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Formation Constants and Partial Formation Constants of Some Metal Ions Coordinated with 8–Hydroxyquinoline by Potentiometric Titration

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Abstract
The association equilibria of HQ and HQ–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 HQ was calculated from the average number of protons attached per repeating unit in the HQ (n_A) at different pH values. This value of pK_a which formed was found to be 6.75.The titration curves revealed that the metal ion replaces protons and coordinates to HQ. 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 : 8-quilonol, in solution were computed and the results were discussed. The value of ń and P_L for the metal ions under investigation were calculated at different pH values. The Formation Constant (log β) of the coordinated 8-quilonol based on HQ–Metal ion were computed using ń– P_L system. Mathematical calculations of differential change of ń (Δń) gave a sharp signal for calculations of formation constant. From ń there are partial formation constant (log β_2, log β_3, log $\beta_4$and log β_5) 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 8-Hydroxyquinoline.

1. Introduction

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 complexities. 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 [1-2] 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.

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. [3]. 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.

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],

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

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

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

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

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):

$$K_n = [ML_n] / [ML_{n-1}] [L] \qquad (5)$$

$$\beta_n = [ML_n] / [M] [L]^n \qquad (6)$$

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]:

$$\beta (M_pH_qL_r) = [M_pH_qL_r] / [M]^p [H]^q [L]^r \qquad (7)$$

Negative q-values for [HL 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] :

$$pH^* = pH_{®} - \delta \qquad (8)$$

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 $M(OH)_2L_2$ (LMPKO or PPKO or DMO)[13].

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 (Ka) of PHQ was calculated from the average number of protons attached per repeating unit in the PHQ matrix (nA) at different pH values. This value of pKa which formed was found to be 7.75.[14]

Kamal and co-workers [15-16], 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 constantsfor 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, ($2PHQ:1M^{n+}$) [17-18].

2. Experimental

2.1. Material

8–Hydroxyquinoline (8–HQ) was obtained from Aldrich (chemical co.,US.).

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

2.3.1. Universal Buffer Solutions

A modified universal buffer series derived from that of Britton [19] 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.

2.3.2. 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 [20].

$NaNO_3$ 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:

$$C^{o}V^{o} + CV \tag{9}$$

Increases proportionally to the added volume (V) (note that the same is not true for the concentration, unless $V \ll V^{o}$) . By expressing this amount in terms of its functional relationship to experimental variable, V and $[H^{+}]$, equation (10) is obtained [21]:

$$F = (V^{\circ} + V)([H^{+}] - \frac{K_w}{[H^{+}]})(1 + \frac{[H^{+}]}{K_a}) = C^{o}V^{o} + CV \tag{10}$$

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" [21] 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 substance (such as HQ) 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 (10) will be reduced to the equation:

$$F = (V^{\circ} + V)([H^{+}] - \frac{K_w}{[H^{+}]})(1 + \frac{[H^{+}]}{K_a}) = C\,V \tag{11}$$

Or

$$F = H(1 + \frac{[H^{+}]}{K_a}) = CV \tag{12}$$

Where

$$H = (V^{\circ} + V)([H^{+}] - \frac{K_w}{[H^{+}]}) \tag{13}$$

With moderately weak acids at moderate dilution $\frac{K_w}{[H^{+}]} = [OH^{-}]$ is negligible with respect to $[H^{+}]$, Then , the equation (13) will be reduced to:

$$H = (V^{\circ} + V)[H^{+}] \tag{14}$$

Therefore, equation (11) can, in most instances, be reduced to the approximate form as:

$$F = (V^{\circ} + V)(1 + \frac{[H^{+}]}{K_a}) = CV \tag{15}$$

Equations (11) – (15) 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 (12) can be written as:

$$H[H^{+}] = K_a(CV - H) \tag{16}$$

Therefore, equation (16) 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 (16), for instance, the equation:

$$K_a = \frac{[H^{+}]^2}{\frac{CV}{V^{\circ} + V} - [H^{+}]} \tag{17}$$

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 (11) to obtain different Linear equation of the form:

$$Y = a + b\,X \tag{18}$$

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:

$$(V^{\circ} + V)[H^{+}]^2 = K_a\left\{CV - (V^{\circ} + V)[H^{+}]\ \right\} \tag{19}$$

3.2. Determination of the pK_a of 8-Hydroxyquinoline (HQ)

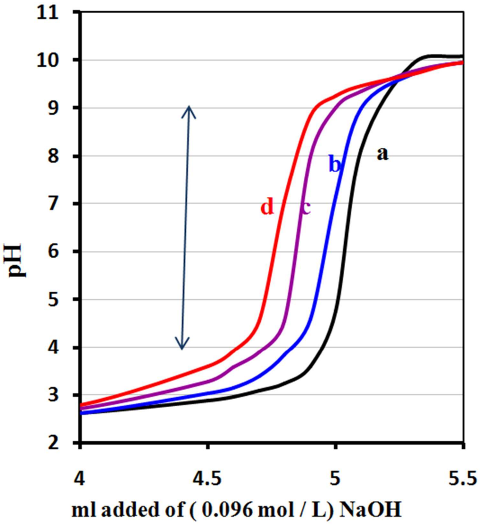

Fig. 1. *Potentiometric titration curves of strong alkali (NaOH) for different concentration of HQ as : a) 0.5, b) 1.0, c) 2.0, and d) 2.5 m mol L^{-1}, respectively.*

Different concentration of HQ 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 6.50. It can be calculated that the pK_a for each concentration of 0.5, 1.0, 2.0 and 2.5 mM of HQ gave pK_a values. From these curves, it can be concluded that, the value of pK_a is not depend (±0.20) on the concentration of HQ.

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 substance under investigation, HQ) was calculated at different pH values given by [22]:

$$n_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V_o + V_1)(T_{cL^\circ})} \tag{20}$$

Where

Y : is the number of dissociable protons in HQ,

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 ofmineral acid (HNO_3) and (HNO_3 + HQ) solutions, respectively.

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

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–HQ formation curves obtained by plotting $n_A$vs. pH is represented in Fig.2.

The value of log K_1^H , the first proton 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 6.75.

The plotting of the differential of the average number of protons associated with HQ,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.

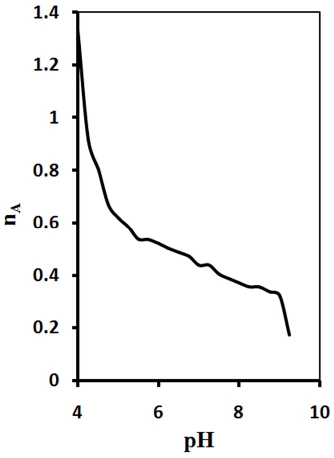

Fig. 2. Variation of the average number of protons associated (n_A) for HQ vs. pH

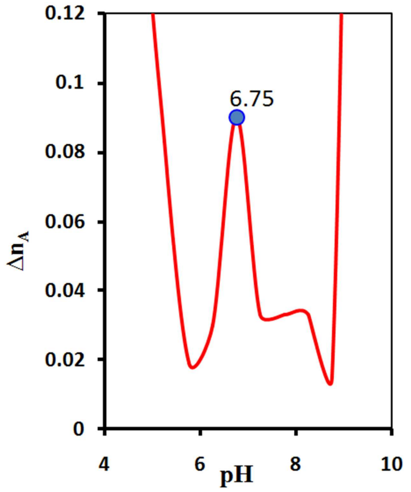

Fig. 3. Variation of the first derivatives of n_A (Δn_A) for HQ vs. pH.

3.4. Potentiometric Titration Studies of HQ–Coordinated with Some Metal IONS

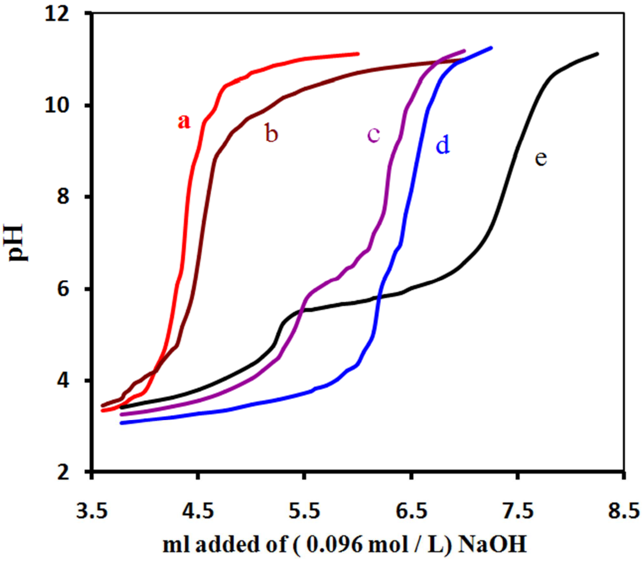

Fig. 4. Potentiometric Titration Curves of HQ–Cu(II) system curves as: a) Free mineral acid (HNO_3), b) HNO_3 + HQ (0.1 m mol L^{-1}), c) b + Cu(II) [1 M^{n+} : 2 HQ], d) b + Cu(II) [1 M^{n+} : 1 PHQ], and e) b + Cu(II) [2 M^{n+} : 1 PHQ].

The potentiometric titration technique was also employed for the determination of the formation constant (log β) of HQ–metal complexes consisted of the pH–metric titration curves of HQ in the absence and presence of metal ion (M^{n+}) under investigation. Thus, the formation constant of binary metal ion – polymer (M–HQ) complex was determined by the titration carried out using different molar ratios of the concentration of metal ions and/or 8- quilonol 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 HQ (HQ : 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 – HQ complex than the HQ alone. This indicates that the strong interaction between each of the metal ions with HQ 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 HQ and formation of the complex (HQ – 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 HQ–Cu(II) system is shown in Fig.4.

Titration curves for some metal ions system, HQ - 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 8-Hydroxyquinoline titration curves (curves b), which also separated from the HQ–metal titration curves due to the alkali consumed for metal–8quinolinol interaction. The different molar ratio curve is curve c which represent HQ - M^{n+} with molar ratio (1 M^{n+} : 2 HQ), curve d for (1M $^{n+}$: 1 HQ) and curve e for (2 M^{n+} : 1 HQ).

3.5. Determination of the Association Constant (pK$_a$) of HQ–Coordinated with Some Metal Ions

The metal–polymer stability constant (log β) were estimated from the analysis of the curves drown between ńand P_L relationship where ń, is the average number of ligand (HQ) attached per metal ion (M^{n+}) and calculated by this equation [22] :-

$$\bar{n} = \frac{(V_3 - V_2)(N° + E°)}{(V_o + V_2) n_A T°_{CM}} \tag{21}$$

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

$$P_L = \frac{1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_j [H^+]^j}{T°_{CL} - \bar{n} T°_{CM}} \cdot \frac{V_o + V_3}{V_o} \tag{22}$$

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), ligand (HQ) + mineral acid and the mineral acid + ligand + metal in potentiometric titration, respectively. The values of ń and P_L for the metal ions under investigation were calculated at different pH values.

From the relation betweenńvs pH as seen in (Fig. 5 a), the half of raising portions which corresponding to the pH value, give the pK$_a$ value for HQ.

This value of pH can determine exactly from First–derivatives treatment ofń (Δ ń), (Fig. 5 b) by the relation of signal vs pH (The differential of ńvalues for constant values of pH) the peak give the certain point of pH value corresponding to pK$_a$.

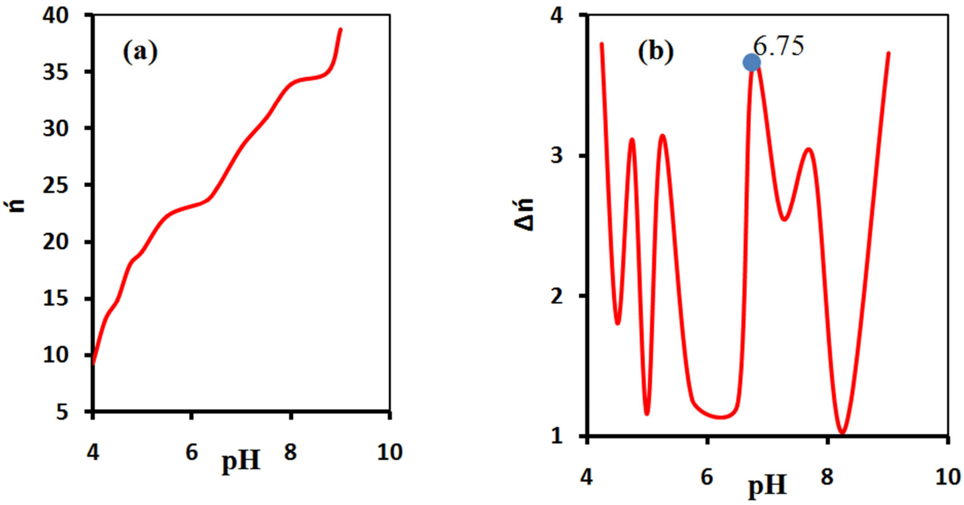

Fig. 5.(a) Variation of the average number of ligand(HQ) attached per metal ion (ń) vs. pH, for HQ-Cu(II) system and (b) first derivative of (a) as (Δ ń) vs. pH.

The values of ń and P_L for the metal ions under investigation were calculated at different pH values. The plots of ń values against P_L were drawn for the solution containing molar ratio 1 : 2, 1 : 1 and 2 : 1(Metal M^{n+}: Ligand HQ) 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 ńand P_L for the metal ions under investigation were calculated at different pH values.

3.6. Determination of the Formation Constants (log β) of HQ–Coordinated with Some Metal Ions Based on (Δń) vs. P$_L$ System

A plotting of Δ ń against P_L ($\Delta P_L = 0.5$), this plotting is advantages thanńvs. 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 Ligand–metal interaction by the number of maxima could be formed. The curves of Δ ń vs P_L for M^{n+} – HQ with the molar ratio (1 : 2, 1 : 1 and 2 : 1) 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 $\beta_{p\,q}$) refers to the reaction [23] as:

$$_{p}M^{j+} + L^{z-} + {}_{q}H^{+} = M_{p}LH_{q}^{(j+p-z)} \tag{23}$$

The results presented that, some metals (for the molar ratio 1 metal : 2 ligand) give two species such as: Ca(II) , Zn(II) , Ni(II) and Fe(III) then have two value of the partial formation constants (log β_1 and log β_2), for example as shown in (Fig. 6 a and b).

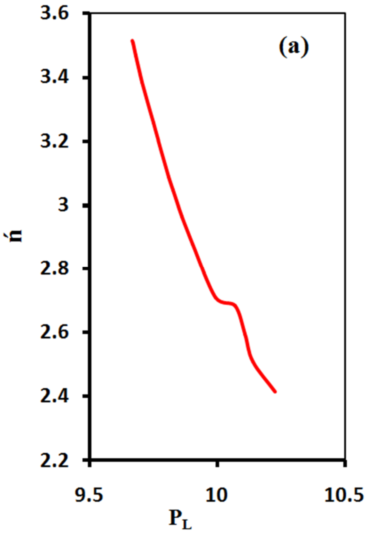

Fig. 6. a). *ń vs P_L of HQ - Fe(III) system, (2 : 1)*

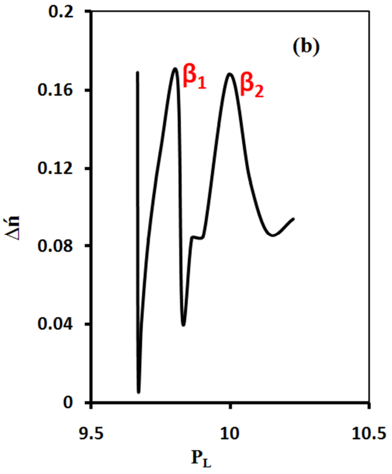

Fig. 6. b). *Δń vs P_L of HQ-Fe(III) system,(2 : 1)*

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

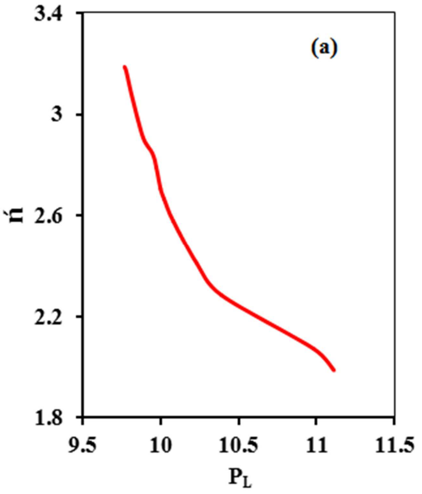

Fig. 7. a). *ń vs PL of HQ-Al(III) system, (2:1)*

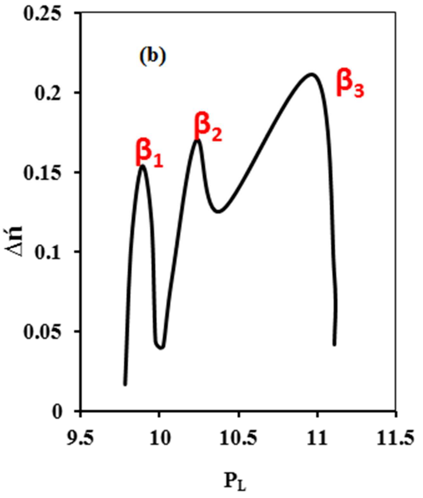

Fig. 7. b). *Δń vs P_L of HQ-Al(III) system, (2:1)*

Both Cu(II) and Pb(II) give four species then have four values of partial formation constant (logβ_1, log β_2, log β_3 and log β_4) respectively, for example as shown in (Fig. 8 a and b).

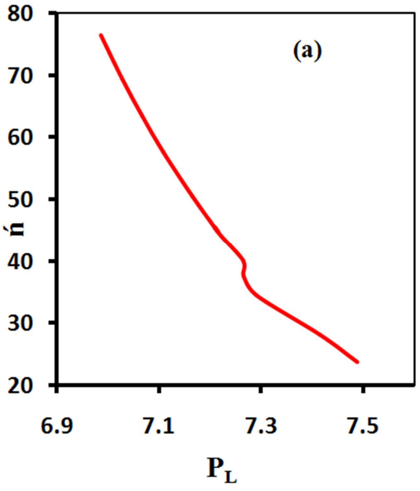

Fig. 8. a). *ń vs P_L of HQ-Pb(II) system,(2:1)*

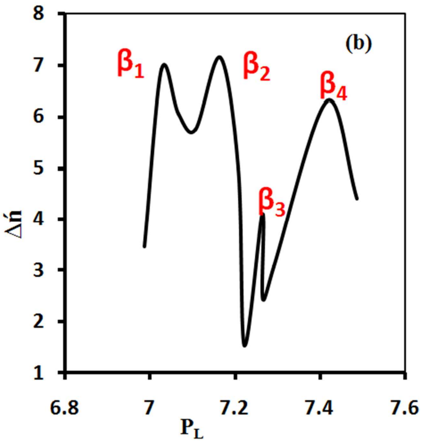

Fig. 8. b). *Δń vs P_L of HQ-Pb(II) system,(2 : 1)*

While, Cd(II) give five species then have five values of partial formation constant (logβ_1, logβ_2, log β_3, log β_4 and log β_5) respectively, for example as shown in (Fig. 9 a and b).

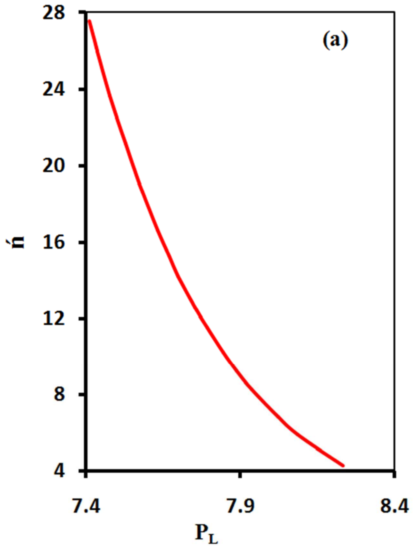

Fig. 9. a). *ń vs P_L of HQ-Cd(II) system,(2 : 1)*

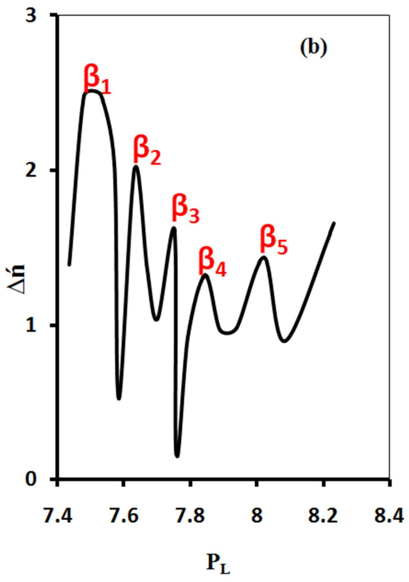

Fig. 9. b). *Δń vs P_L of HQ-Cd(II) system,(2:1)*

Also, The curves of Δ ń vs P_L for M^{n+} – HQ with the molar ratio (1 : 1 and 2 : 1) were studied andthe all values of the formation and partial formation constants for HQ – M^{n+} were listed in Table 1

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

No	**M Ions**	**Ratio M : HQ**	**M-HQ**				
			β_1	**β_2**	**β_3**	**β_4**	**β_5**
1	Ca(II)	1 : 2	9.45	10.06			
		1 : 1	9.434	9.71			
		2 : 1	8.934	9.12	9.397		
2	Zn(II)	1 : 2	9.73	9.95			
		1 : 1	10.74				
		2 : 1	10.03				
3	Fe(III)	1 : 2	9.81	10			
		1 : 1	9.376	9.534	9.793	9.96	
		2 : 1	9.247	9.339			
4	Ni(II)	1 : 2	9.95	10.1			
		1 : 1	10.25	10.987			
		2 : 1	10.023	10.86			
5	Al(III)	1 : 2	9.89	10.23	10.98		
		1 : 1	9.349	9.426	9.552		
		2 : 1	9.027	9.132			
6	Co(II)	1 : 2	9.59	9.66	9.69		

No	M Ions	Ratio M : HQ	M-HQ				
			β_1	β_2	β_3	β_4	β_5
		1 : 1	10.127	10.419	10.845		
		2 : 1	10.031				
7	Mg(II)	1 : 2	8.88	9.07	9.37		
		1 : 1	9.016	9.28	9.907		
		2 : 1	8.88	9.12	9.585	9.917	
8	Cu(II)	1 : 2	8.35	8.43	8.54	8.65	
		1 : 1	8.443	8.497	8.655		
		2 : 1	8.228	8.397	8.564		
9	Pb(II)	1 : 2	7.03	7.17	7.27	7.42	
		1 : 1	8.384	8.56	8.74	8.898	
		2 : 1	8.63	8.734	8.92	9.6778	
10	Cd(II)	1 : 2	7.5	7.63	7.75	7.85	8.02
		1 : 1	8.858	8.667	8.755	8.935	9.142
		2 : 1	8.752	8.825	8.913	9.0	9.242

4. Conclusion

In the present paper protonation constants and complex formation equilibria between 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: Ca(II) , Zn(II) , Ni(II) and Fe(III) (for the molar ratio 1 metal : 2 ligand) have two values of the formation constants log $\beta_1$and log β_2. Other metal ions such as: Al(III) , Co(II), and Mg(II) ions give three partial formation constants (log β_1, log β_2 and log β_3. Both Cu(II) and Pb(II) have four values of partial formation constants log β_1, log β_2, log β_3 and log β_4. While, Cd(II) have five values of partial formation constants (logβ_1, logβ_2, log β_3, log β_4 and log β_5).

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