Asian Journal of Chemistry Vol. 5, No. 4 (1993), 850–856

Stability Constants and Thermodynamic Parameters of Mixed Ligand Chelates of Ni (II) with 5-Phenylazo-8-Quinolinol and 5-(4-Substitued Phenylazo)-8-Quinolinols in the Presence of O,O; O, N and N, N-Donor Ligands in 50% Dioxane-Water Medium

G. BALRAJ, SHIVA RAJ and M.G. RAM REDDY*
Department of Chemistry, Osmania University
Hyderabad-500 007, India.

The equilibria involved in the formation of ternary chelates of Ni(II) with different ligands in presence of N, O donor ligands such as 5-phenylazo-8-quinolinol (PAZOX), 5-(4-methoxyphenylazo)-8-quinolinol (MPAZOX), 5-(4-tolyl phenylazo)-8-quinolinol (TPAZOX) and 5-(4-nitro phenylazo)-8-quinolinol (NPAZOX) have been studied by pH titration technique at 30° ± 1°C and μ = 0.10 M (KNO_3) in 50% dioxane-water medium. The ligands used were (i) glycine (Gly); alanine (ala) (N,O-donors); (ii) catechol (cat); oxalic acid (oxa) (O, O-donors); (iii) 1,10-phenanthroline (1,10-phen), 2,2-bipyridyl (2,2-bipy) (N,N donors). The overall stability constants of ternary chelates are discussed in light of basicity of ligands, nature of donor atoms, metal-ligand d_π–p_π interactions denticity and statistical aspects. The formation constants of mixed ligand complexes have been studied at 20°, 30°, 40°, and 50°C at constant (0.10 M) ionic strength.

INTRODUCTION

Formation constants and thermodynamic parameters of the binary compiexes of 5-phenylazo-8-quinolinol and 5-(4-substituted phenylazo)-8-quinolinols with some divalent transition metal ions in 50% dioxane-water medium reported earlier[1] revealed that the stabilities of 5-(4-methoxy phenylazo)-8-quinolinol and 5-(4-tolyl phenylazo)-8-quinolinols are higher than that of 5-phenylazo-8-quinolinol. This was explained on the basis of electron releasing tendency of $-OCH_3$ and $-CH_3$ groups at fourth position on phenyl ring which causes the decrease in electron withdrawing nature of the phenylazo group. In case of 5-(4-nitro phenylazo)-8-quinolinol the stabilities were lower than that of 5-phenylazo-8-quinolinol and this was due to electron withdrawing capacity of NO_2 group at fourth position, which causes the increase in electron withdrawing capacity of phenylazo group. To understand the nature of the interaction of metal ion with 5-phenylazo-8-quinolinol and 5-(4-X-phenylazo)-8-quinolinols in the presence of secondary ligands a systematic study of mixed ligand complexes in undertaken.

The formation constants of ternary complexes were determined and calculated with known equations[2–5]. The 1 : 1 stability constants of secondary ligands have also been determined at 30°C and 0.10 M ionic strength in 50% dioxane-water medium.

EXPERIMENTAL

All the chemicals used were of A.R. grade. The ligands 5-phenylazo-8-quinolinol and 5-(4-substituted phenylazo)-8-quinolinol dyes were prepared by a method similar to that described by Fox[6].

The stock solutions of ligands were prepared in purified dioxane medium[7]. The following solutions were titrated potentiometrically against carbonate free standard potassium hydroxide solution under nitrogen atmosphere.

1. Acid (4.0×10^{-3} M)
2. Primary ligand (2.0×10^{-3} M) + acid
3. Metal ion (2.0×10^{-3} M) + primary ligand + acid
4. Secondary ligand (2.0×10^{-3} M) + acid
5. Metal ion + secondary ligand + acid
6. Metal ion + primary ligand + secondary ligand + acid

In the ternary systems the metal ligand ratio was maintained as 1 : 1 : 1. The total volume in all systems was maintained at 50 ml. The pH correction of the 50% dioxane-water medium was made by the method of Van Uitert and Haas[8]. The standard deviations have been evaluated and were found to be in the range of 0.02 to 0.05 for the different systems.

RESULTS AND DISCUSSION

In the ternary systems studied, the mixed ligand curves are closely followed those of the 1 : 1 (Ni(II)-A) (where A = PAZOX, NPAZOX, MPAZOX, TPAZOX) binary curves in the lower pH region until the protons of primary ligands are neutralised, indicating the formation of binary Ni–A complexation in this region. The divergence of the ternary curves from the binary Ni–A system above this region revealed the formation of ternary complexes of the type Ni–A–L (where L = gly, ala and cat) in stepwise equilibria. Here the ligands 5-phenylazo and 5-(4-substituted phenylazo)-8-quinolinols acted as primary ligands.

In the case of oxa, 2,2-bipy and 1,10–phen, the ligands PAZOX, MPAZOX, TPAZOX and NPAZOX acted as secondary ligands and the complex formation is occurred in stepwise equilibria[9].

The formation of ternary complexes is further supported by the non-superimposable nature of the theoretical composite curves in the region of mixed ligand complex formation[10]. The formation of ternary complexes were further supported by the distribution curves of various species as a function of pH which were

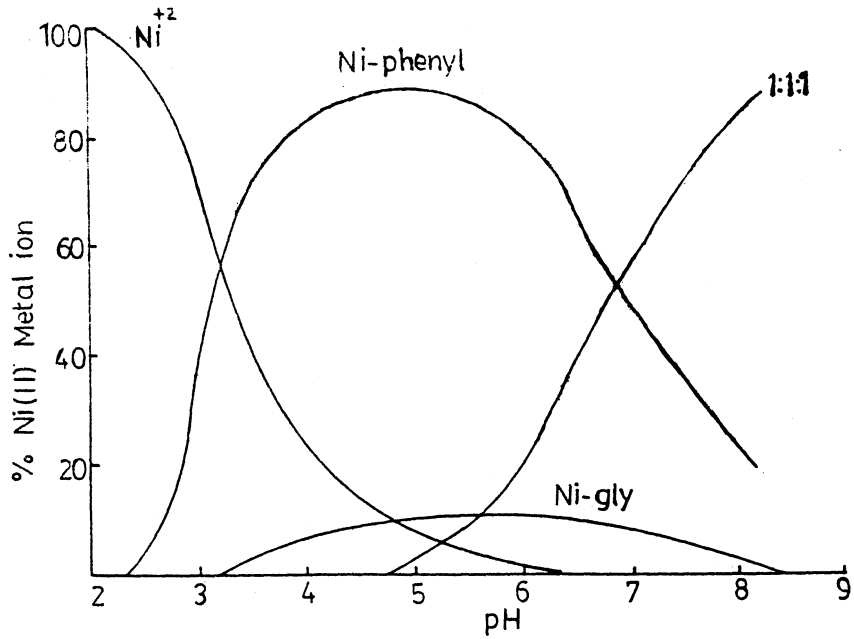

Fig. 1 (a) Relative concentration of binary and ternary complexes species in Ni–5–phenylazo-8–quinolinol-gly systems (0.002 M each) (μ = 0.1 M KNO_3), (temp 30°C ± 1°C).

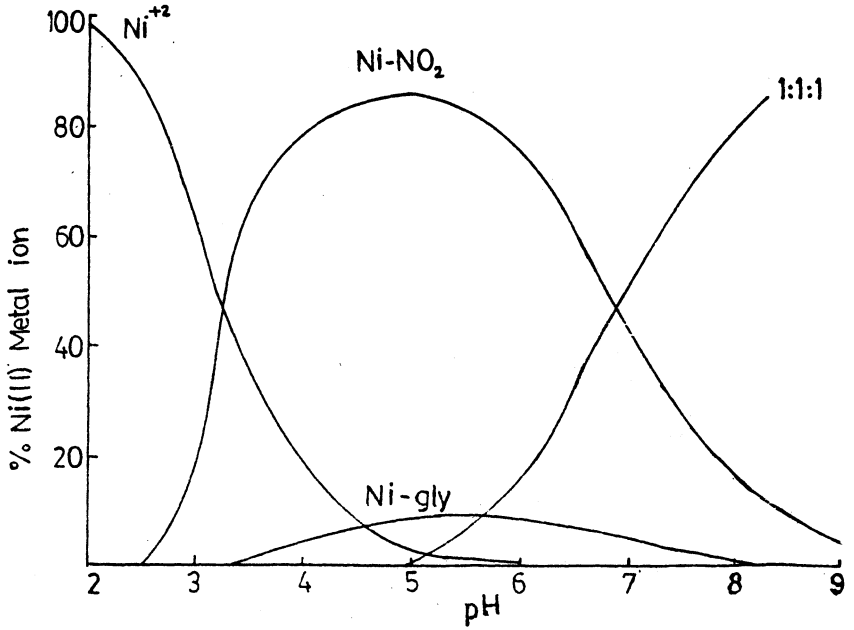

Fig. 1 (b) Relative concentration of binary and ternary complexes species in Ni(II)–5–(4-nitro phenylazo)-8–quinolinol-gly systems (0.002 M each) (μ = 0.1 M KNO_3), (temp 30°C ± 1°C).

calculated using (BEST) computer programme[11] and presented in Fig. 1 (a) and (b). In the lower pH range (2.5 to 6.0) the major contributing species are M(II)–PAZOX/MPAZOX/TPAZOX/NPAZOX, whereas in the higher pH range (5.0 to 80) ternary complex formation predominated over binary complexes.

In order to have uniform and systematic comparison the ligands are classified into several groups based on their donor sites, similarly in structure and denticity of the ligands.

N,N donor ligands: In case of 2,2-bipy and 1, 10-phen the observed order of stabilities of ternary complexes is 2,2-bipy > 1,10-phen. This may be due to steric hinderance of 1,10-phen molecule. The stability constants of ternary complexes (Ni-2,2′-bipy/1,10-phen-NPAZOX) are lower than that of (Ni-2,2′-bipy/1,10-phen–PAZOX), (Ni(II)-2,2′-bipy/1,10-phen-TPAZOX and Ni-2,2′-bipy/1,10-phen-MPAZOX). This may be due to more basic nature of 5-phenylazo-8-quinolinols. The lower negative values of Δ log K are observed in the case of (Ni (II)-2,2′-bipy/1,10-phen-MPAZOX) system may be due to π-interaction between metal-2, 2-bipy/1,10-phen[13]. The ligands 2,2-bipy and 1,10-phen are bound to the metal ion by N–M σ bond, besides there is also M–N π–bond formation by back donation of electrons from the metal dπ-orbitals to the vacant delocalized pπ-orbitals over the ligands. This dπ–pπ interaction does not allow the concentration of the electrons on the metal ion to increase significantly and hence the positive charges on the metal ion is almost same as in M^{2+}. This leads to more stable ternary complexes resulting lower negative values of Δ log K.

N, O donor ligands: The order of stabilities of ternary complexes is (Ni–NPAZOX–gly/ala) > (NiMPAZOX/TPAZOX/PAZOX–gly/ala). This may be due to pronounced effect of electron donating capacity and greater basicity of $-OCH_3$ and $-CH_3$ at fourth position on phenyl ring. The stabilities of (Ni–MPAZOX/ TPAZOX/PAZOX/NPAZOX-ala) are more than that of (Ni–MPAZOX/ TPAZOX/PAZOX/NPAZOX-gly) and this may be due to more basic nature of alanine.

O, O donor ligands: The titration curve indicates that the metal ion first interacts with oxa whereas cat interacts later in the presence of (MPAZOX/ TPAZOX/PAZOX/NPAZOX) and therefore 5-phenylazo-8-quinolinols act as primary ligands in the presence of cat and in the presence of oxa act as secondary ligand. The lower negative value of Δ log K observed in the case of catechol system may be due to the dπ–pπ interaction between metal to vacant pπ-orbitals availabel on cat, resulting in more stable ternary complexes, but in the case of oxa, there is no such pπ-interaction, as it is a open molecule hence Δ log K values are more negative than catechol.

It is observed that binary complexes are more stable than the ternary complexes, resulting in negative Δ log K values for (Ni–L–A) (where L = 2,2′-bipy,1,10-phen, oxa, gly and ala) and (Ni–A–L) (where L = cat) system. Such a lowering of stabilities of ternary complexes compared to that of binary chelates may be

due to the greater destabilization effect[9,11] and caused by ligand repulsion in the mixed ligand complexes than in the binary system coupled with availability of lesser number of coordinating sites. The Δ log K values are presented in Table 1.

TABLE 1
STABILITY CONSTANTS OF TERNARY COMPLEXES OF Ni (II) AT
μ = 0.10 M; temp at 30° ± 1°C in 50% dioxane-water medium.

System	pK_1	pK_2	log K (1 : 1)	log K (1 :1 : 1)	Δ log K
N–O Donors					
Ni (II)–NPAZOX–gly	9.68	—	7.90	7.20	–0.70
Ni (II)–PAZOX–gly			7.90	6.22	–1.68
Ni (II)–TPAZOX–gly			7.90	6.35	–1.55
Ni (II)–MPAZOX–gly			7.90	6.00	–1.90
Ni (II)–NPAZOX–ala	9.70	—	8.65	8.19	–0.46
Ni (II)–PAZOX–ala			8.65	8.08	–0.57
Ni (II)–TPAZOX–ala			8.65	7.98	–0.67
Ni (II)–MPAZOX–ala			8.65	7.20	–1.47
O–O Donors					
Ni (II)–NPAZOX–cat	11.59	9.43	9.25	9.13	–0.12
Ni (II)–PAZOX–cat			9.25	9.07	–0.18
Ni (II)–TPAZOX–cat			9.25	8.99	–0.26
Ni (II)–MPAZOX–cat			9.25	8.90	–0.35
Ni (II)–NPAZOX–oxa	2.78	9.64	9.53	7.67	–1.86
Ni (II)–NPAZOX–oxa	2.98	9.82	9.57	7.80	–1.77
Ni (II)–TPAZOX–oxa	3.02	9.94	9.63	8.20	–1.43
Ni (II)–MPAZOX–oxa	3.10	9.98	9.77	8.41	–1.36
N–N Donors					
Ni (II)–NPAZOX–1,10–phen	2.78	9.64	9.53	9.20	–0.33
Ni (II)–NPAZOX–2,2–bipy			9.53	9.30	–0.23
Ni (II)–PAZOX–1,10–phen	2.98	9.82	9.67	9.27	–0.40
Ni (II)–PAZOX–2,2–bipy			9.67	9.32	–0.35
Ni (II)–TPAZOX–1,10–phen	3.02	9.94	9.63	9.20	–0.43
Ni (II)–TPAZOX–2, 2–bipy			9.63	9.25	–0.38
Ni (II)–MPAZOX–1,10–phen	3.10	9.98	9.77	9.43	–0.34
Ni (II)–MPAZOX–2, 2–bipy			9.77	9.51	–0.26

The potentiometric titration were carried out at 20°, 30°, 40° and 50°C at constant ionic strength 0.10 M. The thermodynamic parameters are given in Table 2. It is observed from the data the stepwise and over all stability constants decrease with rise in temperature, indicating that the formation equilibrium were exothermic in nature. This is also borne out by the fact that ΔH and ΔG are both negative. The ΔS values are positive for the systems indicating that the entropy is favourable for complex formation[14].

TABLE 2
THERMODYNAMIC PARAMETERS FOR TERNARY COMPLEXES OF Ni(II)-5-PHENYLAZO-8-QUINOLINOL AND 5-(4-SUBSTITUTED PHENYLAZO)-8-QUNINOLINOL WITH N, N; N, O; AND O, O, DONOR LIGANDS AT 0.10 M IONIC STRENGTH IN 50% DIOXANE-WATER MEDIUM

System	$-\Delta G$ KJ mol^{-1}	$-\Delta H$ KJ mol^{-1}	ΔS JK^{-1} mol^{-1}
5–Phenylazo–8–quinolinol			
Ni (II)–PAZOX–gly	36.82	25.41	37.65
Ni (II)–PAZOX–ala	46.85	29.04	58.77
Ni (II)–PAZOX–cat	52.59	12.70	131.65
Ni (II)–PAZOX–oxa	45.25	27.22	59.43
Ni (II)–PAZOX–1, 10–phen	50.27	21.78	94.02
Ni (II)–PAZOX–2, 2–bipy	51.14	25.41	84.91
5–(4–nitrophenylazo)–8–quinolinol			
Ni (II)–NPAZOX–gly	41.75	14.52	89.86
Ni (II)–NPAZOX–ala	47.49	16.33	102.83
Ni (II)–NPAZOX–cat	52.94	12.70	132.80
Ni (II)–NPAZOX–oxa	44.47	27.22	56.93
Ni (II)–NPAZOX–1, 10–phen	49.28	19.96	96.76
Ni (II)–NPAZOX–2, 2–bipy	49.86	21.78	92.87
5–(4–tolylphenylazo)–8–quinolinol			
Ni (II)–TPAZOX–gly	36.06	14.52	71.08
Ni (II)–TPAZOX–ala	46.27	19.04	56.86
Ni (II)–TPAZOX–cat	52.13	38.11	36.27
Ni (II)–TPAZOX–oxa	47.55	16.33	103.03
Ni (II)–TPAZOX–1, 10–phen	50.68	21.78	93.37
Ni (II)–TPAZOX–2, 2–bipy	51.02	16.33	114.48
5–(4–methoxyphenylazo)–8–quinolinol			
Ni (II)–MPAZOX–gly	34.79	29.04	18.97
Ni (II)–MPAZOX–ala	41.75	14.52	89.86
Ni (II)–MPAZOX–cat	51.60	21.78	98.41
Ni (II)–MPAZOX–oxa	48.76	18.15	101.10
Ni (II)–MPAZOX–1, 10–phen	53.63	27.78	105.11
Ni (II)–MPAZOX–2, 2–bipy	53.98	12.70	136.27

ACKNOWLEDGEMENT

One of the authors (GB) is thankful to the U.G.C., New Delhi for the award of teacher fellowship.

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(*Received*: 1 March 1992; *Accepted*: 5 February 1993) AJC–542