ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Determination of the Formation Constants of Some Metal Ions Coordinated with poly (8–Hydroxyquinoline)

Mohamed M. Shahata

Environmental affairs Department, Assiut University Hospitals, Assiut University, Assiut, Egypt.

Manuscript Info

Manuscript History:

Received: 25 April 2014
Final Accepted: 23 May 2014
Published Online: June 2014

Key words
Poly(8-Hydroxyquinoline), Potentiometric, Formation constant, Heavy metal ions.

Corresponding Author

Mohamed M. Shahata

Abstract

The association equilibria of PHQ and PHQ–coordinated with some transition metal cations such as: Al(III), Ca(II), Cd(II), Co(II), Cu(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) ions were studied using potentiometric technique. The association constant (K_a) of PHQ was calculated from the average number of protons attached per repeating unit in the PHQ matrix (n_A) at different pH values. This value of pK_a which formed was found to be 7.75.

The titration curves revealed that the metal ion replaces protons and coordinates to the polymer matrix. In addition, the use of such titration curves could be computed of the formation constants (log β) of the different species exist at equilibrium. The formation constant (log β) for different molar ratios of species such as 1 : 2, 1 : 1 and 2 : 1 for metal : polymer matrix, in solution were computed and the results were discussed. The value of $\bar{n}$ and P_L for the metal ions under investigation were calculated at different pH values. The Formation Constant (log β) of the coordinated polymer based on PHQ–Metal ion were computed using $\bar{n}$ – P_L system. Mathematical calculations of differential change of $\bar{n}$ ($\Delta\bar{n}$) gave a sharp signal for calculations of formation constant. From $\bar{n}$ there are partial formation constant (log β_1, log β_2 and log β_3) which indicate to the protonation degree. The analyses of potentiometric data helped us to determine each value of the formation constant and/or partial formation constant for the metal ions such as: Al(III), Ca(II), Cd(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) coordinated with PHQ matrix .

INTRODUCTION

The dissociation constant is one of the most important characteristics of a pharmaceutical chemical moiety which has to be estimated with accuracy. Poor solubility has issues not only with formulating the drug; it also imposes problems in evaluating the physicochemical properties of the molecule itself. Ionization constant (pKa) is one among the parameter to be estimated with accuracy, irrespective of solubility constraints.[1]. The pKa is the negative logarithm of the equilibrium constant (Ka) of the acid-base reaction of the compound of interest. The importance of pKa in biologic systems needs to preserve a relatively constant environment, including control over the pH of the organism's fluids. One way to achieve this is through the use of "buffers". A buffer is a compound which due to its acid-base chemistry reacts to changes in the environment to preserve a near constant pH that is near the pKa of the buffering compound.

Titration with a standard solution of strong base is the method of choice for the characterization of a weak acid. Monitoring the titration progress by means of potentiometric measurements with a pH glass electrode allows the accomplishment of tasks of various complexity. From the simple quantitation of a single solute to the determination of the composition of multi-component mixtures together with the acidity constants of poly functional acids, computer programs [2–3] at various levels of sophistication have been proposed, and are being continuously developed, in order to allow systems of increasing complexity to be dealt with in agreement with the principles of statistical analysis of data.

Potentiometric methods not requiring titration with a base, like sample addition or sample dilution, are seldom used. For instance, pH measurements of sample solutions at a single known concentration of weak acid are sometimes employed to calculate K_a for classification of the acid strength of series of similar substances.

Measured volumes of the sample solution, containing a single weak acid at concentration C, are added stepwise to a known volume V^o of water (the constancy of ionic strength being an important prerequisite for obtaining easily manageable data, an aqueous solution of an inert electrolyte is preferable). In ordered to obtain either the concentration C, or the acidity constant of the sample acid, K_a, or both, the experimental variables V (the total volume of sample added in correspondence of each step) and $[H^+]$ (the corresponding hydronium ion concentration measured by a calibrated glass electrode) can be processed by computational methods according to the basic equation describing the theoretical relation between these quantities [4]. Analytical procedures are greatly simplified and their reliability increased by the possibility of determining the different analysis without the need for tedious, complex separation which are frequently a source of errors. Such an approach requires a new review of well known analytical reagents with well-established properties and features in order to develop procedures for multi component analysis.

The study of 8–hydroxyquinoline (oxine) which has been widely used as an analytical reagent for the determination of metal ions. It forms insoluble complexes with a number of metal ions in aqueous media. In other instances it is necessary previously to remove interference by precipitation or extraction with other reagents to achieve the required selectivity [5]. The determination of different metal ions in the same sample requires working in a sequential manner, which results in prolonged times of analysis. The stepwise protonation equilibria of the ligand were studied (Eqs. 1 to 4) [6] ,

$L^{-1} + H^+ \leftrightarrow HL$ ………..(1)

$HL + H^+ \leftrightarrow H_2L^{2+}$ …………(2)

$H_2L^{2+} + H^+ \leftrightarrow H_3L^{2+}$ ………….(3)

$H_3L^{2+} + H^+ \leftrightarrow H_4L^{2+}$ ……….(4)

According to literature [7], K_1 and K_n can be assigned to the protonation constants of the analyte, while the values are somewhat different from those of free 8–quinolinol . The difference can be attributed to the solvent effect, since, the free 8–quinolinol is insoluble in water and its protonation constants were obtained in the mixture of 1,4–dioxane / water.

The formation constants of metal complexes may be expressed either by the overall stability constants, β_1, β_2, β_3, …… β_n, or by the stepwise stability constants K_1, K_2, ..., K_n as follows (charges are omitted):

$$K_n = [ML_n] / [ML_{n-1}] [L]$$

$$\beta_n = [ML_n] / [M] [L]^n$$

The stepwise stability constants are used for the formation of ML_n complexes. For the formation of protonated, hydroxo, or polynuclear complex species, the overall stability constants are used[8]:

$$\beta (M_pH_qL_r) = [M_pH_qL_r] / [M]^p [H]^q [L]^r$$

Negative q-values for [HI refer to the formation of mixed hydroxo complexes or equilibria in which one or more hydrogen ions which do not normally dissociate are liberated.

The binding properties of average molecular weight towards metal ions in dilute aqueous solutions [9]. It was possible to establish the following order for the different metal ions to form increasingly stable complex species Ni(II) < Cd(II) < Cu(II) < Pb(II). The difference in the average molecular weight did not seem to have any influence on complexation phenomenon .

Potentiometric titration technique can be used to determine the hydrogen ion concentration in solutions at constant ionic medium which contains an excess of, for example, sodium ions, moreover, complex formation M^{n+} (metal) ion and coordinated compound (ligand) in the presence of H^+ can be studied using the glass electrode . The pH values of the mixed solvent-water media were corrected by the method given by Douheret [10] :

$$pH^* = pH_{®} - \delta$$

Where pH* is the corrected reading and $pH_{®}$ is the pH-meter reading obtained in solvent–water mixture. The values δ or the various properties of each organic solvent were determined as recommended previously [9].
The electrical behavior of hydroxyquinoline sulfonic acid and its complexes with Mn(II), Fe(II), Co(II), Ni(II) or Cu(I1) as well as its salts with Li(I), Na(I) or K(I) were studied over the temperature range 294-420K. All compounds behave like semiconductors. The stability constants were calculated at different temperatures in order to determine the thermodynamic parameters ΔH, ΔG and ΔS for the complexes studied.[11]
A series of complexes of divalent transition metal ions with malonyl bis(salicyloylhydrazone) (H_4MSH) have been prepared and characterized with the help of conductometric, potentiometric methods. The proton–ligand and metal–ligand stability constants were obtained pH-metrically. The electrical conductivity of solid complexes was measured at 289 K. The low molar conductance values observed for these complexes indicate that, they are non-electrolytes. They are soluble to a limited extent in DMF and DMSO. The elemental analyses of the complexes indicate that the complexes have 1:1 and 2:1 (M:L) stoichiometry with the existence of water, chloride, acetone molecules inside the coordination sphere as evidence from the IR spectral studies. Further, the complexes have been formulated by comparing C, H, N & metal analysis data [12]. The protonation constants of the ligand and the stability constants of their metal complexes will be evaluated potentiometrically.
The complexation reaction between some oximes including methyl-2-pyridylketone oxime (MPKO), phenyl-2-pyridylketone oxime (PPKO) and diacetyl mono oxime (DMO) with some transition and heavy metal ions: Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+} and La^{3+} has been studied potentiometrically in aqueous solution at 25±0.1 ◦C and ionic strength (μ) of 0.1M supported by KCl. The overall stability constants logβ's of respective species were obtained by computer refinement of pH–volume data. The main species in binary systems are ML, ML_2, MLH, MLH_2, ML_2H, ML_2H_2, M(OH)L, $M(OH)_2L$, $M(OH)L_2$ and $M(OH)_2L_2$ (L =MPKO or PPKO or DMO)[13].
Kamal and co-workers[14-15], have prepared spectro analytical solutions and using several spectroscopic techniques, characterized coordination polymer based on poly(8-hydroxyquinoline) complexed to some metal ions. The insertion of Al(III) cation into poly(8-hydroxyquinoline) (PHQ) instead of some metal ions such as Co(II), Ni(II), Zn(II), Fe(III), Cu(II), Mg(II), Cr(III), Mn(II) and Mo(VI) ions via cation-exchange mechanism has been studied. The stability constants for PHQ coordination polymers with different metal ions were calculated . The calculations indicate that the largest stability constant and free energy change correspond best to the 2:1 stoichiometry, ($2PHQ:1M^{n+}$)[16-17].

2. EXPERIMENTAL

2.1- Material

Materials of polymer: 8–Hydroxyquinoline (8–HQ) was obtained from Aldrich(chemical co.,US.). ploy (vinyl alcohol) (PVA; Mwt =$2.2x10^4$;degree of hydrolysis, 88%) was purchased from chemical co., Japan).

Materials of salts: A copper salt $Cu(NO_3)_2$ was obtained from chemically pure of (Merck). All Materials employed in the present investigation were of analytical reagent products from their Analar grade nitrate salts (BDH) ;

$Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2$, $CaCl_2$, $MgCl_2.6H_2O$, $NH_4Fe(SO_4)_2.12H_2O$, $Al_2(SO_4)_3.16H_2O$, $ZnSO_4.7H_2O$, $Cd(NO_3)_2.4H_2O$, and $Pb(NO_3)_2$.

2.2- Instrumentation

The pH – measurements were made using Jenway 3305 pH–Meter accurate to ±0.01 pH unit with a glass calomel electrode assembly. The pH–meter was standardized against pH 4.0 and pH 10.0 buffers (prepared by dissolving buffer capsules in definite amount of second deionized water).
Magnetic stirrer Jenway1000 was used for stirring the solutions.

2.3- Preparation of the solutions

Universal buffer solutions:

A modified universal buffer series derived from that of Britton [18] was prepared. The constituents of this series of buffer were prepared as follow:-

(a) A solution of 0.4 M of each phosphoric and acetic acids were prepared by accurate dilution of the A.R.concentrated acids .

(b) A solution of 0.4 M boric acid was obtained by dissolving the appropriate weight of the re crystallized acid in bi distilled water.

(c) A stock acid mixture was prepared by mixing equal volumes of the three acids in a large bottle. The total molarity of the acid mixture was thus mentioned at 0.4 M.

A series of buffer solutions (pH 3–12) were prepared as follow: 150 ml of the acid mixture was placed in a 250 ml measuring flask followed by the appropriate volume of 0.4 M NaOH solution and then the flask was completed to mark with bi distilled water. pH was measured with a Fisher Scientific Accument Digital pH meter 810.

Preparation of solutions for potentiometric measurements

Generally, doubly distilled water was used for preparation of all solutions employed.

NaOH solution: Sodium hydroxide (100 m mol L^{-1}) carbonate-free NaOH solution was prepared and standardized by titration against a standard solution of oxalic acid

HNO_3 solution: A stock solution of (100 m mol L^{-1}) HNO_3 was prepared and its molarity was checked by titration with standard KOH solution.

Metal salts solutions: Stock solution of 100 m mol L^{-1} of metals salt studied were prepared and standardized as recommended procedure [19].

$NaNO_3$ solution: A sodium nitrate (0.5 mol L^{-1}) stock solution was also prepared.

The titrations were carried out at constant temperature 25 ± 1^{o}C. The stirring used was relatively long and the stirring rate was relatively low and fixed for all experiments.

3. RESULTS AND DISCUSSION

3.1- Determination of the Stability Constant

When an increasing volume (V) of a solution containing the weak acid HA at concentration (C) is added stepwise to a volume (V^{o}) of solution containing the same acid at concentration $C^{o} > 0$, the amount (moles) of acid in the solution is given by:

$$C^{o}V^{o} + CV$$

Increases proportionally to the added volume (V) (note that the same is not true for the concentration, unless V<< V^{o}) . By expressing this amount in terms of its functional relation ship to experimental variable, V and $[H^{+}]$, equation (1) is obtained [20]:

$$F = (V^{\circ} + V)([H^{+}] - \frac{K_w}{[H^{+}]})(1 + \frac{[H^{+}]}{K_a})$$

$$= C^{o}V^{o} + CV \qquad \text{............(1)}$$

Where $[H^{+}]$ is measured variable of hydronium ion concentration measured as a pH, pK_a, is the acidity constant of the weak acid. This equation defines an auxiliary variable F, which is necessarily a linear function of V, in analogy with the "Rigorous Gran function " [20] for weak acid titration. The case presently of interest, not previously considered, is multiple addition of a sample containing the weak acid or highly conjugated matrix (such as PHQ) at concentration C to a known volume of water or of an aqueous solution of an inert electrolyte. By putting the initial concentration of weak acid in the measured solution, (C^{o}), equal to zero, the equation (1) will be reduced to the equation :

$$F = (V^\circ + V)([H^+] - \frac{K_w}{[H^+]})(1 + \frac{[H^+]}{K_a})$$

$$= CV \qquad \text{……………(2)}$$

or $F = H(1 + \frac{[H^+]}{K_a}) = CV$ ……………(3)

Where $H = (V^\circ + V)([H^+] - \frac{K_w}{[H^+]})$ …………(4)

With moderately weak acids at moderate dilution $\frac{K_w}{[H^+]} = [OH^-]$ is negligible with respect to $[H^+]$, Then , the equation (4) will be reduced to:

$$H = (V^\circ + V)[H^+] \qquad \text{………(5)}$$

Therefore, equation (2) can, in most instances, be reduced to the approximate form as:

$$F = (V^\circ + V)(1 + \frac{[H^+]}{K_a}) = CV \qquad \text{……………(6)}$$

Equations (2) – (6) can be used, in principle, for the determination of the sample concentration C and they can be rearranged to give equations having a different scope or a wider one. For instance, to calculate hydrolysis of water (K_w) when C is known equation (3) can be written as:

$$H[H^+] = K_a(CV - H) \qquad \text{……..……..(7)}$$

Therefore, equation (7) yields the acidity constant (K_a) as the graphical or Least–squares slope of the transformed experimental data. It can be observed that an Equation equivalent to equation (7), for instance, the equation:

$$K_a = \frac{[H^+]^2}{\frac{CV}{V^\circ + V} - [H^+]} \qquad \text{……………(8)}$$

This equation is used when acidity constant (K_a) is calculated from a single measurement of pH. Alternatively, by defining other suitable auxiliary variables X and Y that can be calculated for each pair of experimental data V and $[H^+]$, it is possible to rearrange equation (2) to obtain different Linear equation of the form:

$$Y = a + b X \qquad \text{……..(9)}$$

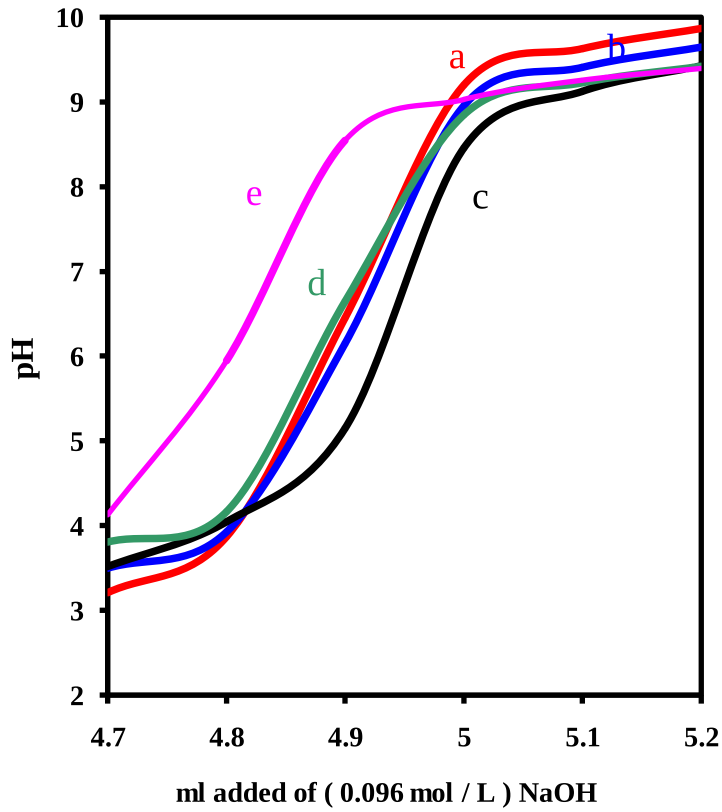
Therefore, C and K_a can be obtained by numerical or graphical linear fit of the values of X and Y, calculated from the experimental data as:

$$(V^\circ + V)[H^+]^2 = K_a\{CV - (V^\circ + V)[H^+]\} \qquad \text{……..(10)}$$

3.2. Determination of the pK$_a$ of PHQ

Different concentration of PHQ which effect on the volume of base consumed to give the same pH value in each concentration, are shown in Fig. 1 . Thus, From the height of the half-pH raising range for these curves which corresponding to the pH 6.75 . Application of eq. (10), it can be calculated that the pK_a for each concentration of 0.5, 1.0, 1.5, 2.0 and 2.5 mM of PHQ gave pK_a values: 9.14, 9.45, 9.53, 9.75 and 9.84 respectively. From these data, it can be concluded that, the value of pK_a is not depend (±0.7) on the concentration of PHQ.

Fig. 1: Potentiometric titration curves of strong alkali (NaOH) for different concentration of PHQ as : a) 0.5, b) 1.0, c) 1.5, d) 2.0, and e) 2.5 m mol L^{-1}, respectively.



3.3. Potentiometric Titration Studies of PHQ

From the potentiometric titration curves, the parameter, (n_A) average number of protons associated with the ligand (the polymer under investigation, PHQ) was calculated at different pH values given by [21]:

$$n_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V_o + V_1)(T_{cL^\circ})} \qquad \ldots\ldots\ldots\ldots..(11)$$

Where

Y : is the number of dissociable protons in the repeating unit of the PHQ,

V_o : is the initial volume,

V_1 and V_2 : are the volume of alkali required to reach the same pH in the presence of mineral acid (HNO_3) and (HNO_3 + PHQ) solutions, respectively.

$T_{cL}{}^{o}$: is the total concentration of the PHQ,

N^{o} : is the normality of the standard alkali and,

E^{o}, is the initial concentration of the free mineral acid (HNO_3).

The proton–PHQ (repeating unit) formation curves obtained by plotting n_A vs. pH is represented in Fig.2. The value of log K_1^H , the first proton–polymer association constant is determined by interplotation at the half (n_A) values from n_A vs. pH graph as seen in Fig.2 . The average value of Acidity constant (pK_a) was found to be 7.75 .

The plotting of the differential of the average number of protons associated with the repeating unit of the polymer Δn_A vs. pH give advantage than the studies of n_A vs. pH. This advantage that the Δn_A – pH graph has a band at certain pH value corresponding to the exact value of association constant, as shown in Fig. 3.

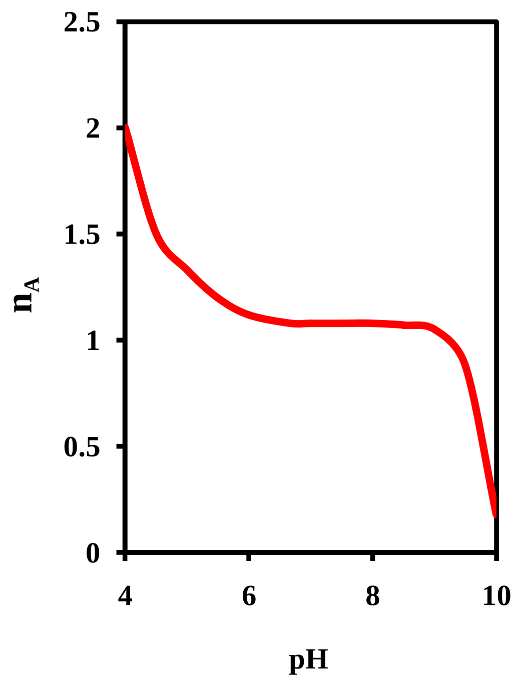


Fig. 2: Variation of the average number of protons associated (n_A) for PHQ vs. pH

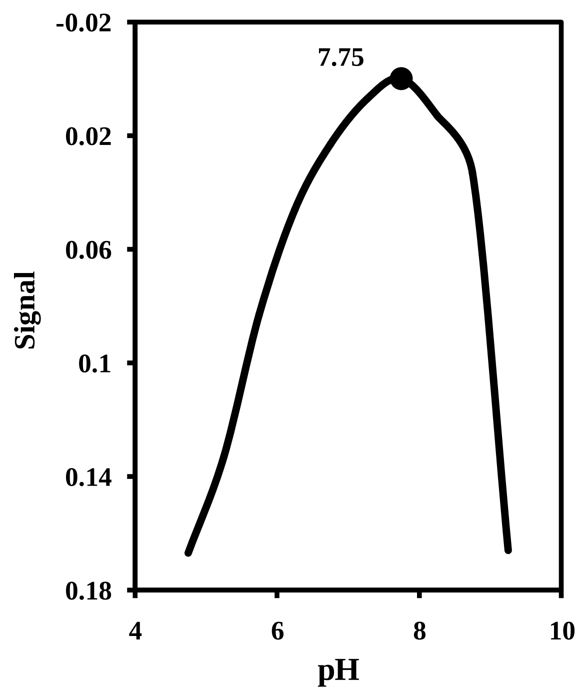
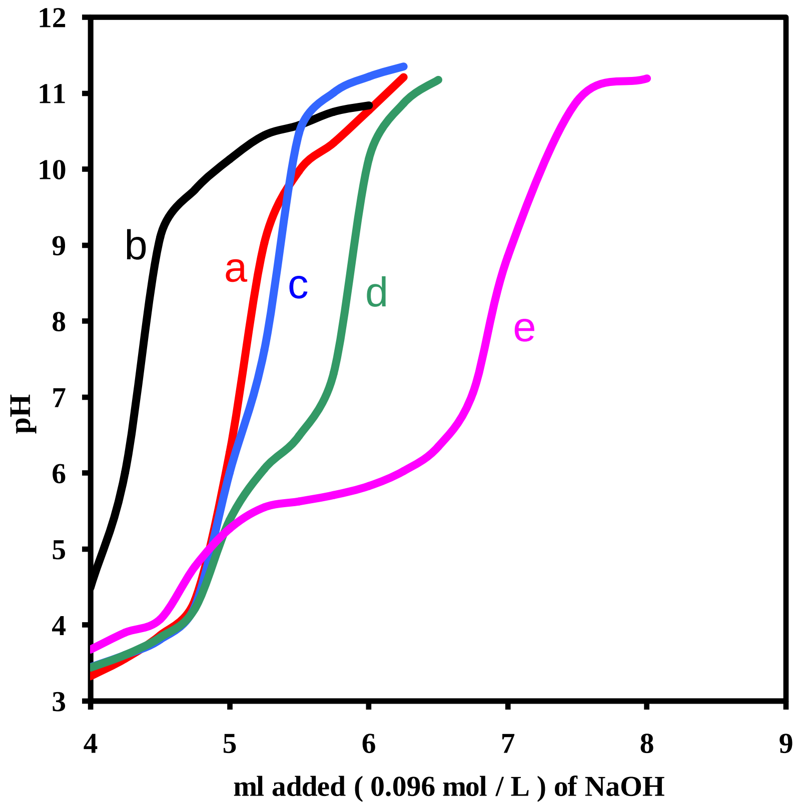


Fig. 3 : Variation of the first derivatives of n_A (Δn_A) for PHQ vs. pH.

3.4- Potentiometric Titration Studies of PHQ–Coordinated with Some Metal Ions

The potentiometric titration technique was also employed for the determination of the formation constant (log β) of PHQ–metal complexes consisted of the pH–metric titration curves of PHQ in the absence and presence of metal ion (M^{n+}) under investigation. Thus, the formation constant of binary metal ion – polymer (M–PHQ) complex was determined by the titration carried out using different molar ratios of the concentration of metal ions and/or repeating unit of the polymer matrix where, in each one the total volume was kept constant (50 ml) aqueous solution. The ionic strength was maintained constant by using 0.1 $molL^{-1}$ of supporting electrolyte ($NaNO_3$). Examination of the various titration curves of the different metal ions (M^{n+}) and PHQ (PHQ : M^{n+}) systems at different molar ratios (1 : 2, 1 : 1 and 2 : 1) show that the higher shift in the volume of alkali added for metal – polymer complex than the polymer alone. This indicates that the strong interaction between each of the metal ions with PHQ matrix via complexation mechanism. The partition coefficient of each metal between the two phases is a complex function of different equilibrium constants involved ionization of polymer (PHQ) and formation of the complex (PHQ – M^{n+}). The pH range (3 – 10) was chosen because it facilitated the complex extraction of the reagent and large number of metal ions and/or transition metal ions. The titration curve of PHQ–Cu(II) system is shown in Fig.4.

Fig.4: Potentiometric Titration Curves of PHQ–Cu(II) system curves as:
a) Free mineral acid (HNO_3),
b) HNO_3 + PHQ (0.1 m mol L^{-1}),
c) b + Cu(II) [1 M^{n+} : 2 PHQ],
d) b + Cu(II) [1 M^{n+} : 1 PHQ], and
e) b + Cu(II) [2 M^{n+} : 1 PHQ].



Titration curves for some metal ions system, PHQ - M^{n+} , such as: Al(III) ,Ca(II) , Cd(II) , Cu(II) , Co(II) , Fe(III) , Mg(II) , Ni(II) , Pb(II) and Zn(II) ions are studied. Thus, the replacement of hydrogen ion is due to complexation mechanism.
From these titration curves, it is clear that the potentiometric titration of free mineral acid curves (as curve a in Fig.4) are well separated from the polymer titration curves (curves b), which also separated from the polymer–metal titration curves due to the alkali consumed for metal–polymer interaction. The different molar ratio curve is curve c which represent PHQ - M^{n+} with molar ratio (1 M^{n+} : 2 PHQ), curve d for (1M $^{n+}$: 1 PHQ) and curve e for (2 M^{n+} : 1 PHQ).

3.5. Determination of the Association Constant (pK_a) of PHQ–Coordinated with Some Metal Ions

The metal–polymer stability constant (log β) were estimated from the analysis of the curves drown between $\bar{n}$ and P_L relationship where $\bar{n}$, is the average number of repeating unit in the matrix (PHQ) attached per metal ion (M^{n+}) and calculated by the equation [21] :-

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V_o + V_2) n_A T^\circ_{CM}} \qquad \ldots\ldots\ldots\ldots\ldots(12)$$

and P_L is the free polymer exponent of at several pH values and can be calculated as follows:-

$$P_L = \frac{1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_j [H^+]^j}{T^\circ_{CL} - \bar{n} T^\circ_{CM}} \cdot \frac{V_o + V_3}{V_o} \qquad \ldots\ldots\ldots(13)$$

Where V_1, V_2 and V_3 are the volumes of alkali required to reach the same pH in the free mineral acid (HNO_3), Polymer + mineral acid and the mineral acid + Polymer + metal in potentiometric titration, respectively. The values of $\bar{n}$ and P_L for the metal ions under investigation were calculated at different pH values.

From the relation between $\bar{n}$ vs pH as seen in (Fig. 5 a), the half of raising portions which corresponding to the pH value, give the pK_a value for PHQ.

This value of pH can determine exactly from First–derivatives treatment of $\bar{n}$ ($\Delta\bar{n}$), (Fig. 5 b) by the relation of signal vs pH (The differential of $\bar{n}$ values for constant values of pH) the peak give the certain point of pH value corresponding to pK_a.

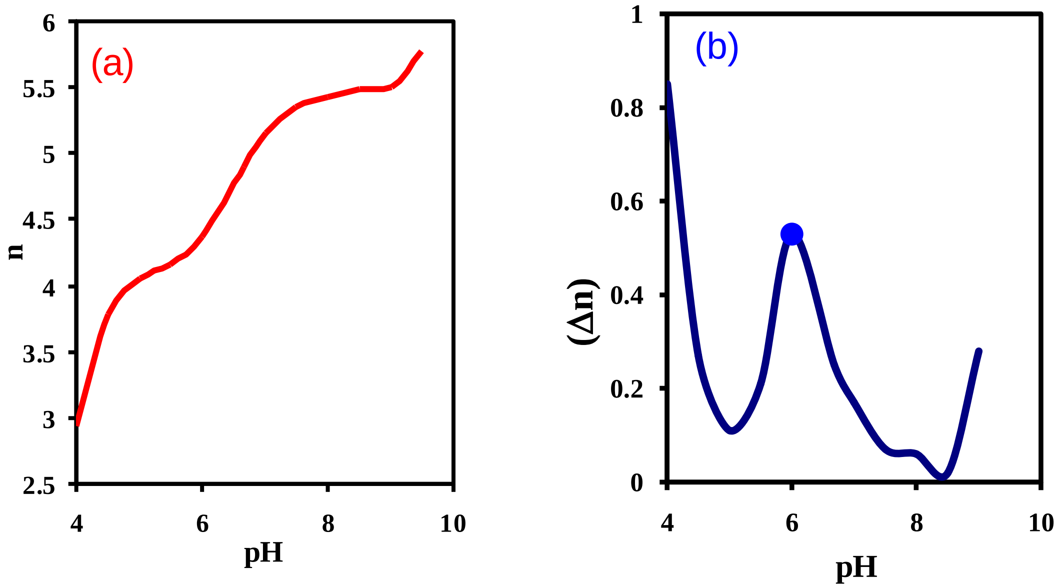


Fig. 5: (a) Variation of the average number of polymer attached per metal ion ($\bar{n}$) vs. pH, for PHQ–Cu(II) system and (b) first derivative of (a) as ($\Delta\bar{n}$) vs. pH.

The values of $\bar{n}$ and P_L for the metal ions under investigation were calculated at different pH values. The plots of $\bar{n}$ values against P_L were drown for the solution containing molar ratio 1 : 2 metal to ligand ratios for some metal ions such as: Al(III), Ca(II), Cd(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) ions.

The values of $\bar{n}$ and P_L for the metal ions under investigation were calculated at different pH values.

3.6. Determination of the Formation Constants (log β) of PHQ–Coordinated with Some Metal Ions Based on ($\Delta\bar{n}$) vs. P_L System.

A plotting of $\Delta\bar{n}$ against P_L ($\Delta P_L = 0.5$), this plotting is advantages than $\bar{n}$ vs. P_L since that gives us maxima at the value of the formation constant (log β) and also described the number of species could be formed from polymer–metal interaction by the number of maxima could be formed. The curves of $\Delta\bar{n}$ vs P_L for metal – PHQ with the molar ratio (1 : 2) were studied.

The analysis of potentiometric data presented that, in all the investigated systems are formed according to the protonation degree then give formation constant (log β) and partial formation constant (log β_{pq}) refers to the reaction [22] as:

$$_pM^{j+} + L^{z-} +_q H^+ = M_pLH_q^{(j+p-z)} \quad \text{……………..(14)}$$

The results presented that, some metals (for the molar ratio 1 metal : 2 polymer) give one species such as: Cu(II) , Zn(II) , Ni(II) and Al(III) then have one value of the formation constant (log β_1), for example as shown in (Fig. 6 a and b).

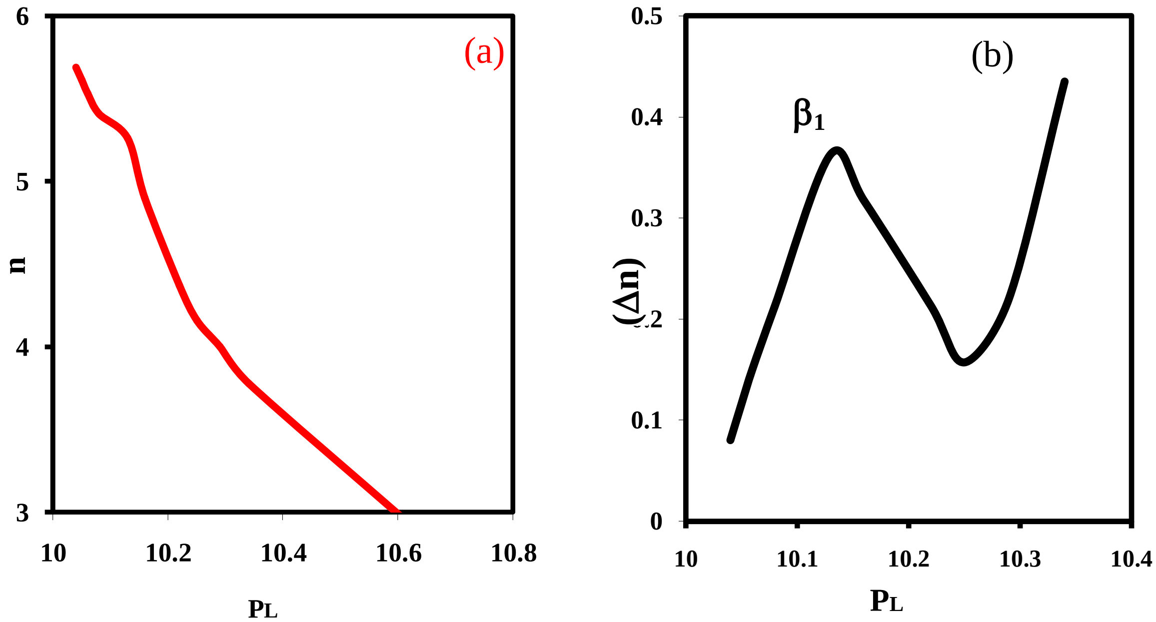


Fig. 6: (a) $\bar{n}$ **vs. P_L Experimental formation constant of PHQ – Cu(II) system,**

(b) Variation of $\bar{n}$, ($\Delta\bar{n}$) vs. P_L of (a).

Other metal ions give two species such as: Fe(III) , Pb(II) , Co(II) and Mg(II) ions. These species indicate that there are two partial formation constant (log β_1) and (log β_2), for example as shown in (Fig. 7 a and b).

Both Ca(II) and Cd(II) give three species then have three values of partial formation constant (log β_1), (log β_2) and (log β_3) respectively, for example as shown in (Fig. 8 a and b).

The values of the formation and partial formation constants for PHQ – M^{n+} matrix were listed in Table 1

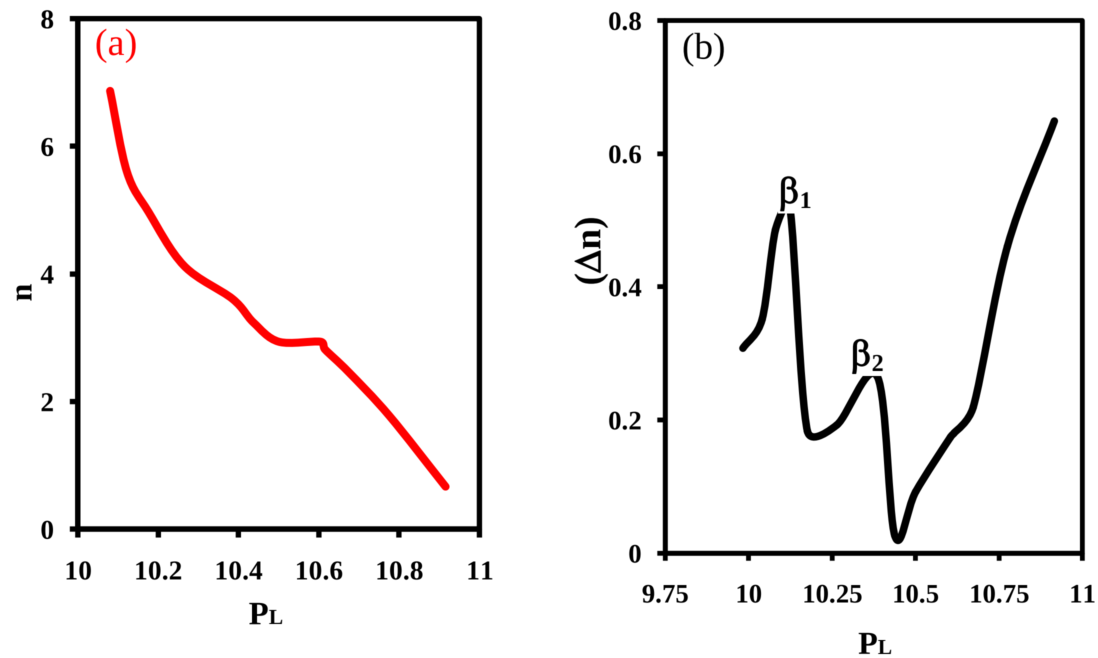


Fig. 7: (a) $\bar{n}$ **vs.** P_L **Experimental formation constant of PHQ – Mg(II) system,**
(b) Variation of $\bar{n}$, ($\Delta\bar{n}$) vs. P_L of (a).

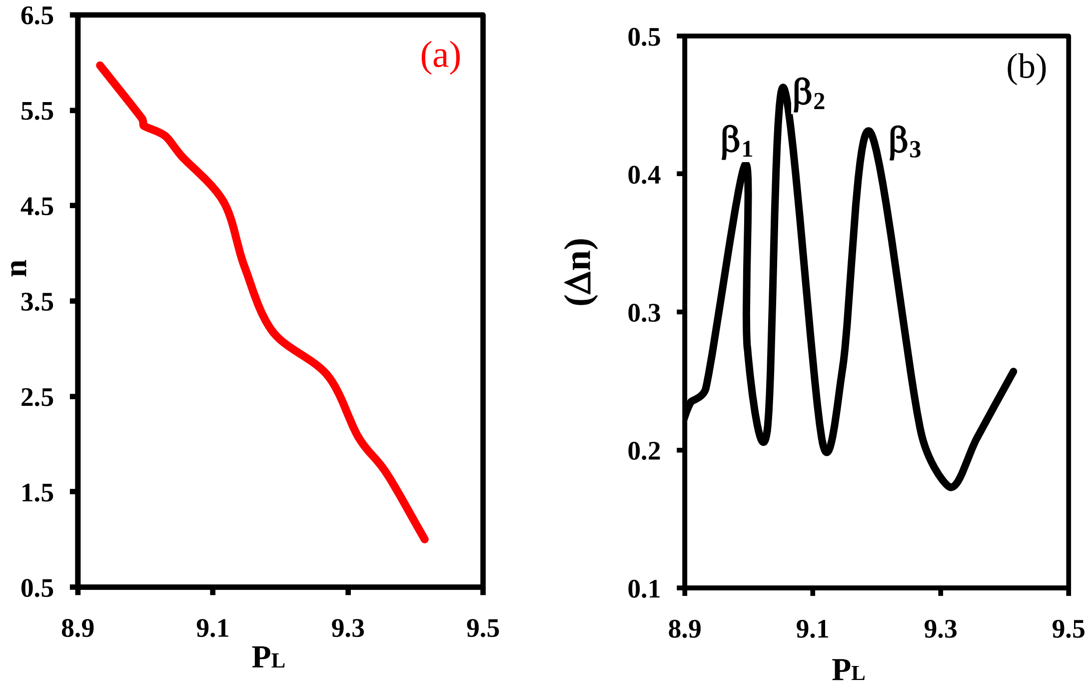


Fig. 8: (a) $\bar{n}$ **vs.** P_L **Experimental formation constant of PHQ – Cd(II) system,**
(b) Variation of $\bar{n}$, ($\Delta\bar{n}$) vs. P_L of (a).

Table 1
Formation constants (log β) and partial formation constants (log $\beta_{p\,q}$) values for metals coordinated with PHQ at different ratios of Metal : polymer.

No.	Coordination Polymer	Formation and partial formation constants		
		log β_1	log β_2	log β_3
1	PHQ – Cu(II)			
	2 : 1	10.13	----	----
	1 : 1	9.87	----	----
	1 : 2	9.72	----	----
2	PHQ – Zn(II)			
	2 : 1	10.43	----	----
	1 : 1	10.50	----	----
	1 : 2	11.67	----	----
3	PHQ – Ni(II)			
	2 : 1	10.65	----	----
	1 : 1	10.83	----	----
	1 : 2	12.15	----	----
4	PHQ – AL(III)			
	2 : 1	10.71	----	----
	1 : 1	8.72	----	----
	1 : 2	9.73	9.85	----
5	PHQ – Fe(III)			
	2 : 1	10.82	11.25	----
	1 : 1	10.20	10.41	10.58
	1 : 2	9.93	10.16	10.27
6	PHQ – Pb(II)			
	2 : 1	8.99	9.09	----
	1 : 1	10.06	10.45	----
	1 : 2	9.66	10.12	----
7	PHQ – Co(II)			
	2 : 1	10.62	10.71	----
	1 : 1	10.72	----	----
	1 : 2	11.00	----	----
8	PHQ – Mg(II)			
	2 : 1	10.38	10.60	----
	1 : 1	10.58	11.17	----
	1 : 2	10.46	11.43	----
9	PHQ – Ca(II)			
	2 : 1	8.88	8.92	8.98
	1 : 1	10.25	10.37	10.86
	1 : 2	10.18	10.40	10.86
10	PHQ – Cd(II)			
	2 : 1	9.00	9.15	9.27
	1 : 1	10.22	10.59	11.21
	1 : 2	10.03	10.49	12.21

4. CONCLUSION

In the present paper protonation constants and complex formation equilibria between poly(8-Hydroxyquinoline) with some transition and heavy metal ions including Al(III), Ca(II), Cd(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) ions have been studied in aqueous solution at 25.0±0.1 ◦C, using glass electrode potentiometrically. The protonation constants of the ligands and formation constants of the resulting complexes were computed from titration data.

The overall protonation constants of ligands and the stability of their metal complexes were calculated from computer refinement of the pH–volume data. The results presented that, some metals such as: Cu(II) , Zn(II) , Ni(II) and Al(III) (for the molar ratio 1 metal : 2 polymer) have one value of the formation constant (log β_1). Other metal ions such as: Fe(III) , Pb(II) , Co(II) and Mg(II) ions give two partial formation constant (log β_1) and (log β_2). Both Ca(II) and Cd(II) have three values of partial formation constant (log β_1), (log β_2) and (log β_3).

5- REFERENCES

1- Ravichandiran, V., Devarajan, V., Masilamani, K.(2011). Determination of ionization constant (pka) for poorly soluble drugs by using surfactants: a novel approach. Der Pharmacia Lettre, 3 (4)183-192.
2- Legget, D. J. (1985). Computational methods for the determination of formation constants, Plenum Press, New York,.
3- Martell, A. E. and Motekaitis, R. J.(1988). VCH, New York.
4- Macca, C. (1990). Linearized multiple standard additions for the potentiometric determination of weak acids. Talanta, 37, 1141-1149.
5- Blanco, M., Coello, J., Gonzalez, F., Iturriaga, H. and Maspoch, S.(1989). Simultaneous determination of metal ions: Spectrophotometric determination of binary, ternary and quaternary mixtures of aluminium, iron, copper, titanium and nickel by extraction with 8-hydroxyquinoline. Anal. Chim. Acta, 226, 271–279.
6- Xun-Cheng Su, Zhi-Fen Zhou and Hua-Kuan Lin.(2001). Novel 8-hydroxyquinoline substituted open chain dioxotetraamine and its metal complexes: Synthesis and property studies in aqueous solution. Indian Journal of Chemistry, 40 A, 533–537.
7- Stevenson, R. L. and Freiser, H.(1976). Tridentate ligands derived from substitution in the methyl group of 8-hydroxyquinaldine. Anal. Chem., 39(12), 1354- 1358.
8- Laurih. J. Lajunen, Roberto Portanov, Juha Piispanen and Marlena Tolazzi.(1997).Hydroxycarboxylic acid complexes with protons and metal ions and the accompanying enthalpy changes- Part I: Aromatic ortho-Hydroxycarboxylic acid. Pure &Appl. Chem., Vol. 69, No. 2, 329-381.
9- Catherine Morlay, Monique Cromer, Yolande Mouginot and Olivier Vittori. (1999). Potentiometric study of Cd(II) and Pb(II) complexation with two high molecular weight poly(acrylic acids); comparison with Cu(II) and Ni(II). Talanta, 48, 1159–1166.
10- Douheret, G. (1975). Medium effects in aqueous organic solvents. Influence of solute on transfer parameters. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 61(2), 228–232.
11- Abd El Wahed, M.G., El Manakhly, K.A., El Kososy, N. (1995). . Physicochemical studies of hydroxyquinoline sulfonic acid and its transition metal complexes. Materials Chemistry and Physics 41, 117-122.
12- Askar, E.I., Shokry, H., Al. Hashmy, D. ,(2010). Potentiometric and conductometric studies of malonyl bis(salicyloylhydrazone) and divalent metal complexes. Journal of Saudi Chemical Society, 14, 175–182.
13- Hamid Reza Rajabi, Marzieyeh Sadat. Niband. (2008). Potentiometric study of binary complexes of methyl 2-pyridyl ketone oxime, phenyl 2-pyridyl ketone oxime and diacetyl monooxime with some transition and heavy metal ions in aqueous solution. Spectro chimica Acta Part A 71, 655–662.
14- Mostafa M. Kamal, Seddique M. Ahmed, Mohamed M. Shahata and Yassien M. Temerk. (2002). Differential Pulse Polarographic (DPP) of Poly (8–Hydroxyquinoline) Matrix. Anal. and Bioanal. Chem., 372, 843 – 848.
15- Ahmed, Seddique M., Shahata, Mohamed M., Kamal, Mostafa M.(2003). Spectrophotometric Studies of the Coordination polymers Based on Poly(8-Hydroxyquinoline) Matrix. J. Inorg. Organomet. Polym. 13, 171-192.
16- Kamal, Mostafa M., El- Sayed, Abd El-Aziz Y., Ahmed, Seddique M., Omran, Ahmed I., Shahata, Mohamed M.(2009). Cation exchange mobility on Poly(8-hydroxyquinoline) matrix. J. Inorg. Organomet. Polym. 19, 501- 506.
17- Mohammed. M. Shahata, Seddique. M. Ahmed and Mostafa M. Kamal. (2013). Cathodic Stripping Differential Pulse Voltammetric Determination of Poly(8–Hydroxyquinoline) Matrix. IJPAC-International Journal of Pure and Applied Chemistry, 8 (3), 209-216.
18- Britton, H.T.S. (1952). “Hydrogen Ions” Fourth Edition.
19- Vogel A. I. (1989). Text book of quantitative inorganic analysis, 5th edn. EIBS – Longman. London, p. 326.
20- Carlo Macca and Merkoci. (1994). Potentiometric characterization of weak acids by multiple sample addition—I. Linear equations and intrinsic performance of the method. Talanta, 41, (12), 2033–2042.
21- Irving, H. and Rossotti, H. S. (1954). The calculation of formation curves of metal complexes from pH titration curves in mixed solvents. J. Chem. Soc., 2904- 2910.

22- Alessandro De Roberties, Concetta De Stefano, Antonio Gianguzza and Silvio Sammartano. (1999). Binding of polyanions by biogenic amines III Formation and stability of protonated spermidine and spermine complexes with carboxylic ligands. Talanta, 48, 119–126.