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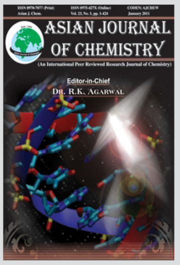

Thermodynamics and Solution Studies on Some Quaternary Metal Complexes and their Comparison with Binary and Ternary Complexes

DHARA D. PATEL[1], SANGITA SHARMA[1], K.R. PATEL[2,*] and V.D. PATEL[2]

[1]Department of Chemistry, Hemchandracharya North Gujarat University, Patan-384 265, India
[2]School of Research, Suresh Gyan Vihar University, Jaipur-302 004, India

*Corresponding author: E-mail: kirti3183@yahoo.co.in

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Equilibrium studies on quaternary metal complexes of type M_1M_2AB where M_1 and M_2 are Cu(II) and Ni(II) or Cd(II) or Co(II) or Pb(II), L_1 = *o*-phenylenediamine and L_2 = salicylic acid were carried out using Irving Rossotti titration technique at 30 ± 0.1, 40 ± 0.1 and 50 ± 0.1 ºC at fixed ionic strength, $\mu = 0.2$ mol dm^{-3} ($NaClO_4$). The separation of titration curves demonstrate the formation of mixed metal mixed ligand complexes of stoichiometry $M_1M_2L_1L_2$. All metal ion formation constant of the complexes, $M_1M_2L_1L_2$ in addition to $M_1L_1L_2$, $M_2L_1L_2$, $M_1(L_1)_2$, $M_1(L_2)_2$, $M_2(L_1)_2$ and $M_2(L_2)_2$ type of complexes for all metal ions were evaluated using for the Fortran IV computer program and the complex formation equilibrium data were pruned with the aid of speciation curves plotted with aid of Fortran IV computer program SPEPLOT. The stability order of metal complexes and solution structure of heterobinuclear $M_1M_2L_1L_2$ complexes have been discussed on the basis of basicity of ligands and coordination sphere of complexation.

Key Words: *o*-Phenylenediamine, Salicylic acid, Stoichiometry, Formation constant, SPEPLOT, Metal complexes.

INTRODUCTION

The ever increasing the importance of ternary complexes especially those involving ligands containing functional groups[1,2] identical with those present in the enzymes *viz*., -COOH, $-NH_2$, $-CONH_2$, *etc*., is obvious form the application of such complexes in many analytical and biological reactions[3]. Diamines are widely studied in binary systems but so far literature does not support where diamines are used as primary ligand in ternary system and also in quaternary systems. We reported herein the solution and equilibria studies on binary, ternary, quaternary complexes of Cu(II), Co(II), Pb(II), Ni(II) metal ions with *o*-phenylenediamine and salicylic acid ligand using pH metry in aqueous medium[4-6]. The relevant stability constants have been evaluated using FORTRAN II computer program. The stability constants of binary ternary and quaternary complexes are determined at 30 ± 1, 40 ± 1 and 50 ± 1 ºC and at ionic strength $\mu = 0.2$ M ($NaClO_4$). The studies are carried on 1:1:1 (M -*o*-phenylenediamine-salicylic acid) ternary and 1:1:1:1 (M_1-M_2-*o*-phenylenediamine salicylic acid) quaternary complexes with a view to introduce stability parameters for comparing the stabilities at a particular temperature[7,8].

EXPERIMENTAL

All chemicals used were of reagent grade. The standard solutions were prepared by using doubly distilled CO_2 free water. Metal salts were standardized by complexometric EDTA titration method. Digital μ 361 pH meter with readability ± 0.001 with combined glass calomel electrode have been used for pH metric study. Stoichiometrically 1:1:1 concentration of M_1, M_2, L_1 and L_2 were maintained in the solution. Metal ligand mixtures of following compositions were prepared for titration keeping total volume 50 mL in each case ($\mu = 0.2$ M $NaClO_4$). The concentration of ligand and metal solution were checked by pH metric titration against 0.2 N carbonate free sodium hydroxide solution.

Metal ligand formation constants have been evaluated by FORTRAN IV computer program. The values of formation constants were supplied to the computer as input data to obtain distribution curves of the complexes occurring at different pH value. Using SPEPLOT a representative titration set for quaternary system for Cu-Ni-*o*-phenylene diamine-salicylic acid is shown in Fig. 1.

The order of stability of mixed ligand complex is explained in term of basicity and strctre of primary ligand and secondary ligand. Tables 1-4 shows the ligand formation constant parameter in aqueous solution for binary, ternary and quaternary formation constant.

Thermodynamic parameters ΔG, ΔH and ΔS for ternary complexes shown in Table-5 and thermodynamic parameters ΔG, ΔH and ΔS for quaternary complexes shown in Table-6.

TABLE-1
PROTON LIGAND FORMATION CONSTANT IN AQUEOUS SOLUTION. Temp. = 30 ± 1 ºC, $\mu = 0.2$ mol dm^{-3} ($NaClO_4$)

	Cu	Ni	L_1	L_2	log β
L_1	1	0	0	0	0
L_1H	1	0	1	0	4.61
L_1H_2	1	0	2	0	6.42
L_2	0	1	0	0	0
L_2H	0	1	1	0	11.20
L_2H_2	0	1	2	O	14.23

TABLE-2
MIXED LIGAND BINARY, TERNARY AND QUATERNARY FORMATION CONSTANTS OF CU AND NI IN AQUEOUS SOLUTION. Temp. = 30 ± 1 ºC, $\mu = 0.2$ mol dm^{-3} ($NaClO_4$)

Metal complex	Cu	Ni	L_1	L_2	t	log β
CuL_1	1	0	1	0	0	2.78
$Cu(L_1)_2$	1	0	2	0	0	5.01
NiL_1	0	1	1	0	0	2.32
$Ni(L_1)_2$	0	1	2	0	0	5.81
CuL_2	1	0	0	1	0	6.70
$Cu(L_2)_2$	1	0	0	2	0	12.11
NiL_2	0	1	0	1	0	6.84
$Ni(L_2)_2$	0	1	0	2	0	12.34
CuL_1L_2	1	0	1	1	0	10.90
NiL_1L_2	0	1	1	1	0	10.11

TABLE-3
FORMATION CONSTANT FOR TERNARY COMPLEXES AT DIFFERENT TEMPERATURE. $\mu = 0.2$ mol dm^{-3} ($NaClO_4$)

Metal	log β		
	30 ºC	40 ºC	50 ºC
Cu	10.90	10.78	10.56
Ni	10.11	10.05	9.98
Cd	11.28	11.25	11.1
Co	9.49	9.37	9.27
Pb	9.97	9.67	9.47

TABLE-4
FORMATION CONSTANT FOR QUATERNARY COMPLEXES AT DIFFERENT TEMPERATURE. $\mu = 0.2$ mol dm^{-3} ($NaClO_4$)

Metal	log β		
	30 ºC	40 ºC	50 ºC
Cu-Ni	13.76	13.58	13.40
Cu-Cd	13.89	13.87	13.70
Co-Cd	10.43	10.40	10.37
Pb-Cd	10.97	10.91	10.83

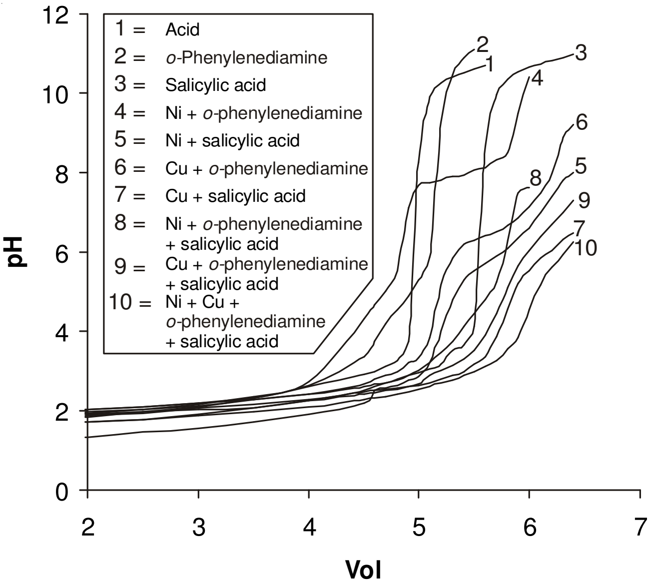


Fig. 1. Titration set for quaternary system for Cu-Ni-*o*-phenylenediamine-salicylic acid

RESULTS AND DISCUSSION

Species present in binary 1:1 system during complexation equilibrium are M^{2+}: L_1 (1:1) are L_1H, L_1H_2, M_1L_1, M_2L_1, M_1L_2,M_2L_2, like wise for M^{2+} : L_2 (1:1) system species of the type exist however metal hydroxo species are also present in the form $ML_1(OH)$, $ML_2(OH)$ the pH range of 9-12.

Ternary species are detected form in mononuclear ternary M^{2+}: L_1:L_2 (1:1:1) system along with some binary species discussed above speciation curves indicate the formation according to the following equation.

$$M^{2+} + L_1H_2 + L_2H_2 \rightarrow [ML_1L_2] + 4H^+$$

$$[ML_1] + L_2H_2 \rightarrow [ML_1L_2] + 2H^+$$

In hetronuclear quaternary $(M_1)^{2+}$:$(M_2)^{2+}$: L_1:L_2 (1:1:1:1) systems appreciable concentration is $M_1M_2L_1L_2$ however some amount of M_1L_1, M_2L_2, $M_1(L_2)_2$, $M_2(L_2)_2$ species is in the range 3-11 are found and species $M^1M^2L_1L_2$ reaches steadily to maximum extent *ca.* 50 % at pH 7 Their formation may be explained by the following equilibrium.

$$(M_1)^{2+} + (M_2)^{2+} + L_1H_2 + L_2H_2 \rightarrow [M_1M_2L_1L_2] + 4H^+$$

TABLE-5
THERMODYNAMIC PARAMETERS ΔG, ΔH, ΔS FOR TERNARY COMPLEXES

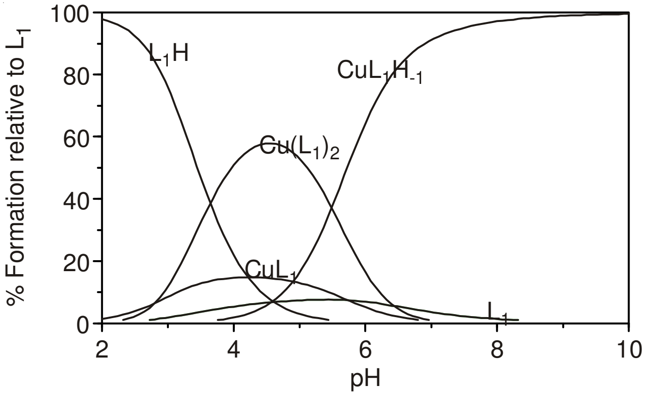
Metal ion	ΔG (K cal mol^{-1})			ΔH (K cal mol^{-1})		ΔS (K cal. mol^{-1})	
	303 K	313 K	323 K	313 K	323 K	313 K	323 K
Cu	-1.5113	-1.5440	-1.5468	-6	-22	0.0240	0.063
Ni	-1.4017	-1.4394	-1.4751	-3	-7	0.0049	0.017
Cd	-1.5650	-1.6113	-1.6406	-1.5	-15	0.0035	0.041
Co	-1.3158	-1.3420	-1.3701	-6	-10	0.0140	0.026
Pb	-1.3823	-1.3850	-1.3997	-15	-20	0.0430	0.057

TABLE-6
THERMODYNAMIC PARAMETERS ΔG, ΔH, ΔS FOR QUATERNARY COMPLEXES

Metal ion	ΔG (K cal mol^{-1})			ΔH (K cal mol^{-1})		ΔS (K cal mol^{-1})	
	303 K	313 K	323 K	313 K	323 K	313 K	323 K
Cu-Ni	-1.9078	-1.945	-1.9806	-1.86	-3.56	0.0023	0.0048
Cu-Cd	-1.9259	-1.9894	-2.0249	-3.17	-3.55	0.0037	0.0017
Co-Cd	-1.4461	-1.4895	-1.5327	-2.16	-4.32	0.0021	0.0089
Pb-Cd	-1.521	-1.5626	-1.6007	-2.08	-3.81	0.0071	0.0068

Both ligands L_1 and L_2 are bidentate in nature. The stability constants value for ML_2 are more than ML_1 indicated for higher stability of ML_2 complex basicity of ligand L_2 is more than L_1 but [M-(*o*-phenylenediamine)$_n$]$^{2+}$ can be compared with [M-(H_2O)$_n$]$^{2+}$ complexes so as per literature in ternary and quaternary complexes [M-*o*-phenylenediamine]$^{2+}$ is first formed and than salicylic acid attaches.

Figs. 2 and 3 showed the binary complexes of Cu(II) and Ni(II)-*o*-phenylenediamine (1:1) with respect of ligand L_1. Fig. 4 shows the formation of ternary complex of Cu(II) (1:1:1). Fig. 5 shows the formation of ternary complex of Ni(II) (1:1:1). Fig. 6 shows the quaternary complexes of Cu in C-Ni-*o*-phenylene diamine-salicylic acid. Fig. 7 shows the quaternary complexes of Ni in C-Ni-*o*-phenylene diamine-salicylic acid.



Fi. 2. Binary complexs of Cu(II)-*o*-phenylenediamine (1:1)

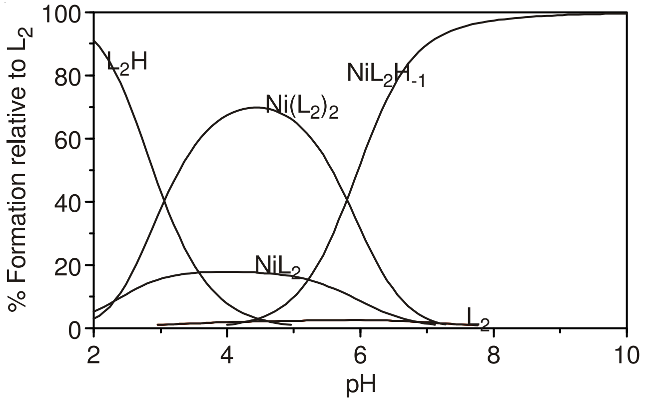


Fig. 3. Binary complexs of Ni(II)-*o*-phenylenediamine (1:1)

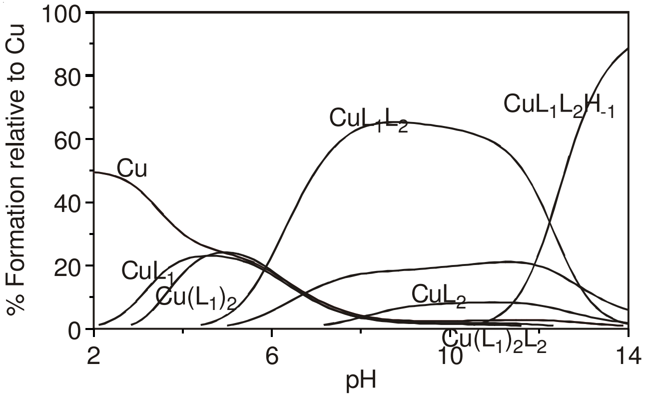


Fig. 4. Ternary complexes of Cu(II) 1:1:1

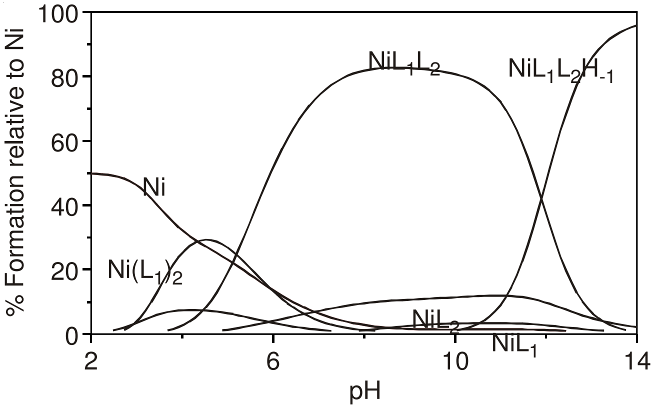


Fig. 5. Ternary complexes of Ni(II) 1:1:1

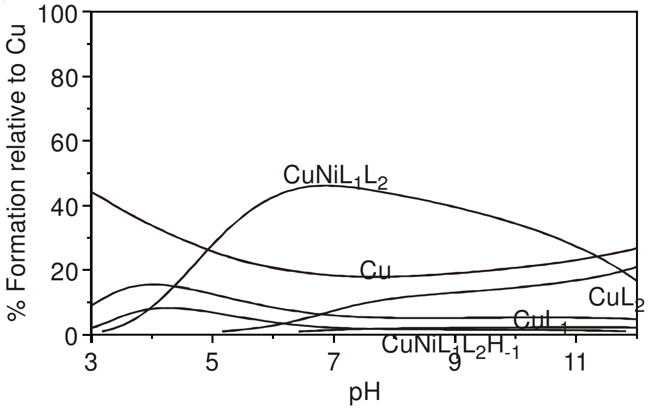


Fig. 6. Quaternary complexes Cu-Ni-*o*-phenylenediamine-salicylic acid

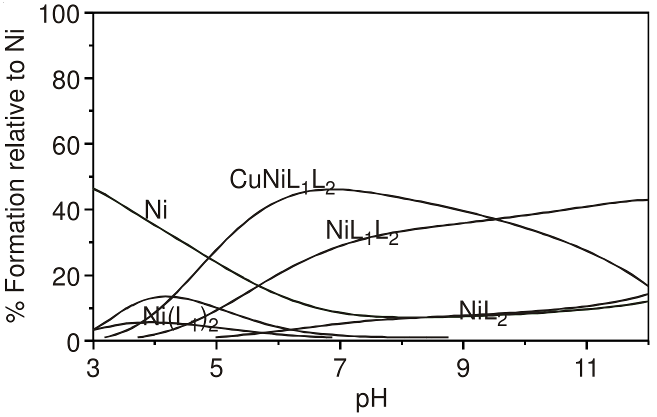


Fig. 7. Quaternary complexes Cu-Ni-*o*-phenylenediamine-salicylic acid

Formation constants of binary and ternary are in order of Cd > Cu > Ni > Pb > Co and formation constants of quaternary complexes are found in the following general order of Cu - Cd > Cu - Ni > Cd - Pb > Cd - Co.

The negative ΔH and ΔG values indicate that these factors responsible for the spontaneity of the reaction. In all the cases the positive value of entropy ΔS indicate that the complexation reactions are favoured by entropy.

Conclusion

pH-metric studies on some quaternary metal complexes (transition metal with *o*-phenylenediamine and salicylic acid).

A binary and ternary metal complex reaches steadily to maximum extent *ca.* 60-80 % at pH 3-11 at high pH hydroxyl also formation taken place. Quaternary metal complexes maximum extent *ca.* 50 % at pH 7 thermodynamic studies have shown that the reactions are exothermic in nature. The complexation reactions are favoured by entropy.

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