Potentiometric and thermodynamic studies of N, N'-bis(4-hydroxyacetophenone) ethylenediamine and its Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Mn^{2+} complexes

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Abstract: Studying the stability constants of metal complexes offers significant insights into their applications in analytical chemistry, pharmaceuticals, catalysis, environmental science, and material science. The protonation constants of N, N'-bis(4-hydroxyacetophenone) ethylenediamine (BHAEN) and the stability constants of a number of transition metal complexes have been studied potentiometrically at 20, 25, 30 and 40ºC, in water solution at 0.1 M ionic strength (KNO_3), using the mole ratios (1:1) and (2:1), (L:M), where M = Cu^{2+}, Ni^{2+}, Co^{2+} , Fe^{3+}, and Mn^{2+}. The calculations are performed by operating the computer program SUPERQUAD. From the values of the stability constants of the complexes at the different four temperatures, the thermodynamic functions G, H and S were evaluated. The order of stability of the complexes agrees the Irving - Williams order. The positive values of H for the BHAEN complexes, especially for the most stable complexes species, (ML) in the case with Cu(II) and Fe(III), (MHL) in the case of Ni(II) & Co(II) and (ML_2) in the case of Mn(II), reveal that the stability of these species is mainly due to the S values which are highly positive.

Key words: Potentiometric Titrations – Stability Constants – Complexes – Schiff bases.

دراسات الجهدية والحرارية الديناميكية لـ N، N'-bis(4-hydroxyacetophenone) ethylenediamine ومجمعاته Cu^{2+} وNi^{2+} وCo^{2+} وFe^{3+} وMn^{2+}

الملخص: إن دراسة ثوابت استقرار المركبات المعدنية تقدم رؤى مهمة في تطبيقاتها في الكيمياء التحليلية والمستحضرات الصيدلانية والحفز والعلوم البيئية وعلوم المواد. تمت دراسة ثوابت بروتونات N و-N'-bis(4-hydroxyacetophenone) ethylenediamine (BHAEN) وثوابت استقرار عدد من مركبات المعادن الانتقالية بطريقة جهدية عند 20 و 25 و 30 و 40 درجة مئوية، في محلول مائي بقوة أيونية 0.1 M (KNO_3)، باستخدام النسب المولية (1:1) و(2:1)، (L:M)، حيث M = Cu^{2+} و Ni^{2+} و Co^{2+} و Fe^{3+} و Mn^{2+}. يتم إجراء الحسابات عن طريق تشغيل برنامج الكمبيوتر SUPERQUAD. من قيم ثوابت استقرار المركبات عند أربع درجات حرارة مختلفة، تم تقييم الدوال الديناميكية الحرارية G و H و S. يتوافق ترتيب استقرار المركبات مع ترتيب إيرفينج - ويليامز. إن القيم الإيجابية لـ H لمجمعات BHAEN، وخاصة بالنسبة لأكثر أنواع المجمعات استقرارًا، (ML) في حالة Cu(II) وFe(III)، و (MHL) في حالة Ni(II) و Co(II) و (ML_2) في حالة Mn(II)، تكشف أن استقرار هذه الأنواع يرجع بشكل أساسي إلى قيم S التي تعتبر إيجابية للغاية.

1. Introduction

Schiff-base ligands have performed a significant role in the evolution of contemporary coordination chemistry, Because of their importance in a variety of interdisciplinary study domains,[1]

particularly as corrosion inhibitors,[2] catalysts for activation of small molecules[3-4] and in biological systems.[5-12] These wide applications of Schiff bases have generated a great deal of interest in metal complexes, kinetics of formation and hydrolysis as well as electronic spectra and acidity constants. Tetradentate Schiff bases, especially those with a N_2O_2 donor set, resulting from the condensation of aliphatic diamines such as ethylenediamine or derivatives with Acetylacetone or salicylaldehyde, have been extensively studied.[13] In view of recent interest in the energetics of metal ligand binding in metal chelates involving N, O donor ligands[14] we started to study Schiff base complexes derived from N,N'-bridged tetradentate ligands involving an N_2O_2 donor atoms.

Equilibrium studies for salicylaldimines are in general scarce due mainly to their insolubility in water which is the most common solvent for potentiometric determination of stability constants.[13] The majority of the thermodymanic data reported on stability constants and/or protonation constants of Schiff bases are related to bidentate bases with a NO donor set mainly derived from salicylaldehydes or benzaldehydes or their derivatives, anilines or substituted anilines. Tetradentate Schiff bases have been less studied. The stability constants for the Cu(II), Ni(II) and Fe(III) complexes of the tetradentate H_2salen have been reported[15] in DMSO–water 80:20 wt./wt. Martell et al. also carried out studies of H_2salen in dioxane–water 70:30 v/v in order to determine the oxygenation constants of the complex Co(salen) which can reversibly bind molecular oxygen.[16]

The present work reports the results of potentiometric investigation on BHAEN and its complexes of Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{2+}. The potentiometric method is used to determine the protonation constants of the free ligand as well as the stoichiometries and the stability of its complexes in the appropriate solutions and with the two mole ratios, (1:1) and (2:1), (L:M). The computer program SUPERQUAD is used to evaluate these constants. To study the effect of temperature on the stability of these complexes, the determination of the stability constants of these complexes is carried out at four different temperatures, 20, 25, 30 and 40°C and from the data obtained, the thermodynamic functions G, H and S are evaluated.

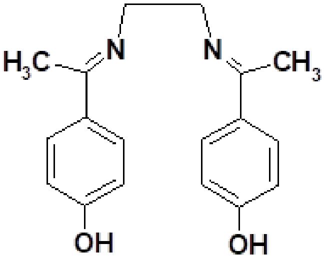
2. Experimental

Materials and Solutions. Ethylenediamine (B.P.=118°C) and 4-hydroxyacetophenone (M.P. = 95-97°C) were Prolabo and Fluka products. All other reagents used were of analytical grade (Merck, Darmstadt, Germany). Carbonate free KOH was prepared in double-distilled water, and standardized potentiometrically with potassium hydrogen phthalate solution. 1M KNO_3 solution was prepared in double-distilled water. Stock solutions of the metal salts, were prepared in double-distilled water and standardized by complexometric EDTA titration.[17] Stock solutions of the studied ligands (0.01 M) were prepared by dissolving an appropriate amount of a given ligand in double-distilled water.

Preparation of N, N'-bis(4-hydroxyacetophenone) ethylenediamine (BHAEN).
BHAEN was prepared as already described in [18].

Instruments. The potentiometric measurements were performed with Metrohm 702 SM Titrino, Metrohm Ltd. CH-9101 Herisou, Switzerland. The titrino was supplied by 727-titration stand, with built-in magnetic stirrer.

The electrode, combined pH glass electrode, was calibrated using aqueous standard buffers of pH 4.0 and 7.0 at 20, 25, 30 and 40ºC. The titrations were performed in a double-wall glass cell through the outer jacket of which water circulated from a controlled temperature bath. The temperature was controlled with the thermostat Digiterm100, J. P. Selecta, S. A., Barcelona, Spain, with a temperature uncertainty of (0.1 °C).



BHAEN

Computer Programs. VESUV, Verification Support for Validation, is PC software for Metrohm titrators allowing the optimal cooperation between the titrino and PC. SUPERQUAD 91, the calculations on the pH-metric data were performed with the aid of the SUPERQUAD[19] computer program.

Potentiometric measurements. The following mixtures were prepared for the determination of the protonation constants of BHAEN and titrated against standard CO_2-free potassium hydroxide (0.094 M) solution. (i) (6×10^{-3} M) HNO_3 + (3×10^{-3} M) L, (ii) (4×10^{-3} M) HNO_3 + (2×10^{-3} M) L and (iii) (2×10^{-3} M) HNO_3 + (1×10^{-3} M) L. The total volume was kept at 50 ml in each case and the temperature was adjusted at the desired temperature. For the determination of the stability constants of the metal complexes of BHAEN, the following mixtures were prepared and titrated against standard CO_2-free potassium hydroxide (0.094 M) solution. For the mole ratio (1:1) ligand-metal (L-M*). (a) (4×10^{-3} M) HNO_3, (b) (4×10^{-3} M) HNO_3 + (2×10^{-3} M) L and (c) (4×10^{-3} M) HNO_3 + (2×10^{-3} M) L + (2×10^{-3} M) M*. For the mole ratio (2:1), ligand-metal. (d) (8×10^{-3} M) HNO_3, (e) (8×10^{-3} M) HNO_3 + (4×10^{-3} M) L and (f) (8×10^{-3} M) HNO_3 + (4×10^{-3} M) L + (2×10^{-3} M) M*. The total volume was adjusted to 50 ml by adding double-distilled water in each case. The titration curve obtained from (a) or (d) is a calibration curve for the electrode system; it provides data used to calculate the standard electrode potential, E_o, and the dissociation constant for water. These values were used to calculate the hydrogen ion concentration from potential readings.[20]

3. Results and discussion

Proton – Ligand (BHAEN) equilibria. Protonation constants of BHAEN, which may be considered as a triprotic acid H_3L^+, were determined. The potentiometric titration curves of BHAEN using the different concentrations at 25°C are presented in the Figures 1. The titration curves showed two inflections. The first inflection indicates the neutralization of the excess hydrogen ions, whereas the second inflection indicates the formation of different deprotonated species. Since there are four protonation sites (two phenolic groups and two tertiary amine groups) for BHAEN, models with LH_n (n = 1 – 4) were tried for refinement process. But the best-fit model gave only for three protonated species (H_3L^+, H_2L and HL^-) in the experimental pH region.

The equilibrium reactions for protonation constants are proposed by the following equation (charges are omitted for simplicity):

$$L + nH = H_nL, \qquad \beta_n = (H_nL) / (L)(H)^n \qquad (1)$$

Differences between the various log β values give the stepwise protonation constants K_n^H defined by equations (2 - 4)

$$H^+ + L^{2-} \rightleftharpoons HL^{-1} \qquad K_1^H = (HL^{-1})/(H^+)(L^{2-}) \qquad (2)$$

$$H^+ + HL^{-1} \rightleftharpoons H_2L \qquad K_2^H = (H_2L)/(H^+)(HL^{-1}) \qquad (3)$$

$$H^+ + H_2L \rightleftharpoons H_3L^+ \qquad K_3^H = (H_3L^+)/(H^+)(H_2L) \qquad (4)$$

The first two protonation constants obtained in the experimental region may be assigned to the phenolic protons as their values, and the pH range (5 - <10) in which they exist, are in agreement with the protonation constants of other phenols. [21-22] And the third protonation constant may be assigned to one of the imine groups.

	(21)	**(22)**	**Present work**
Log K_1^H	**8.20**	**8.62**	**8.57**
Log K_2^H	**7.45**	**7.36**	**7.74**

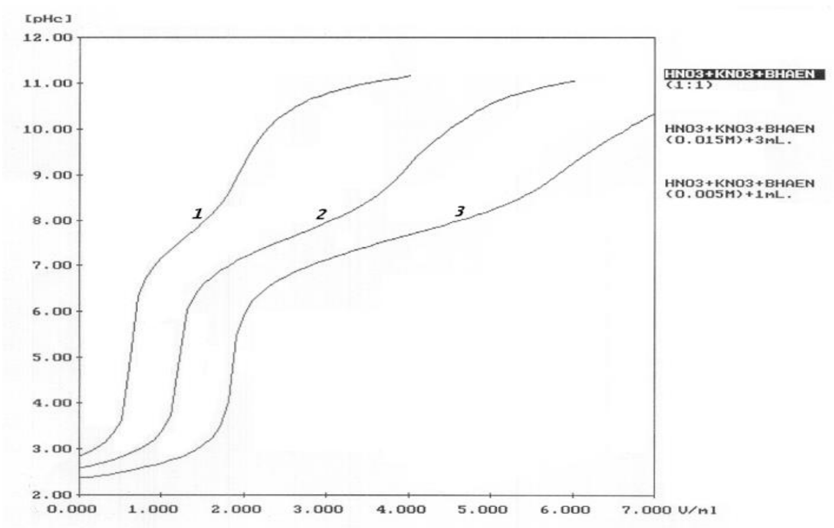
The protonation constants are reported in Table 1, where the highest values were found to be at 40°C indicating that the protonation reactions are favorable at high temperature.

Table 1. Protonation constants (log β's) of BHAEN

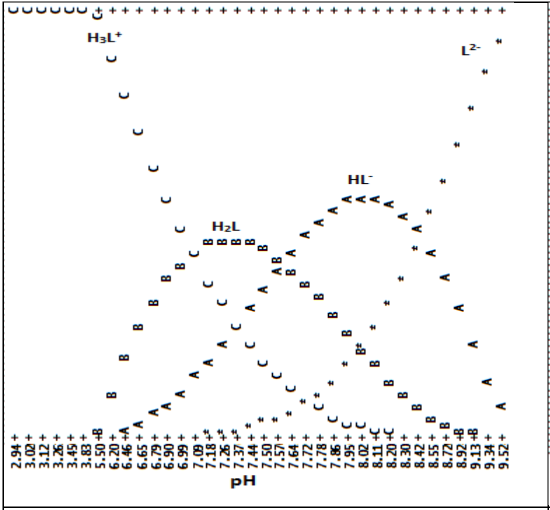
	H: L	***20°C***	***25°C***	***30°C***	***40°C***
The mean values of log β's	**HL**	**8.343 (0.029)**	**8.571 (0.028)**	**8.536 (0.023)**	**8.619 (0.025)**
	H_2L	**16.007(0.023)**	**16.318(0.023)**	**16.291(0.020)**	**16.528(0.023)**
	H_3L	**23.111(0.033)**	**23.457(0.033)**	**23.359(0.028)**	**23.581(0.031)**

*(Standard deviations are given in parentheses)

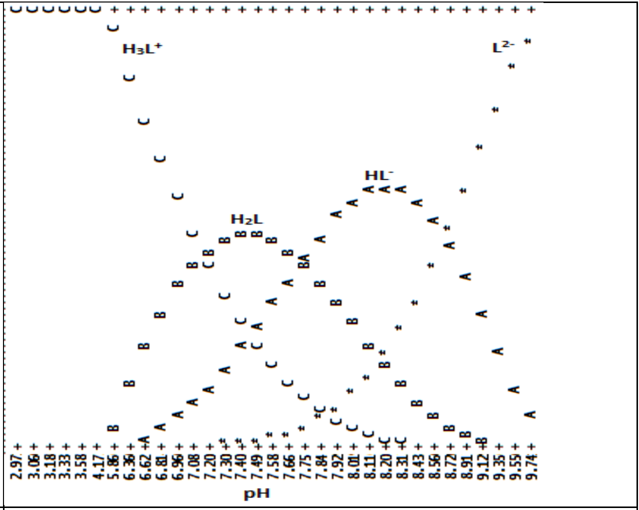
The concentration distribution of various species formed in solution (formation %) as a function of pH was obtained by the use of the SUPERQUAD 91 program throughout the present work. The species distribution diagrams for BHAEN based on the fitted equilibrium constants, Figures 2-5, indicate that at lower pH values, the only existing species is H_3L^+ at all the temperatures studied, whereas in the pH range ≈ 5 – 9.7 the species H_2L, HL^- and L^{2-} coexist. The species H_2L starts at pH ≈ 5.5, 5.9, 6 and 4.9 at 20, 25, 30, and 40ºC, respectively, and then increases rapidly attains a maximum value (≈ 50%) at pH ≈ 7.4 at all the temperatures studied and then decreases gradually with the increasing of the species HL^- which started at pH ≈ 6.5. The concentration of the species HL^- increases with the increasing of the pH reaches a maximum (≈ 60%) at pH ≈ 8.2 and then decreases with the increasing of L^{2-} species.



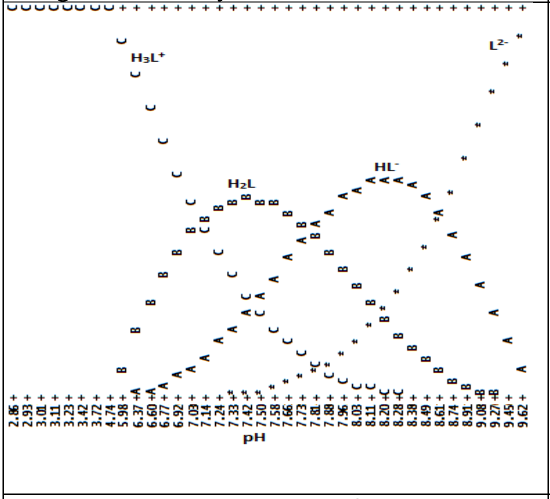
etric titration curve of H+/ BHAEN system at 25ºC: (1) BHAEN (0.005M), (
N (0.01M), (3) BHAEN (0.015M).



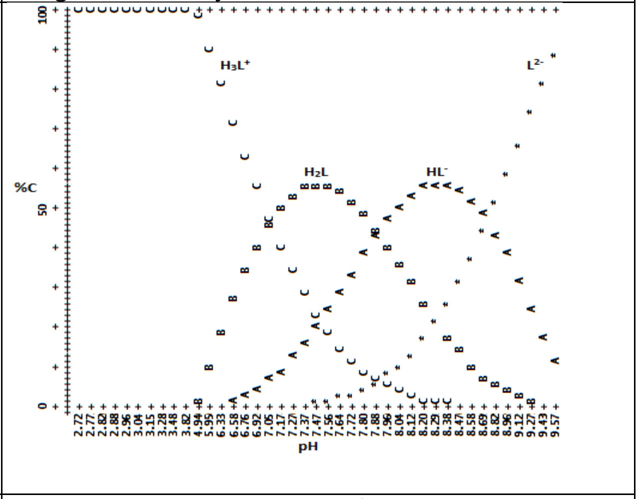
n diagram for the system H^+-L^{-2} at 20° C



n diagram for the system H^+- L^{-2} at 25°C

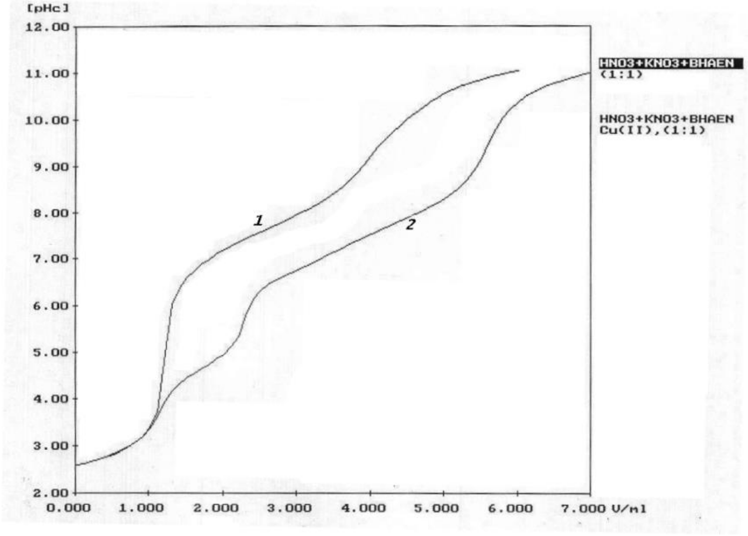


n diagram for the system H^+-L^{-2} at 30°C

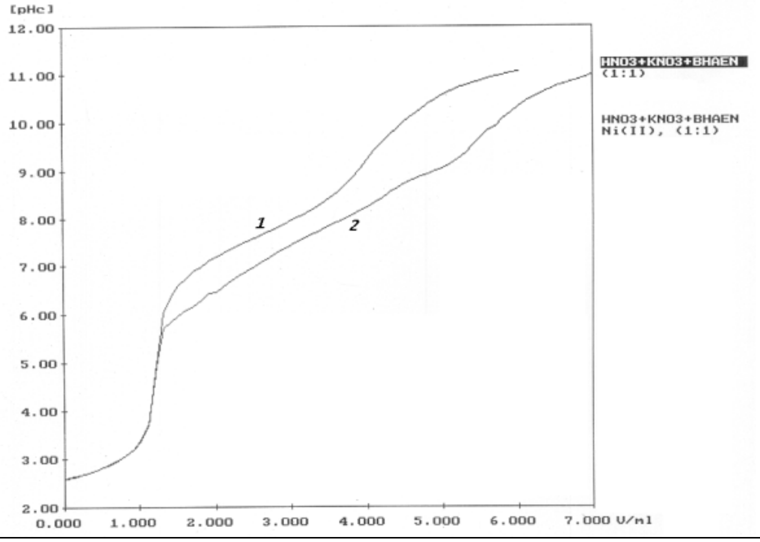


n diagram for the system H^+- L^{-2} at 40°C

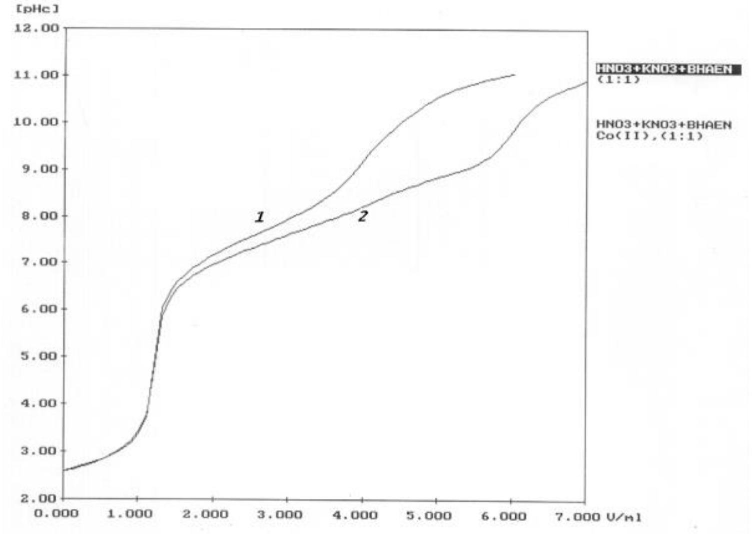
Stability constants of the complexes. The stoichiometries and stability constants of M – BHAEN complexes, using the molar ratios 1:1 and 2:1, (L:M), at the four different temperatures 20, 25, 30, and 40°C and under the conditions described in the experimental part are reported in Table 2. A number of models were examined in sequence using the SUPERQUAD 91 program and the reported stability constants are for the best models examined. A displacement was noticed in each curve of the titration curves for M– ligand mixtures, Figures 6-10, compared with that for the free ligand. This indicates the release of protons, which in turn depends on the reaction between the ligand and M ion.



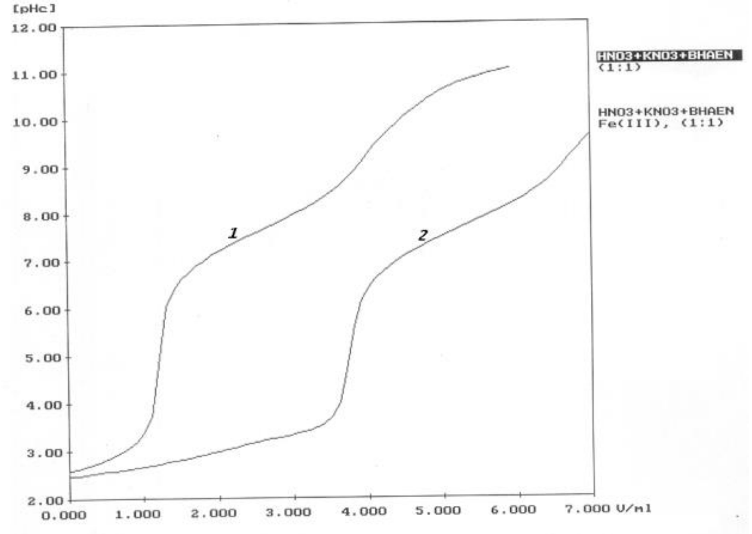
etric titration curves of Cu^{2+}/BHAEN system at 25ºC: (1) BHAEN, (2) Cu^{2+}/ B
x



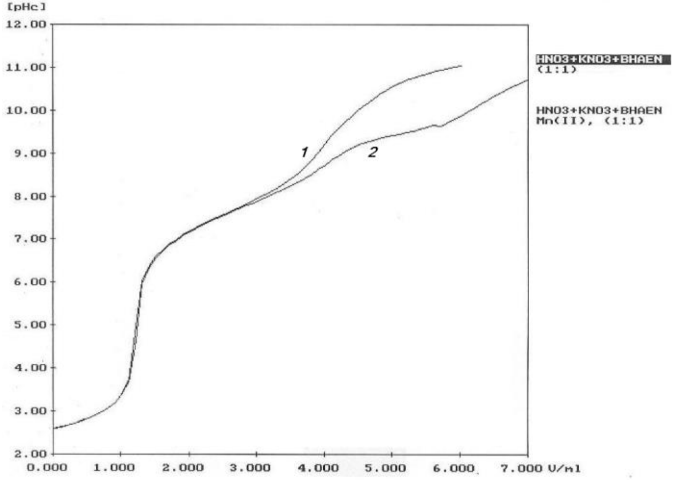
etric titration curves of Ni^{2+}/BHAEN system at 25ºC: (1) BHAEN, (2) Ni^{2+}/B
x



etric titration curves of Co^{2+}/BHAEN system at 25ºC: (1) BHAEN, (2) Co^{2+}/
x



etric titration curves of Fe^{3+}/BHAEN system at 25ºC: (1) BHAEN, (2) Fe^{3+}/
x



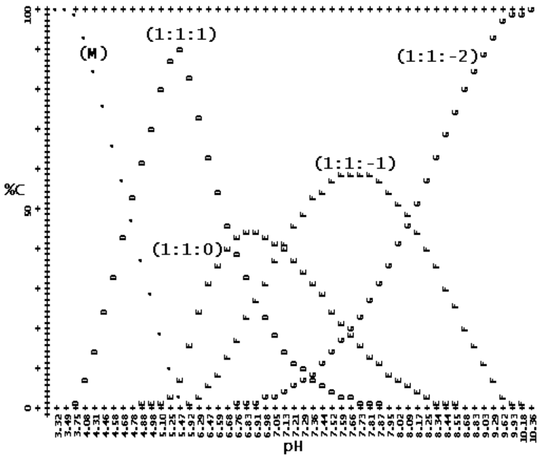
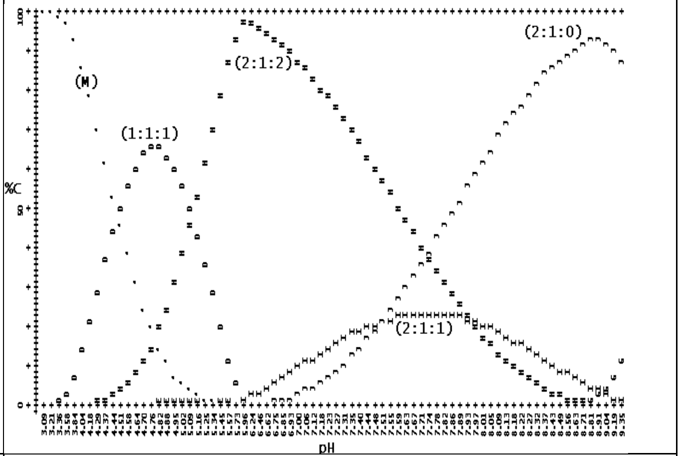
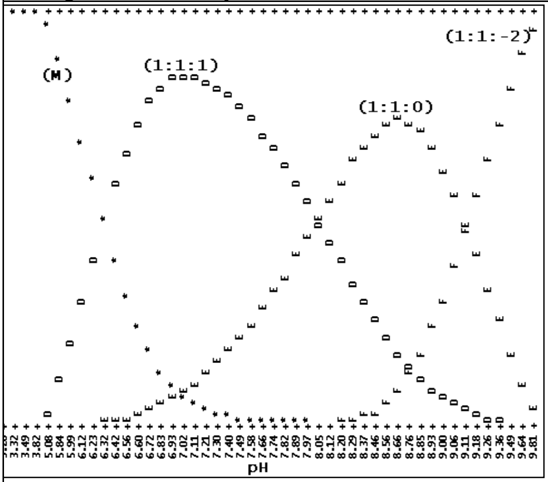
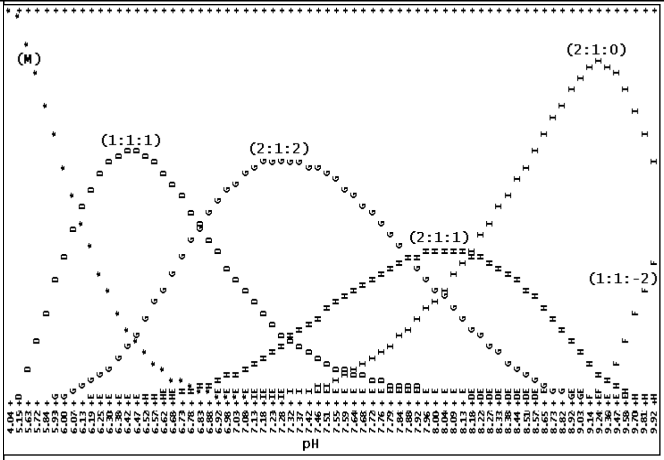
**metric titration curves of Mn^{2+}/BHAEN system at 25ºC: (1) BHAEN, (2) Mn^{2+}/B
x**

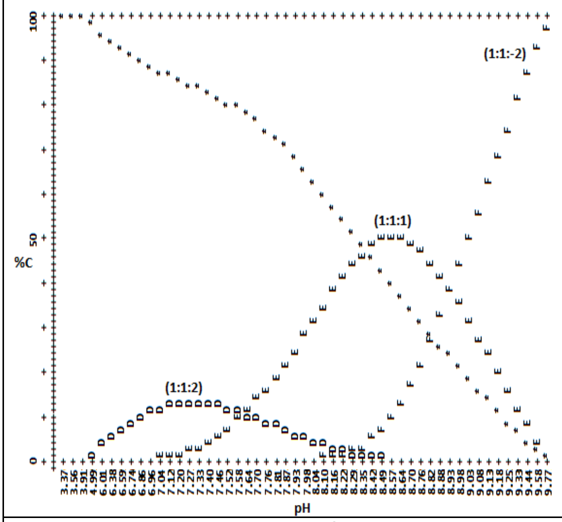
Table 2. The stoichiometries and stability constants (log$_s$) for the metal complexes.

Stoichiometry (L:M:H)	Stability Constants (log□’$_s$) 20ºC	25ºC	30ºC	40ºC
Copper(II) complexes				
1:1:1	16.757(0.039)	16.792(0.032)	16.956(0.025)	17.247(0.026)
1:1:0	9.961(0.088)	10.062(0.092)	10.286(0.077)	10.758(0.072)
1:1:-1	2.877(0.072)	2.917(0.098)	3.286(0.079)	3.887(0.088)
1:1:-2	-5.005(0.109)	-5.206(0.149)	-4.683(0.128)	-4.179(0.141)
2:1:2	31.974(0.053)	32.412(0.019)	32.622(0.021)	33.091(0.033)
2:1:1	-----	24.459(0.061)	24.664(0.062)	25.364(0.090)
2:1:0	17.150(0.083)	16.935(0.028)	17.172(0.029)	17.614(0.051)
2:1:-2	0.899(0.107)	-----	-----	-----
Nickel(II) complexes				
1:1:1	13.104(0.153)	13.584(0.033)	13.867(0.027)	14.186(0.031)
1:1:0	6.807(0.076)	5.539(0.071)	6.104(0.051)	6.119(0.048)
1:1:-2	-11.385(0.079)	-12.741(0.101)	-11.710(0.065)	-11.441(0.049)
2:1:2	------	25.994(0.038)	26.744(0.051)	27.292(0.035)
2:1:1	18.989(0.107)	18.099(0.081)	19.099(0.086)	19.359(0.041)
2:1:0	10.659(0.134)	9.921(0.037)	10.135(0.054)	10.007(0.089)

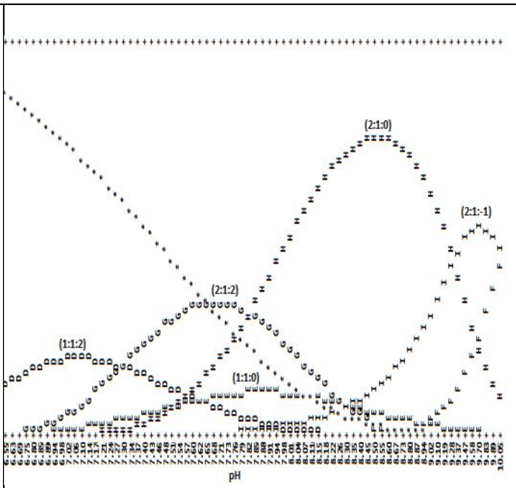
Cobalt(II) complexes				
1:1:2	**------**	**18.548(0.159)**	**18.945(0.066)**	**19.226(0.034)**
1:1:1	**11.457(0.081)**	**------**	**11.466(0.033)**	**11.517(0.048)**
1:1:0	**------**	**3.300(0.101)**	**3.752(0.066)**	**3.557(0.083)**
1:1:-2	**-14.917(0.059)**	**-14.559(0.092)**	**-13.990(0.072)**	**-14.086(0.079)**
2:1:2	**------**	**23.032(0.019)**	**23.775(0.028)**	**22.990(0.054)**
2:1:1	**------**	**------**	**------**	**14.937(0.062)**
2:1:0	**7.597(0.0344)**	**7.378(0.0230)**	**7.905(0.036)**	**6.915(0.026)**
2:1:-1	**-0.833(0.0279)**	**-1.941(0.041_**	**-1.008(0.098)**	**------**
2:1:-2	**-9.452(0.0581)**	**------**	**------**	**------**
Iron(III) complexes				
1:1:1	**19.310(0.105)**	**19.631(0.080)**	**19.607(0.118)**	**19.904(0.148)**
1:1:0	**16.028(0.034)**	**16.295(0.035)**	**16.740(0.023)**	**17.383(0.019)**
2:1:4	**45.514(0.084)**	**-----**	**------**	**-----**
2:1:2	**-----**	**36.009(0.099)**	**36.708(0.077)**	**37.530(0.092)**
2:1:0	**20.761(0.121)**	**22.115(0.099)**	**22.934(0.097)**	**22.931(0.107)**
Manganese(II) complexes				
1:1:-1	**-----**	**-4.682(0.04)**	**-4.913(0.043)**	**-4.891(0.150)**
2:1:2	**-----**	**-----**	**-----**	**22.506(0.022)**
2:1:0	**5.172(0.153)**	**5.364(0.113)**	**5.545(0.117)**	**6.478(0.044)**
2:1:-2	**-12.322(0.150)**	**-----**	**-----**	**-----**

The concentration distribution of various complex species formed in solution (formation %) as a function of pH was obtained by means of the SUPERQUAD 91 program. The distribution diagrams for the systems M / BHAEN and M / 2BHAEN based on fitted stability constants at the four different temperatures are depicted in Figures 11- 19.

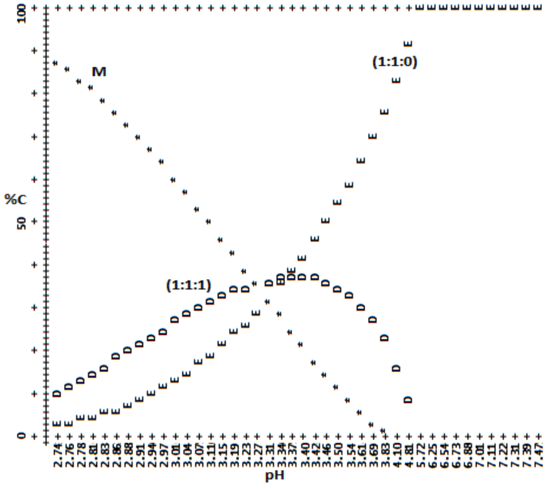
	
n diagram for the system Cu^{2+}/BHAEN at 25ºC	**n diagram for the system Cu^{2+}/2BHAEN at 25ºC**
	
n diagram for the system Ni^{2+}/BHAEN at 25ºC	**n diagram for the system Ni^{2+}/2BHAEN at 25ºC**



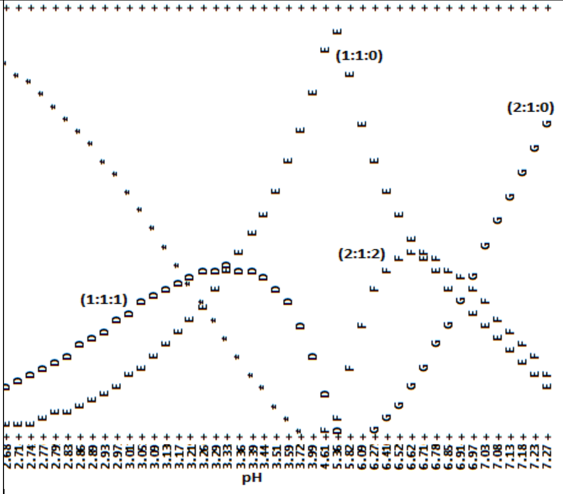
n diagram for the system Co^{2+}/BHAEN at 25ºC



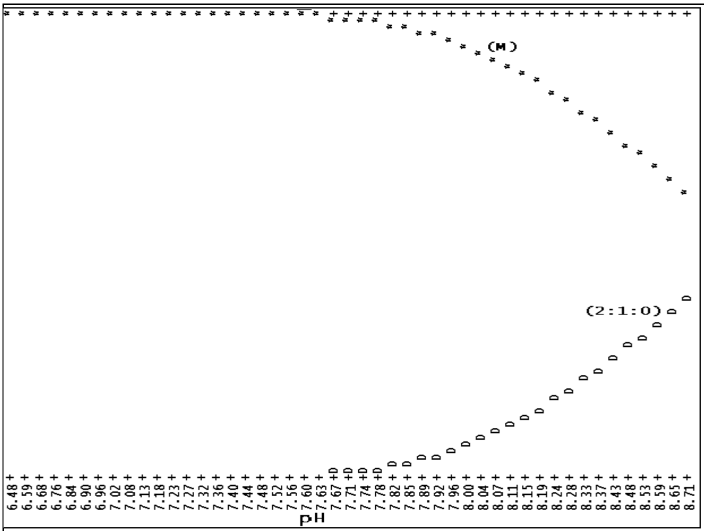
n diagram for the system Co^{2+}/2BHAEN at 25ºC



n diagram for the system Fe^{3+}/BHAEN at 25ºC



n diagram for the system Fe^{3+}/2BHAEN at 25ºC



n diagram for the system Mn^{2+}/2BHAEN at 25ºC

Enthalpies and entropies of protonation of BHAEN

From Arrhenius plots of $\log K_1$, $\log K_2$, and $\log K_3$, Table 3, vs. 1/T (ºK), Figure 20, the stepwise enthalpy changes ΔH'$_S$ were deduced, and these are given in Table 3. The free energy changes ΔG'$_S$ were also evaluated at 25ºC using the expression,

$$-\Delta G = 2.303RT \log K \qquad (1)$$

Similarly, the entropy changes ΔS'$_S$ were evaluated using the following relationships,

$$\Delta S = (\Delta H - \Delta G)/ T \qquad (2)$$

$$-RT \ln K = \Delta H - T\Delta S \qquad (3)$$

Table 3. The stepwise enthalpy changes □H'$_S$, the free energy changes G'$_S$ and the stepwise entropy changes S(C) & S(g).

	20 ºC	*25 ºC*	*30 ºC*	*40 ºC*	*H (kcal/mole)*	*G (kcal/mole)*	*S(g) (cal/mole. deg)*	*S(C) (cal/mole. deg)*
log K_1	**8.343**	**8.571**	**8.536**	**8.619**	***4.870***	***-11.452***	***55.066***	***54.772***
log K_2	**7.664**	**7.747**	**7.755**	**7.909**	***4.944***	***-10.519***	***52.238***	***51.890***
log K_3	***7.104***	***7.139***	***7.068***	***7.053***	***-1.446***	***-9.751***	***27.829***	***27.869***

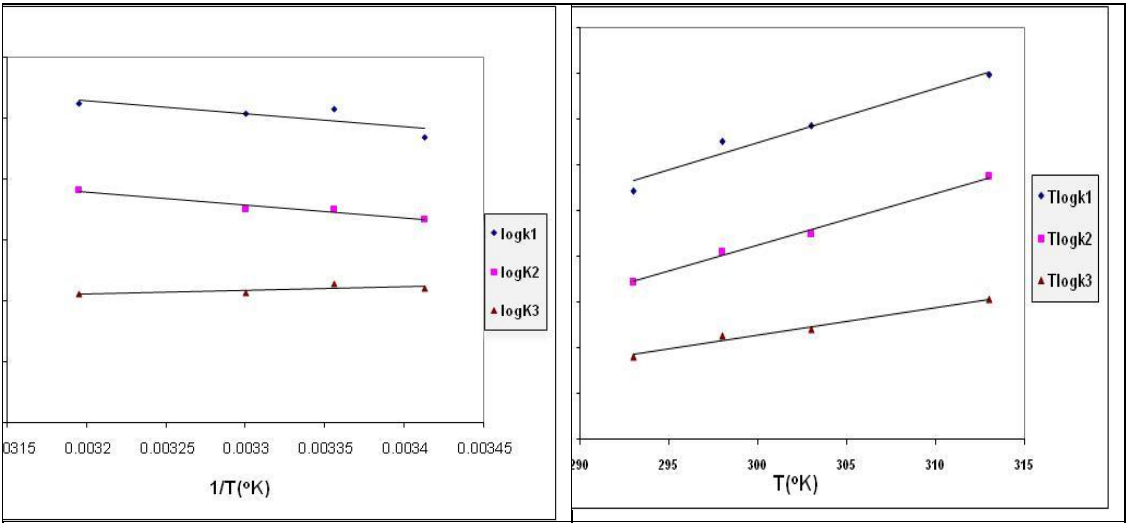


Figure 20. Relationship between logk anip between Tlogk and T

The stepwise entropy changes for BHAEN were evaluated from equation (2), □S(C) and from the slope of TlogK vs. T plots, □S(g), Figure 21. The values of □S calculated by the two methods are in good agreement, Table 3.

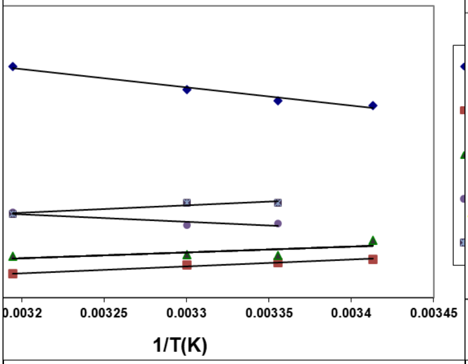
The positive values of □H’$_S$ for the first and the second protonation reactions indicate that these reactions are endothermic, i.e., the reaction is enhanced with increasing temperature, and The negative value of □H for the third protonation reaction indicates that this reaction is exothermic, i.e., the reaction is enhanced with decreasing temperature. The large negative values of □G’$_S$ for the three protonation reactions indicate that these reactions proceed spontaneously, the value of □G for the third reaction is less than that for the first two reactions as supported by the values of □S’$_S$. This latter value is less positive for the third reaction than the first two reactions.

Enthalpies and entropies of chelation of BHAEN with metal cations

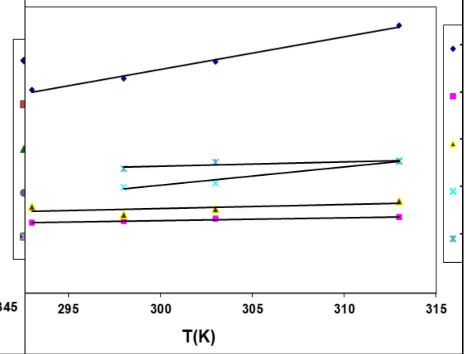
The stepwise thermodynamic functions □G, □H, and □S for the M/BHAEN complexes were calculated from the stepwise stability constants obtained at the four different temperatures used, Table 4. The values of these thermodynamic functions of the complexes are summarized in Table 4. Arrhenius plots are presented in Figures 22-24-26-28-30. to obtain □H’S values of the complexes formed. The stepwise entropy changes for the formation of M/BHAEN complexes were evaluated from equation (2), □S(C), and from the slope of TlogK vs. T plots, □S(g), Figures 23-25-27-29-31. The values of □S calculated by the two methods agree, Table 4.

Copper(II) complexes

ure (22). Relationship between logk and 1/T

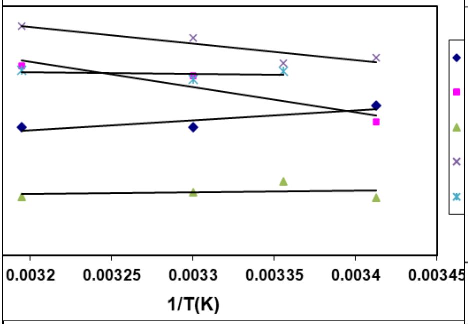


ure (23). Relationship between Tlogk and T

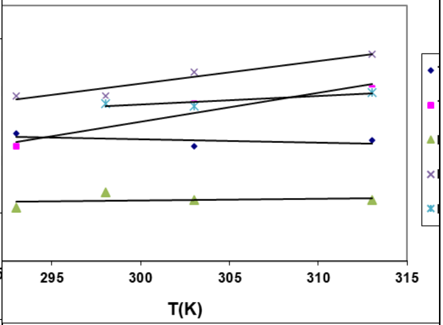


Nickel (II) Complexes

(24). Relationship between logk and 1/T

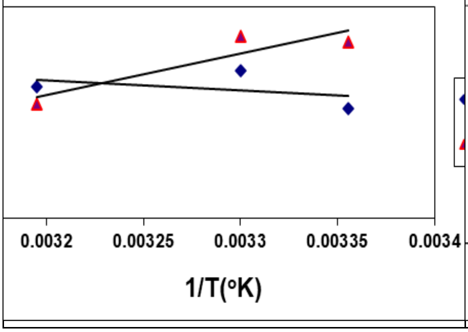


e (25). Relationship between Tlogk and T

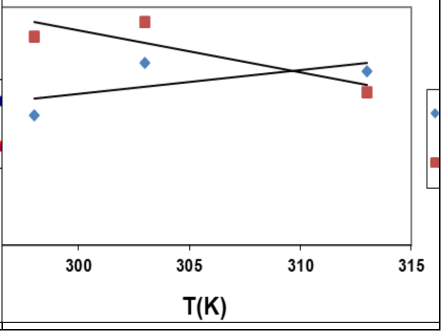


Cobalt (II) Complexes

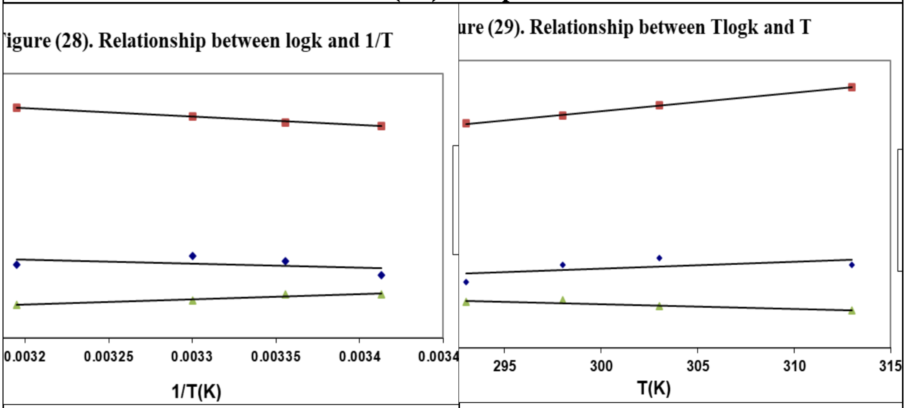
igure (26). Relation between logk and 1/T.



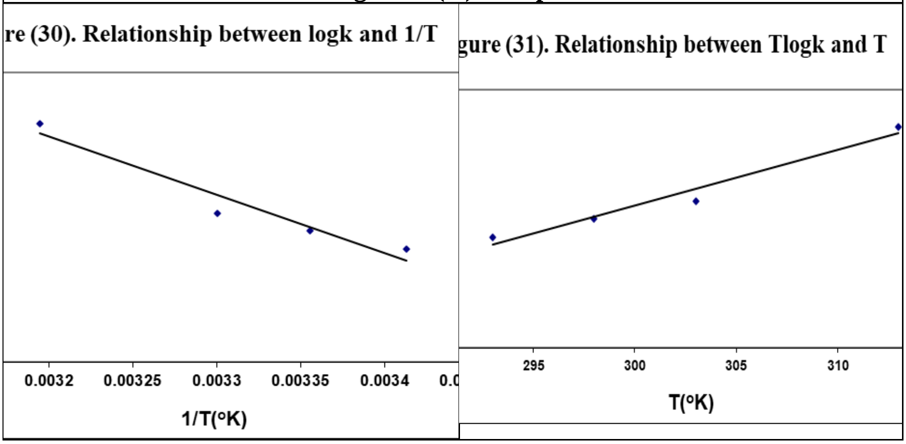
igure (27). Relationship between Tlogk and



Iron (III) Complexes



Manganese (II) Complexes



Figures 22-31. Plots of log K vs. 1/T and T log K vs. T

For the Cu(II) complexes the large negative values of G obtained for all the species indicate that the formation reaction of these species proceed spontaneously. The species (ML) has the highest negative value of G, although it has a positive enthalpy change, but this was outweighed by the large positive S value, which is favorable to chelation. The S value obtained for the species (ML_2) indicates that the formation of 1:2 complex is not entropy favorable compared with 1:1 complex, which has a large positive S value.

For the Ni(II) complexes The high negative value of H for the formation of the species (ML) indicates that this chelating reaction is exothermic, i.e., the reaction is enhanced with decreasing temperature. Also, it is obvious from the concentration distribution diagrams that the concentration of this species decreases with the temperature increasing.

The formation of the species (ML_2) has a small negative value of H, this may be explained by the enhancement of the reaction from 20°C to 25°C, then decreases after that with the increasing of temperature. The positive value of H'$_S$ for the formation of the other species indicates that these reactions are endothermic, i.e., the reaction is enhanced with the increasing of temperature. The negative values of G'$_S$ obtained for all the species indicate that the formation reaction of these species proceed spontaneously. The species (MHL), (MHL_2) an (MH_2L_2) have the highest negative values of G'$_S$. Moreover, these species are entropy favorable.

The species (MHL) has the highest positive entropy value, indicates the stability of this species. This can also be observed from the concentration distribution curves for the systems of the mole ratio (1:1) and, it is also present in the systems of the mole ratio (2:1) with a relatively high concentration.

In the case of Co(II) complexes the positive value of H'$_S$ for the formation of the species with the mole ratio (1:1), indicate that these reactions are endothermic, i.e., the reaction is enhanced with the increasing of temperature. The negative value of H for the formation of the species (ML_2) indicates that this reaction is exothermic, i.e., the reaction is enhanced with the decreasing of temperature. The negative values of G'$_S$ obtained for all the species indicate that the formation reaction of these species proceed spontaneously. The species (MHL), (MH_2L) have the highest negative values of G'$_S$, although they have positive enthalpy changes, but these were outweighed by the large positive S'$_S$ values, which is favorable to chelation.

The negative S value obtained for the species (ML_2) indicates that the formation of 1:2 complex is not entropy favorable compared with 1:1 complex, which has a large positive S value. This may explain the appearance of species with the mole ratio 1:1 in the concentration distribution curves of the systems with the mole ratio 1:2, M:L.

For the Fe(III) complexes The positive values of H'$_S$ for the formation of the species (ML) and (ML_2), indicate that these reactions are endothermic, i.e., the reaction is enhanced with the increasing of temperature. The negative value of H for the formation of the species (MHL) indicates that this reaction is exothermic, i.e., the reaction is enhanced with the decreasing of temperature. The negative values of G'$_S$ obtained for all the species indicate that the formation reaction of these species proceed spontaneously. The species (ML) has the highest negative value of G , although it has positive enthalpy changes, but this was outweighed by the large positive S value, which is favorable to chelation.

The S value obtained for the species (ML_2) indicates that the formation of 1:2 complex is not entropy favorable compared with 1:1 complex, which has a large positive S value. The low stability of the species (ML_2) compared with that of (ML), logK = (logKML – logKML$_2$) = 10.475, Table (14), may be attributed to steric hindrance effect. This may explain the appearance of the species (ML) in the concentration distribution curves in all systems and at all temperatures with a large concentration value (≈ 100%).

For the Mn(II) complexes The positive value of H for the formation of the species (ML_2), indicates that this reaction is endothermic, i.e., the reaction is enhanced with the increasing of temperature. The negative values of G obtained for the species (ML_2) indicate that the formation reaction of this species proceeds spontaneously. The species (ML_2) has a negative value of G, although it has positive enthalpy changes, but this was outweighed by the large positive S value, which is favorable for chelation.

4. Conclusion

From the obtained results, it can be concluded that the order of stability of the complexes formed between BHAEN and transition ions, Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} investigated in this study is in the expected Irving - Williams order [23]: $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$.

A large value of charge/radius ratio for a central ion means that the central ion will form more stable complexes.[24] The correlation between charge/radius ratio for the central metal ions and the stability of their complexes with BHAEN is shown in Table 5 and Figure 32.

Table 5.

The ion	***Radius (A°)***	***Charge/radius (Z/r***	***Stability constant at 20°C (L:M)***	
			(1:1)	***(2:1)***
Cu^{2+}	**0.57**	**3.509**	**10.062**	**16.935**
Ni^{2+}	**0.69**	**2.899**	**5.539**	**9.921**
Co^{2+}	**0.72**	**2.778**	**3.3**	**7.378**
Mn^{2+}	**0.91**	**2.198**	**---**	**5.364**

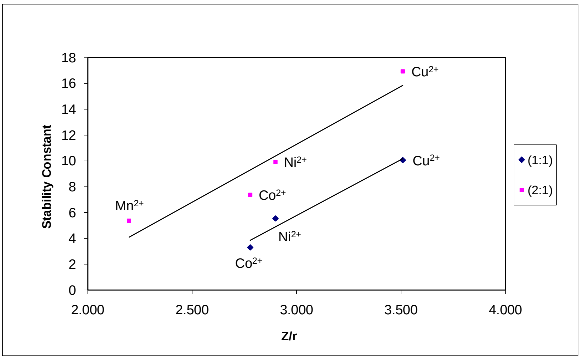


Figure (32). Relation between stability constant and charge/radius ratio

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Table 4. The stepwise stability constants (logKs) and the values of the thermodynamic functions *ΔH*, *ΔG,* and *ΔS* of the complexes of Cu(II), Ni(II),Co(II), Fe(III), Mn(II).

	Cu(II)			
	$20^{o}C$	***$25^{o}C$***	***$30^{o}C$***	***$40^{o}C$***
logKML	**9.961**	**10.062**	**10.286**	**10.758**
logKMHL	**6.796**	**6.730**	**6.670**	**6.489**
$logKMH_2L$	**---**	**---**	**---**	**---**
$logKML_2$	**7.189**	**6.873**	**6.886**	**6.856**
$logKMHL_2$	**---**	**7.524**	**7.492**	**7.750**
$logKMH_2L_2$	**---**	**7.953**	**7.958**	**7.727**
	ΔH (kcal/mole	***ΔG (kcal/mole***	***S(g) (cal/mole.deg***	***ΔS(C) (cal/mole.deg)***
logKML	**17.357**	**-13.810**	**105.190**	**104.590**
logKMHL	**-6.497**	**-9.238**	**9.089**	**9.197**
$logKMH_2L$	**---**	**---**	**---**	**---**
$logKML_2$	**-5.782**	**-9.434**	**13.442**	**12.253**
$logKMHL_2$	**7.105**	**-10.330**	**58.566**	**58.499**
$logKMH_2L_2$	**-6.950**	**-10.920**	**13.259**	**13.310**

	Ni(II)			
	$20^{o}C$	***$25^{o}C$***	***$30^{o}C$***	***$40^{o}C$***
logKML	**6.807**	**5.539**	**6.104**	**6.119**
logKMHL	**6.297**	**8.045**	**7.763**	**8.067**
$logKMH_2L$	**---**	**---**	**---**	**---**
$logKML_2$	**3.852**	**4.382**	**4.031**	**3.888**
$logKMHL_2$	**8.330**	**8.178**	**8.964**	**9.352**
$logKMH_2L_2$	**---**	**7.895**	**7.645**	**7.933**
logKML	***ΔH (kcal/mole)***	***ΔG (kcal/mole***	***S(g) (cal/mole.deg***	***ΔS(C) (cal/mole.deg)***
logKMHL	**-14.692**	**-8.822**	**-18.241**	**-18.757**
$logKMH_2L$	**37.640**	**-11.630**	**156.592**	**157.411**
$logKML_2$	**---**	**---**	**---**	**---**
$logKMHL_2$	**-2.472**	**-5.605**	**9.368**	**10.009**
$logKMH_2L_2$	**24.852**	**-13.483**	**122.775**	**122.473**
	2.603	**-11.437**	**45.262**	**44.857**

	Co(II)			
	20^{o}C	25^{o}C	30^{o}C	40^{o}C
logKML	---	3.300	3.752	3.557
logKMHL	---	---	7.714	7.960
logKMH$_2$L	---	---	7.479	7.709
logKML$_2$	---	4.078	4.153	3.358
logKMHL$_2$				
logKMH$_2$L$_2$				
	ΔH (kcal/mole	ΔH (kcal/mole	ΔH (kcal/mole)	ΔH (kcal/mole)
logKML	5.268	5.268	5.268	5.268
logKMHL	10.746	10.746	10.746	10.746
logKMH$_2$L	10.047	10.047	10.047	10.047
logKML$_2$	-22.481	-22.481	-22.481	-22.481
logKMHL$_2$	5.268	5.268	5.268	5.268
logKMH$_2$L$_2$	Co(II)	Co(II)	Co(II)	Co(II)

	Fe(III)			
	20^{o}C	25^{o}C	30^{o}C	40^{o}C
logKML	16.028	16.295	16.74	17.383
logKMHL	3.282	3.336	2.867	2.521
logKML$_2$	4.733	5.820	6.194	5.548
	ΔH (kcal/mole)	ΔG (kcal/mole)	ΔS(g) (cal/mole.deg)	ΔS(C) (cal/mole.deg)
logKML	29.280	-22.366	173.685	173.309
logKMHL	-17.928	-4.579	-45.886	-44.795
logKML$_2$	13.937	-7.988	68.301	73.577

	Mn(II)			
	20^{o}C	20^{o}C	20^{o}C	20^{o}C
logKML	---	---	---	---
logKMHL	---	---	---	---
logKML$_2$	5.172	5.172	5.172	5.172
	ΔH (kcal/mole)	ΔH (kcal/mole)	ΔH (kcal/mole)	ΔH (kcal/mole)
logKML	---	---	---	---
logKMHL	---	---	---	---
logKML$_2$	27.811	27.811	27.811	27.811