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Analysis of stability constants of 2-carboxy ethyl-3-hydroxy-4(3h) quinazolinone with transition metal

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Abstract

This paper deals with stability constants of binary and ternary complexes of 2-carboxyl ethyl-3-hydroxy-4(3H) quinazolinone [CEHQO] with Co(II), Ni(II), Cu(II) and Zn(II). in presence of Glycine (gly), α -Alanine (ala), Proline (pro), Histidine (hist), Iminodiacetic acid (IMDA), Nitrilotriacetic acid (NTA), 2,2'-Bipyridyl (bipy) and Ethylene-diamine(en) at 30°C and ionic strength of 0.1M KNO₃. It also deals with binary and ternary complexes at different temperatures.

Keywords: 2-carboxy ethyl-3-hydroxy-4(3h)

Introduction

The Cyclic hydroxamic acids are known for biological activity ^[1,2] such as anti-helminthic agents, anti-microbial, bactericidal, analgesic, hypnotic, anti-convul-sant, anti-inflammatory, CNS depressants and also have gained significant importance as anti-pyretic, anti-allergic, anti-ulcer, anti-cancer, anti-tumor. Anti-HIV drugs. Besides these also act as a good chelating agents. Survey of literature reveals that little work has been done on chelating tendencies of these compounds with transitional metal ions.

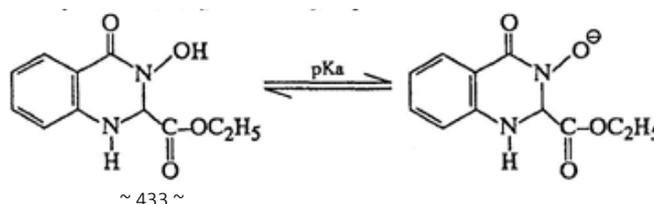
Recently ^[3,4] studies have been made on binary and ternary complexes of 2-phenyl-3-hydroxy quinazolin-4-one and 2-chloro-3-hydro quinazolin-4-one with Co(II), Ni(II), Cu(II) and Zn(II).

Material and Method

CEHQO is prepared and purified by the method of Kuniyoshi Tanaka *et al.* ^[5]. The solution of the CEHQO was prepared in distilled ethyl alcohol. The metal solutions were prepared by dissolving metal nitrate of AR grade in double distilled water and standardized ^[6]. The other reagents HNO₃, gly(E. Merck), ala, pro, hist, IMDA, NTA, en (Sigma), bipy, KNO₃(BDH) of AR grade were used. Double distilled water was used throughout. Commercial ethanol was distilled by the procedure given by Vogel ^[7]. Titration were carried out under nitrogen atmosphere. pH meter readings in 10% (v/v) ethanol-water were corrected by the method of Van Uiter and Haas ^[8]. Proton-ligand and metal-ligand formation constants of CEHQO were determined pH metrically by Irving-Rosotti ^[9] titration technique. The formation constants of ternary systems were determined by the method of Ramamoorthy and Santhappa ^[10, 11]. The formation of various metal ligand species in solutions with the variation of pH has been calculated by using the computer programme Best ^[12]. The values are further refined by the programme Scogs ^[13].

Results and Discussion

Binary systems: The pKa value for CEHQO was determined pH metrically for the first time. The RH values (0.1-1.0) for CEHQO indicating the liberation of one proton, which is due to the dissociation of proton from hydroxamic group as shown below.



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\bar{n} values (0.1 < n < 1.9) obtained for M(II)-CEHQO system indicate the formation of both 1:1 and 1:2 complexes in solution. The acid dissociation constants and binary formation constants so obtained are presented in Table 1. It was established that the carbonyl oxygen and -OH groups are participating in bonding with the metal ion. The releasing of protons in the pH range of above 3 in the present investigation indicates that -OH group is participating in bonding with the metal ion. From these studies it was established that these ligands act as 0-0 donors. The order of formation constants of metal chelates under investigation are Co(II) < Ni(II) < Cu(II) > Zn(II) which are in the conformity with the Irving -William natural order of stabilities [14]. The formation of various metal ligand species in solutions with the variation of pH has been calculated by using the computer Program Best [15]. As a representative case, Ni(II)-CEHQO distribution diagram is given in the Fig. 1.

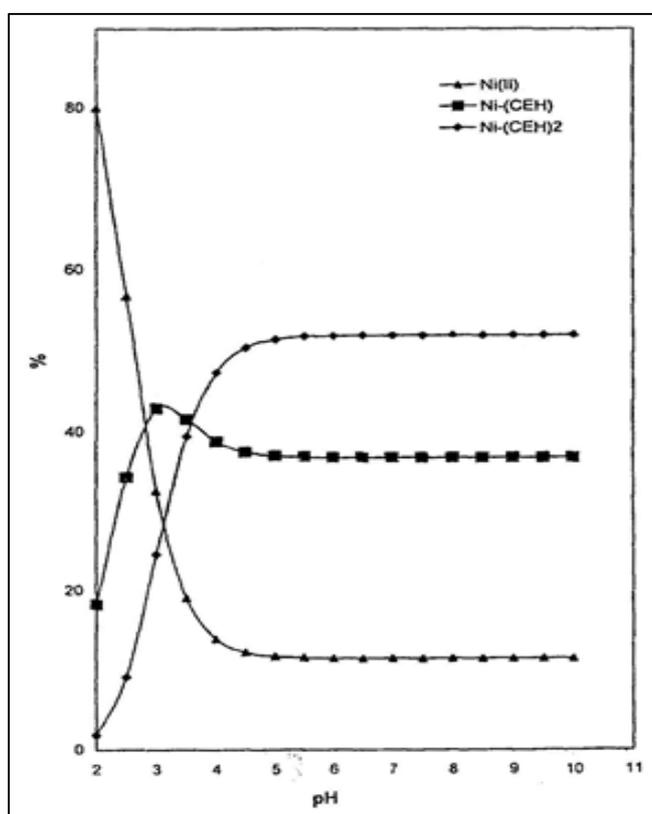


Fig 1: Distribution Diagram of Ni(II)-CEHQO

Table 2: Stability constants of Ternary metal complexes of M(II) ions with CEHQO in presence of other chelating agents
Temp: 303 K, I=0.1 M KNO₃, Medium: 10%(v/v) aq. Ethanol

CEHQO	gly		ala		pro		en		IMDA		NTA		bipy		hist	
	log K ^{ML} _{MLA}	ΔlogK														
Co(II)	4.56	-0.05	4.64	0.33	5.04	-0.06	4.94	-1.31	8.82	-1.75	8.65	1.41	8.65	-0.65	7.15	-3.35
Ni(II)	5.7	0.12	5.36	-0.04	6.02	0.07	5.51	-1.45	10.77	-0.5	10.11	1.82	8.64	-0.82	7.4	-4.61
Cu(II)	8.15	-0.01	8.15	0.02	8.1	-0.73	7.64	-2.81	13.33	-0.95	12.17	-1.95	9.55	-2.53	8.94	-4.92
Zn(II)	5.37	0.07	0.07	-0.25	6.11	0.46	4.91	-0.9	9.46	-0.7	9.05	0.17	7.85	-0.77	7.15	-2.82

The order of stability of [M-A-CEHQO] ternary complexes with respect to secondary ligands A are pro > gly > ala > en as shown in Table 2. The trends in the case of secondary ligands are almost all in conformity with the basicity sequence of the ligands under investigation. gly forms more stable complex than ala because of the absence of any alkyl side chain, which may produce an unfavourable steric effect

Table 1: Stability Constants of binary complexes of CEHQO with M(II) ions at different temperatures and 0.1 M Ionic strength in 10% (v/v) aqueous Ethanol medium

Metal Ion	Stability Constants	Different Temperatures		
		20°C	30°C	40°C
H ⁺	pKa	4.07	3.7	3.75
Co(II)	Log K1	3.47	3.33	3.20
	Log K2	3.10	2.92	2.81
Ni(II)	Log K1	3.76	3.62	3.47
	Log K2	3.13	3.01	2.85
Cu(II)	Log K1	3.82	3.70	3.57
	Log K2	3.44	3.33	3.16
Zn(II)	Log K1	3.54	3.44	3.31
	Log K2	3.11	2.97	2.83

Ternary Complexes: In the formation of ternary complexes [M(II)-CEHQO-A], CEHQO coordinated with metal ions [where M(II) = Co(II), Ni(II), Cu(II) and Zn(II), A = gly, ala, pro, en] in stepwise manner. The mixed ligand curves of [M(II)-CEHQO-A] closely follow the 1:1 M(II)-CEHQO curves in the lower pH region, until the protons of CEHQO were neutralised, indicating that the binary [M(II)-CEHQO] complexes predominate in this region. Above this region the divergence of the ternary curve from those of binary M(II)-CEHQO systems reveals the formation of ternary complexes of the type [M(II)-CEHQO-A] in step wise equilibria. Here, CEHQO acts as a primary ligand. Such a stepwise formation of ternary complex is confirmed from the distribution diagram (Fig. 2), that in the lower pH range the major species are the free metal ion and the [M-CEHQO] species, whereas in the higher pH range the major species are [M-CEHQO] and [M-CEHQO-A].

In the case of A (where A = IMDA, NTA, bipy and hist) CEHQO coordinated with metal ions in simultaneous manner. The mixed ligand curves of [M(II)-A-CEHQO] neither followed [M-CEHQO] binary curve nor [M-A] binary titration curves. The equilibria involved in the ternary complex formation of the type [M(II)-A-CEHQO] can be represented by the following equation (charges are omitted for the sake of clarity).



(where A = IMDA, NTA, hist and bipy)

It is observed from the distribution diagram that the [M-A-CEHQO] species is predominated in the entire pH range over [M-A] and [M-CEHQO] which confirms the formation of complexes simultaneously.

in other amino acids studied. Perusal of log K data reveals that many chelates formed by en are less stable than those of gly, ala, pro. Probably, this may be due to the fact that in the case of en the interaction occurs between neutral en and unipositive [M-CEHQO]⁺ primary species. Whereas in case of aminoacids, the interaction is between uni negative aminoacid A⁻ and unipositive [M-CEHQO]⁺ primary

species. Therefore the attraction between en and $[M-CEHQO]^+$ is less than the attraction between amino acid A- and $[M-CEHQO]^-$. Thus the stability of ternary complexes of en is less stable than those of gly, ala, pro. A log K data also reveals that ternary complexes formed by gly are more favourable than ala which is reversal to their basicity values. Methyl group on ala may be responsible for destabilization of its ternary complexes. In the present investigation the

order of stabilities of $[M-A-CEHQO]$ ternary complexes formed in simultaneous equilibria, is as follows $[M-IMDA-CEHQO] > [M-NTA-CEHQO] > [M-bipSt-CEHQO] > [M-hist-CEHQO]$
 The relative order of stabilities with respect to metal ions in all the CEHQO ternary complex systems $[Co(II) < Ni(II) < Cu(II) > Zn(II)]$ is in agreement with the Irving-William natural order of stability [14]. The extent of favoured formation of the ternary complexes can be inferred.

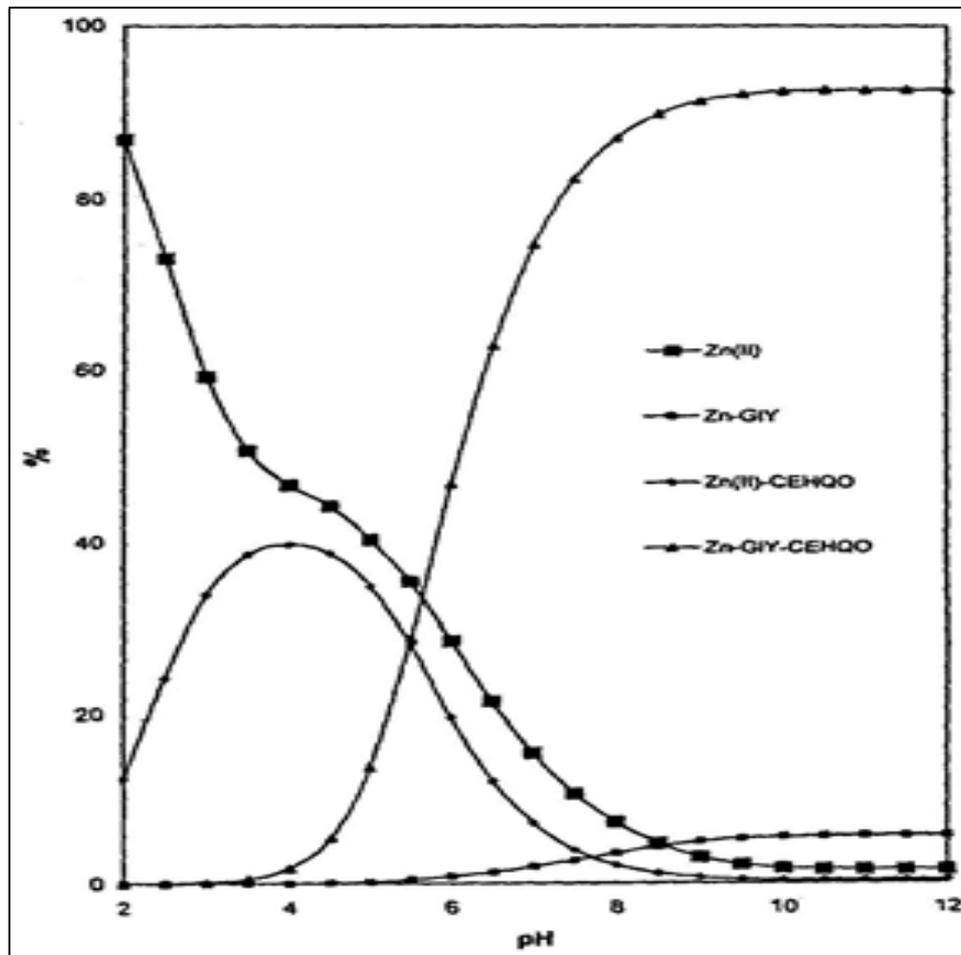


Fig. 2: Distribution Diagram of Zn(II)-Gly-CEHQO (1:1:1)

from. A log K values. The negative A log K values as shown in Table 2 reveal that the formation of ternary complexes is not favoured over that of binary complexes.

Effect of Temperature : In the present study, the complexation equilibria of CEHQO were studied with the transition metal ions Co(II), Ni(II), Cu(II) and Zn(II) at three different temperatures 20°C, 30°C and 40°C at constant ionic strength of 0.1M KNO₃. The formation constant data of binary metal complexes $[M(ID-CEHQO)]$

are presented in Table 1. The stability constants data obtained at different temperatures has been used in the evaluation of thermodynamic parameters accompanying the formation of metal complexes.

The All values thus obtained were refined by using the algebraic equation. The values of overall change in the free energy (ΔG), Enthalpy (ΔH) and the Entropy (ΔS) for the complex-ation reactions of CEHQO with the transition metal ions are reported in the Table 3.

Table 3: Thermodynamic parameters for the formation of 1:1 and 1:2 metal chelates of CEHQO
 Temp: 30°C, I = 0.1 M KNO₃, Medium : 10% (v/v) Aq. Ethanol

Metal Ion	1:1 Complex			1:2 Complex		
	-ΔG K Cal/mole	-ΔH K Cal/mole	-ΔS K Cal/mole	-ΔG K Cal/mole	-ΔH K Cal/mole	-ΔS K Cal/mole
Co(II)	776.34	667.67	85.70	665.55	461.30	161.12
Ni(II)	726.21	571.72	121.85	657.54	467.41	149.95
Cu(II)	787.85	609.25	140.85	726.21	622.78	81.57
Zn(II)	745.72	553.75	151.40	17.15	236.83	173.25

The data shows that the acid dissociation constants pK_a of the ligand and their stability constants with metal ions decreases with the increase in the temperature, indicating that the formation equilibria are exothermic in nature. This is also evident from the negative values of the Enthalpy (ΔH). The negative values of Free energy (ΔG) and the positive values of Entropy (ΔS) indicate that these factors are major driving force for the spontaneity of the binary

chelates. The results obtained in the present cases suggested that the metal-ligand bonds are fairly strong as evidenced by their negative enthalpy changes. The formation constants of the ternary complexes $[M-A-CEHQO]$ (where $M = Cu(II)$ and $Ni(II)$, $A = gly, ala, pro, hist, bipy, en, IMDA$ and NTA) were evaluated at $20^\circ C$, $30^\circ C$ and $40^\circ C$ at $0.1M$ ionic strength and presented in Table 4.

Table 4: Formation Constants of $M(II)-A-CEHQO$ ternary complexes at $0.1 M KNO_3$ and at different temperatures

A	Cu(II)-A-CEHQO			Ni(II)-A-CEHQO		
	20°C	30°C	40°C	20°C	30°C	40°C
gly	8.32	8.13	7.93	6.07	5.7	5.67
ala	8.37	8.14	7.93	5.54	5.35	5.15
pro	8.26	8.1	7.91	6.21	6.03	5.83
hist	9.2	8.95	8.75	7.73	7.4	7.04
en	7.87	7.65	7.42	5.72	5.51	5.27
IMDA	13.82	13.32	12.77	11.17	10.75	10.20
NTA	12.75	12.17	11.62	10.67	10.11	9.52

The thermodynamic parameters enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) were calculated are presented in Table 5.

Table 5: Thermodynamic parameters for the Formation of Ternary metal complexes of CEHQO
Temp: $30^\circ C = 0.1 M KNO_3$, Medium: 10% (v/v) Aq. Ethanol

A	Cu(II)-A-CEHQO			Ni(II)-A-CEHQO		
	$-\Delta G$ K Cal/mole	$-\Delta H$ K Cal/mole	$-\Delta S$ K Cal/mole	$-\Delta G$ K Cal/mole	$-\Delta H$ K Cal/mole	$-\Delta S$ K Cal/mole
gly	1262.64	407.10	674.85	1068.84	559.23	401.96
ala	1263.37	512.05	592.62	1011.04	582.77	337.80
pro	1259.67	387.80	687.72	1081.95	518.96	444.06
hist	1320.45	657.13	523.21	1205.24	792.60	325.50
en	1225.25	522.64	554.21	1027.64	659.94	290.03
IMDA	1559.21	650.17	717.02	1430.67	691.36	583.13
NTA	1505.33	823.61	529.04	1393.15	967.72	335.55

The formation constants of all the systems were found to decrease with increase in temperature, indicating that the reactions are exothermic in nature and enthalpy favoured. The negative ΔH and ΔG values indicate that these factors are responsible for the spontaneity of the reaction in all the cases. The positive values of entropy (ΔS) indicate that the complexation reactions are also favoured by entropy. The more positive values of (ΔS) for the ternary systems, compared to binary systems indicate that the formations of ternary complexes are more favoured by entropy.

Formation of binary complex of $[Ni(II)-CEHQO]$ is also supported by the spectral data. The ligand contains hydroxyl group at 3-position. The characteristic band of the hydroxyl group at $3400-3600\text{ cm}^{-1}$ is absent and instead a broad band at $3200-3100\text{ cm}^{-1}$ appears which can be attributed to a hydrogen bonded type of hydroxyl group with oxygen of amide carbonyl group. The disappearance of this band in the complexes indicates deprotonation followed by coordination to the metal ion. In addition to this ligand display a band around 1700 cm^{-1} characteristic of carbonyl group. This shifts by $20-40\text{ cm}^{-1}$ towards lower wave numbers in the complexes indicating that the oxygen of carbonyl group is also involved in coordination. The ^1H-NMR spectra of CEHQO display a down field signal at $\delta 10.2$ indicating that the hydroxyl proton is hydrogen bonded. The disappearance of this signal in the complex confirms deprotonation and participation of oxygen in the $M-CEHQO$ bond formation.

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