)methane (THAM)	Mono-amine	

In case of monoamines only one steep plunge of graph is seen and thus these have one pK_b value. Following graph (Figure 2) shows the graph of all mono-amines tested for pK_b. From the graph it is seen that 2-Amino-2-methyl-1-propanol (AMP), 2-(Methylamino)ethanol (MAE), 2-(Ethylamino)ethanol (EAE), Diisopropanolamine (DIPA) and 2-(Dimethylamino)ethanol (DMAE) have larger value of pK_b. It is because all of these show comparatively lesser interaction with protons. Nitrogen atom in these amines amine is surrounded by bulky groups and less protonation occurs. Monoethanolamine (MEA) has least pK_b value because it is highly basic in nature and show high interaction with protons. The pK_b calculated from the graph are given in Table 3.

pK_b value of any amine shows its basic strength. From the Table 3 it is clear that out of the Mono-amines used in this study 2-(Ethylamino) ethanol (EAE) is the least basic in nature and Monoethanolamine (MEA) is the most basic in nature. Other amines like Diethanolamine (DEA), Triethanolamine (TEA) and N-Methyldiethnaolamine (MDEA) also show good basic character. Rest of the amines has comparatively less basic character.

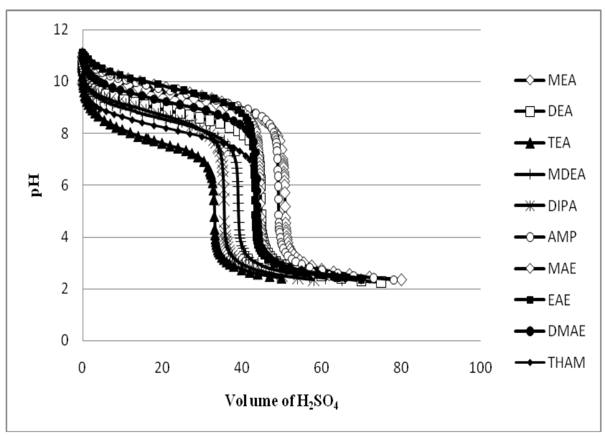


Figure 2: pH graph of all Mono-amines used to find out the pK_b value

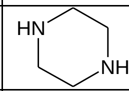
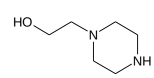
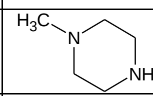
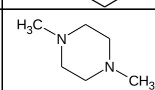
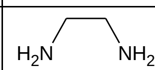
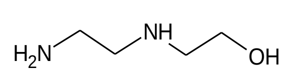
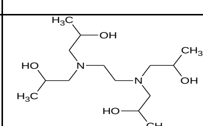
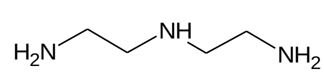
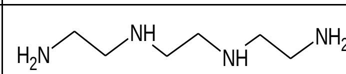
Table 3: pK_b values of mono-amines

S. No.	Amine	pK_b (Determined)	pK_b (Literature Value)
1	Monoethanolamine (MEA)	4.89	4.66[12]
2	Diethanolamine (DEA)	5.23	5.12[12]
3	Triethanolamine (TEA)	5.54	5.52[12]
4	N-Methyldiethnaolamine (MDEA)	5.42	5.48[12]
5	Diisopropanolamine (DIPA)	5.71	5.76[12]
6	2-Amino-2-methyl-1-propanol (AMP)	5.63	5.58[12]
7	2-(Methylamino)ethanol (MAE)	5.74	-
8	2-(Ethylamino)ethanol (EAE)	6.01	-
9	2-(Dimethylamino)ethanol (DMAE)	5.86	-
10	Tris(hydroxymethylamino)methane (THAM)	5.80	-

Di-amines

Di-amines are those amines in which two nitrogen atoms are bonded to two different sites of carbons in the structure of the amine. Due to presence of two aminic nitrogen atoms, these are di-acidic bases. The structures of di-amines used for the study are given in Table 4. It is seen from the structures, that piperazine is less bulky di-amine and N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine (THED) is the most bulky di-amine. The amount of protonation will be more in case of Piperazine. Other derivatives of Piperazine like 1-(2-Hydroxyethyl)piperazine (HEP), N-Methylpiperazine (MP) and 1,4-Dimethylpiperazine (DMP) have one nitrogen is more bulky than other. In all the cases of Piperazine and its derivatives, the protonation will be more for Piperazine. In all the amines, Ethylenediamine (ED) is the least bulky diamines.

Table 4: Structures of Polyamines used for pK_b study

S. No	Amine	Type of amine	Structure
1	Piperazine (PIP)	Di-amine	
2	1-(2-Hydroxyethyl)piperazine (HEP)	Di-amine	
3	N-Methylpiperazine (MP)	Di-amine	
4	1,4-Dimethylpiperazine (DMP)	Di-amine	
5	Ethylenediamine (ED)	Di-amine	
6	(2-Aminoethylamino)ethanol (AEAE)	Di-amine	
7	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine (THED)	Di-amine	
9	Diethylenetriamine (DETA)	Tri-amine	
10	Triethylenetetramie (TETA)	Tetramine	

7% (w/v) solutions of all the di-amines were taken for the pH titration study. 40 ml of each amine solution is taken and titrated with standard 0.25N H_2SO_4. After taking the pH readings by adding standard H_2SO_4, graph has been plotted. Plots drawn for all of the di-amines are given in the following graph (Figure 3).

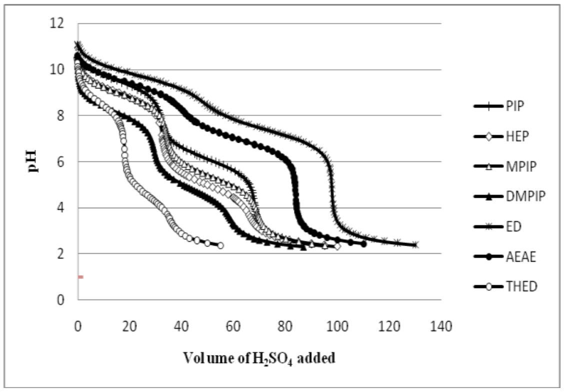


Figure 3: pH graph of all Di-amines used to find out the pK_b value

From the above graphs, pK_b values of di-amines are calculated by tangent draw method. Both pK_b1 and pK_b2 values of all di-amines are given in Table 4.

Di-amines have two pK_b values. pK_b1 values generally represents the strength of the bases. From the Table 4, it is clear that 1-Methylpiperazine is the most basic and ethylenediamine (ED) is least basic. Two pK_b values show that one of the amino groups has greater affinity towards proton than other in aqueous solution. Firstly one of the two amino groups binds completely with proton and then other amino group starts to bind. Therefore two distinct steep plunges are seen in the graph of di-amines. Other amines like N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenedi-amine (THED), Diethylenetriamine (DETA) and Diethylenetriamine (DETA) also show good basic character.

Table 4: pK_b values of di-, tri- and tetra-amines

S. No	Amine	pK_b1	pK_b2
1	Piperazine (Pip)	4.15	7.98
2	N-Hydroxyethylpiperazine (HEP)	4.07	6.97
3	1-Methylpiperazine (MP)	3.98	7.56
4	1,4-Dimethylpiperazine (DMP)	4.12	6.62
5	Ethylenediamine (ED)	5.02	8.75
6	2-(2-Aminoethylamino)ethanol (AEAE)	4.68	8.34
7	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenedi-amine (THED)	3.54	6.53
8	Diethylenetriamine (DETA)	3.81	7.56
9	Triethylenetetramine (TETA)	3.95	8.20

Tri- and Tetra-amines

There is only one tri-amine i.e. Diethylenetriameie (DETA) and one tetra-amine i.e. Triethylenetetramine (TETA) which are studied for pK_a determination. The structures of these amines are given in Table 4. The comparative plots of Diethylenetriamine (DETA) and Triethylenetetramine (TETA) are given in the following graph (Figure 4).

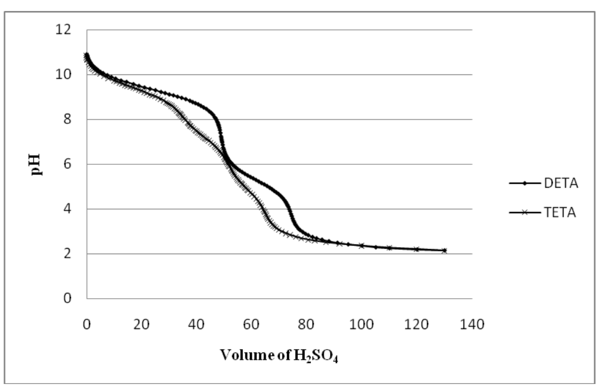


Figure 4: pH graph of all Tri-amine and Tetra-amines used to find out the pK_b values

Both Diethylenetriamine (DETA) and Triethylenetetramine (TETA) show good basic character as their pK_b are very near as well as very less. DETA is tri-amine but it show only two steep plunges in its graph and hence two pK_b values. The reason behind this is the structure of DETA in which two of three nitrogens are equivalents and far apart from each other. Thus it can be concluded that DETA has only two types of nitrogen atoms with different nature. So it shows only two pK_b values. Likewise TETA is a tetra amine containing four nitrogen atoms but it has two types of nitrogen atoms by nature. Hence it gives only two pK_b values. From the graph (Figure 4) it can be noted that DETA has two distinct steep plunges but TETA show less clear plunges. This can be explained on the basis of structure. The structure of TETA is a long chain structure, which is something coiled in nature and thus nitrogen atom becomes hindered and therefore gets less protonated.

Conclusion

In this paper mono-amines and polyamines are studied for the determination of pK_b values and also analysed for the basic character. This study will be beneficial for those, who are working on organic bases in the laboratory or in research laboratories. Most of the amines are very costly therefore should not be wasted in determination of such type of studies. This study is the first study of its kind in pH-metric determination pK_b of all types of amines. It is very clear the results are surprisingly good. Further study is needed by using other methods for pK_b determination.

Acknowledgement
The authors are grateful to the Vice Chancellor, Uttarakhand Technical University, Dehradun, who permitted and allowed to carry out the research work on the topic. Support of Uttaranchal College of Science and Technology, Dehradun, is also acknowledge for providing the library and IT facility.

References

1. Marshall W.L., Frank E.U., Ion product of water substance, 0-1000 ºC, 1-10000 bars, new international formulation and its background. *J. Phys. Chem. Ref. Data.,* **10 (2)**, 295 (**1981**).

2. Reijenga J., Hoof A.V., Loon A.V., Teunissen B., Development of Methods for the Determination of pK_a Values. *Analytical Chemistry Insights*., **8**, 53 (**2003**).

3. Manderscheid M., Eichinger T., Determination of pK_a values by liquid charamatography. *Journal of Charomatographic Science*., **41**, 323 (**2003**).

4. Rob J.L., Martinus B., Gerdine J.K., Dissociation Constants of Some Alkanolamines at 293, 303, 318, and 333 K, *J. Chem. Eng. Data.,* **35**, 276, (**1990**)

5. Reijenga J., Hoof A.v., Loon A. v., Teunissen B, Development of Methods for the Determination of pK_a Values, *Analytical Chemistry Insights.,* **8**, 53 (**2013**).

6. Shalaeva M., Kenseth J., Lombardo F., Bastin A., Measurement of Dissociation constants (pK_a Values) of Organic Compounds by Multiplexed Capillary Electrophoresis Using Aqueous and Cosolvent Buffers, *Journal of Pharmaceutical Sciences*., **97**, 2581 (**2008**).

7. Serjeant E. P., Dempsey B., Ionization Constants of Organic Acids in Aqueous Solution, *Pergamon, Oxford.,* (**1979**).

8. Perrin D. D., Dissociation Constants of Organic Bases in Aqueous Solution, *Butterworths, London, 1965, Supplement.,* (**1972**).

9. Perrin D. D., Dempsey B., Serjeant E. P., pK_a Prediction for Organic Acids and Bases, *Chapman and Hall, London.,* (**1981**).

10. Zhao Y.H., Yuan X., Yang L.H., Wang L.S., Quantitative structure-activity relationships of organic acids and bases, *Bull Environ Contam Toxicol.,* **57(2)**, 242 (**1996**).

11. Reich H.J., Rigby J.H., Handbook of Reagents for Organic Synthesis, Acidic and Basic Reagents, *John Wiley and Sons,* New York, (1999).

12. Khalili F., Henni A., East A. L. L., pKa values of some piperazines at (298, 303, 313 and 323) K, *Journal of Chem. Engg. Data.,* **54(10)**, 2914 (**2009**).