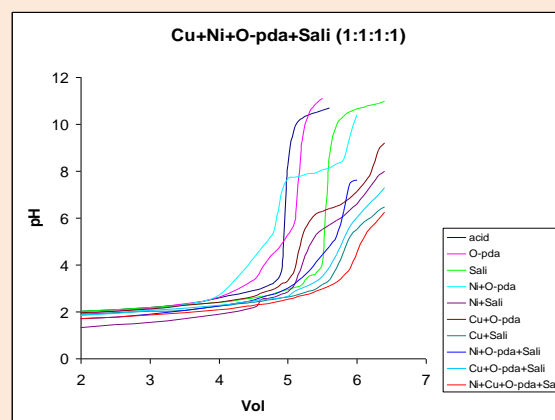


Research Article

Thermodynamics and Solution State Studies on Binary, Ternary and Quaternary Complexes of Cu^{II} , Ni^{II} , Cd^{II} , and Co^{II} and their ComparisonSangita Sharma^{1*} and Dhara D.Patel²¹Department of Chemistry, Hemchandracharya North Gujarat University, Patan- 384 265, Gujarat, India²General department, M.L.I.D.S. Bhandu, Gujarat, India**Abstract**

Equilibrium studies on quaternary metal complexes of type $\text{M}^1\text{M}^2\text{L}_1\text{L}_2$ where M^1 and M^2 are Cu^{II} and Ni^{II} or Cd^{II} or Co^{II} , $\text{L}_1 = o$ -phenylenediamine and $\text{L}_2 = \text{Salicylic acid}$ were carried out using Irving Rossotti titration technique at 30 ± 0.1 , 40 ± 0.1 and $50 \pm 0.1^\circ\text{C}$ and at fixed ionic strength, $\mu = 0.2 \text{ mol dm}^{-3}$ (NaClO_4). The separation of titration curves demonstrate the formation of binary, ternary and quaternary (mixed metal mixed ligand) metal complexes. Stability constant of the complexes, $\text{M}^1\text{M}^2\text{L}_1\text{L}_2$ in addition to $\text{M}^1\text{L}_1\text{L}_2$, $\text{M}^2\text{L}_1\text{L}_2$, $\text{M}^1(\text{L}_1)_2$, $\text{M}^1(\text{L}_2)_2$, $\text{M}^2(\text{L}_1)_2$, and $\text{M}^2(\text{L}_2)_2$ type of complexes for all metal ions were evaluated using for the Fortran IV computer program. The complex formation equilibrium data were pruned with the aid of Fortran IV computer program SPEPLOT and speciation curves were evaluated. The stability order of metal complexes and solution structure of Binary, Ternary and Quaternary hetero binuclear $\text{M}^1\text{M}^2\text{L}_1\text{L}_2$ complexes have been discussed on the basis of basicity of ligands and coordination sphere of complexation.

Keywords: Equilibrium, Binary, Ternary, Quaternary, Complexation, Binuclear

***Correspondence**

Author: Sangita Sharma

Email: smridhee2000@yahoo.co.in

Introduction

The ever increasing importance of ternary complexes especially those involving ligands containing functional groups identical with those present in the enzymes viz. $-\text{COOH}$, $-\text{NH}_2$, $-\text{CONH}_2$ etc is obvious from their applications of such complexes in many analytical and biological reactions [1–16]. 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 report here the solution and equilibria studies on binary, ternary, quaternary complexes of Cu^{II} , Co^{II} , Pb^{II} , Ni^{II} metal ions with ligands o -phenylenediamine and salicylic acid ligand using pH metry technique in aqueous medium.

The relevant stability constants have been evaluated using FORTRAN II computer program. The stability constants of binary, ternary and quaternary complexes are determined at $30 \pm 1^\circ\text{C}$, $40 \pm 1^\circ\text{C}$ and $50 \pm 1^\circ\text{C}$ and at ionic strength $\mu = 0.2 \text{ M}$ (NaClO_4). The studies are carried on 1:1 ($\text{M} - o$ -pda or $\text{M} - \text{Salicylic acid}$) binary, 1:1:1 ($\text{M} - o$ -pda - salicylic acid) ternary and 1:1:1:1 ($\text{M}^1\text{-M}^2$ - opda- salicylic acid) quaternary complexes with a view to introduce stability parameters for comparing the stabilities at a particular temperature.

Experimental

All chemicals used were of analytical grade. Their standard solutions were prepared by using doubly distilled, CO₂ free Conductivity water. Metal salt were standardized by complexometric EDTA titration method. Digital μ 361 pH meter having combined glass calomel electrode with readability ± 0.01 has been used for pH metric study. 1:1:1:1 Stoichiometry was maintained in the solution concentration for M₁, M₂, L₁ and L₂. Metal ligand mixtures were prepared for titration keeping total volume 50ml in each sample and ionic strength was maintained 0.2M using NaClO₄. The concentration of ligand and metal solution were checked by pH metric titration against 0.2N sodium hydroxide solution.

The following titration sets were prepared for study of binary, ternary and quaternary complexes and these were titrated against CO₂ free standardized 0.2N NaOH.

1. Known amount of HClO₄.
2. Free HClO₄ + known amount of ligand. L₁.
3. Free HClO₄ + known amount of ligand.L₂.
4. Free HClO₄+ known amount of ligand L₁+ known amount of metal [M¹].
5. Free HClO₄ + known amount of ligand L₂+ known amount of metal [M¹].
6. Free HClO₄ + known amount of ligand L₁+ known amount of metal [M²].
7. Free HClO₄ + known amount of ligand L₂+ known amount of metal [M²].
8. Free HClO₄ + known amount of ligand L₁+ known amount of ligand L₂ + known amount of metal [M¹].
9. Free HClO₄ + known amount of ligand L₁ + known amount of ligand L₂+ known amount of metal [M²].
10. Free HClO₄ + known amount of ligand L₁+ known amount of ligand L₂+ known amount of metal [M¹] + known amount of metal [M²].

A representative graph from titration data of quaternary system for Cu-Ni-opda-Salicylic acid is shown in **Figure 1**. Stability constants for binary, ternary and quaternary are calculated by using FORTRAN IV computer program known as BEST [17]. The values of stability constants were fed to the computer as input data to obtain distribution curves for these complexes as function of pH value using SPEPLOT program [18]. In these equilibria following type of complexes are expected,

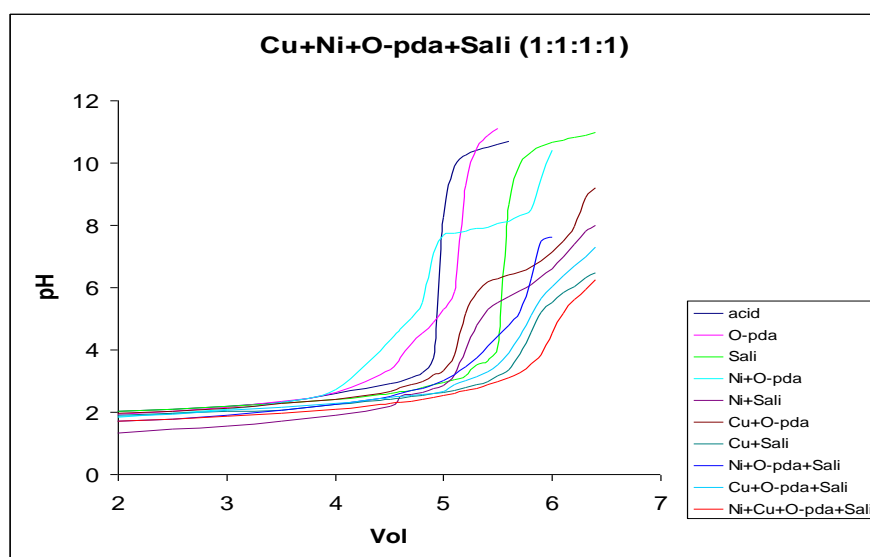


Figure 1 pH metric titration curves for the [M₁-M₁-Opd-Salicylic acid] binary system

1. M¹L₁ or M¹L₂ and M²L₁ or M²L₂ \longrightarrow 1:1 Binary Complexes

2. $M^1 L_1 L_2$ and $M^2 L_1 L_2 \longrightarrow 1:1:1$ ternary complexes

3. $M^1 M^2 L_1 L_2 \longrightarrow 1:1:1:1$ quaternary mixtures.

where M^1 or $M^2 = Co^{II}$ &/or Cd^{II} &/or Cu^{II} &/or Ni^{II} as required and $L_1 =$ O-Phenylenediamine and $L_2 =$ Salicylic acid.

Results and Discussion

The stability constant values of the binary, ternary and quaternary complexes formed between Cu^{II} and Ni^{II} or Cd^{II} or Co^{II} ions with opda and salicylic acid has been calculated by measuring the magnitude of the proton liberated during the titration of the ligand in absence and in presence of metal against standard sodium hydroxide solution. The calculated Proton ligand formation constants and stability constants for $M(II)$ complexes in aqueous medium from titration data considering a BEST FIT model at temperatures $30 \pm 0.1^\circ C$ are given in **Table 1** and **Table 2** respectively. Species distribution diagrams (**Figures 2–4**) $M(II)$ -ligand system were drawn using SPEPLOT program [18] in pH range between 0–12. 'S' minimum values for all the selected binary systems are calculated, S_{min} is the same statistical distribution as χ^2 with K degrees of freedom and with weights reported in accordant with Fletcher and Powell [19–20]. S_{min} can be equated to χ^2 .

Both ligands namely o-phenylene diamine (L_1) and Salicylic acid (L_2) are bidentate in nature. The stability constant values for ML_2 are more than ML_1 that indicates for higher stability of ML_2 complexes. Basicity of ligand L_2 is more than L_1 but $[M - (opda)_n]^{2+}$ can be compared with $[M - (H_2O)_n]^{2+}$ complexes. It is anticipated that in ternary and quaternary complexes $[M-opda]^{2+}$ is first formed and then salicylic acid coordinates as secondary complex.

Stability constants of binary and ternary are in order of $Cd > Cu > Ni > Co$ and stability constants of Quaternary complexes are found in the following general order of

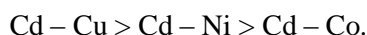


Table 1 Proton Ligand Formation Constants in of O-phenylene diamine and Salicylic acid at temperature = $30 \pm 1^\circ C$, $\mu = 0.2 \text{ mol dm}^{-3} (\text{NaClO}_4)$

	L_1	L_2	H	OH	$\log\beta$
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	0	14.23

Table 2 BEST Fit data for Equilibrium study on stability constants of Binary, Ternary and Quaternary metal complexes at $30 \pm 1^\circ C$ temperature and at $\mu = 0.2 \text{ mol dm}^{-3} (\text{NaClO}_4)$

Metal complex	M_1	M_2	L_1	L_2	OH	$\log\beta$	No. of data points	pH Scale	S minimum
CdL_1	1	0	1	0	0	3.41	48	2–12	0.9786
$Cd(L_1)_2$	1	0	2	0	0	5.13	43	1–11	0.8999
$Cd(L_1)(OH)$	1	0	1	0	1	-1.25	47	1–11	0.8754
CuL_1	1	0	1	0	0	2.93	39	2–12	0.9902
$Cu(L_1)_2$	1	0	2	0	0	4.97	42	1–11	0.9987

Cu(L₁)(OH)	1	0	1	0	1	-1.78	49	2-11	0.8765
NiL₁	1	0	1	0	0	2.82	35	1-12	0.9999
Ni(L₁)₂	1	0	2	0	0	4.81	45	2-12	0.8777
Ni(L₁)(OH)	1	0	1	0	1	-1.98	46	2-11	0.9876
CoL₁	1	0	1	0	0	2.59	48	1-11	0.8543
Co(L₁)₂	1	0	2	0	0	4.31	36	2-12	0.8324
Cd(L₁)(OH)	1	0	1	0	1	-1.35	47	2-11	0.9642
CdL₂	1	0	0	1	0	8.32	44	1-11	0.9230
Cd(L₂)₂	1	0	0	2	0	10.45	39	2-12	0.9031
Cd(L₂)(OH)	1	0	0	1	1	-1.35	35	1-11	0.8753
CuL₂	1	0	0	1	0	8.24	44	1-12	0.8021
Cu(L₂)₂	1	0	0	2	0	10.54	41	2-12	0.9980
Cu(L₂)(OH)	1	0	0	1	1	-1.76	35	2-11	0.8890
NiL₂	1	0	0	1	0	7.70	40	1-11	0.9880
Ni(L₂)₂	1	0	0	2	0	9.98	37	1-12	0.8855
Ni(L₂)(OH)	1	0	0	1	1	-1.90	42	2-12	0.9595
CoL₂	1	0	1	0	0	7.51	45	1-11	0.9201
Co(L₂)₂	1	0	2	0	0	9.01	48	1-12	0.8012
Co(L₂)(OH)	1	0	0	1	1	-1.89	40	2-12	0.9999
CdL₁L₂	1	0	1	1	0	11.28	41	1-11	0.8540
CuL₁L₂	1	0	1	1	0	10.90	38	2-11	0.8765
NiL₁L₂	1	0	1	1	0	10.11	46	1-12	0.9605
CoL₁L₂	1	0	1	1	0	09.49	35	2-12	0.9777
CdL₁L₂(OH)	1	0	1	1	1	-4.00	44	2-11	0.8888
CuL₁L₂(OH)	1	0	1	1	1	-4.10	40	1-12	0.8765
NiL₁L₂(OH)	1	0	1	1	1	-4.23	43	1-11	0.9430
CoL₁L₂(OH)	1	0	1	1	1	-4.40	39	2-12	0.9329
Cd-Cu L₁L₂	1	1	1	1	0	13.89	45	2-12	0.8901
Cd-Ni L₁L₂	1	1	1	1	0	12.76	35	2-11	0.8743
Cd-Co L₁L₂	1	1	1	1	0	11.24	40	1-11	0.9911

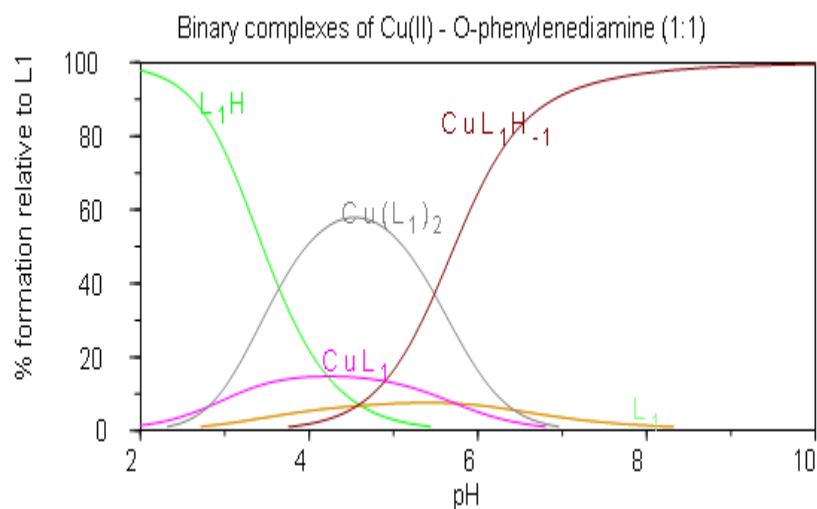


Figure 2 Species distribution curves as function of pH calculated for binary Cu(II)-O-phenylene systems in ratio of 1:10 at 30 ± 0.1 °C, $\mu = 0.2 \text{ mol} \cdot \text{L}^{-1}$ (NaClO_4). Cu- opd= ML_1 , Cu- opd₂= $\text{M(L}_1)_2$, $\text{CuL}_1\text{H}_{-1}$ = $\text{ML}_1(\text{OH})$

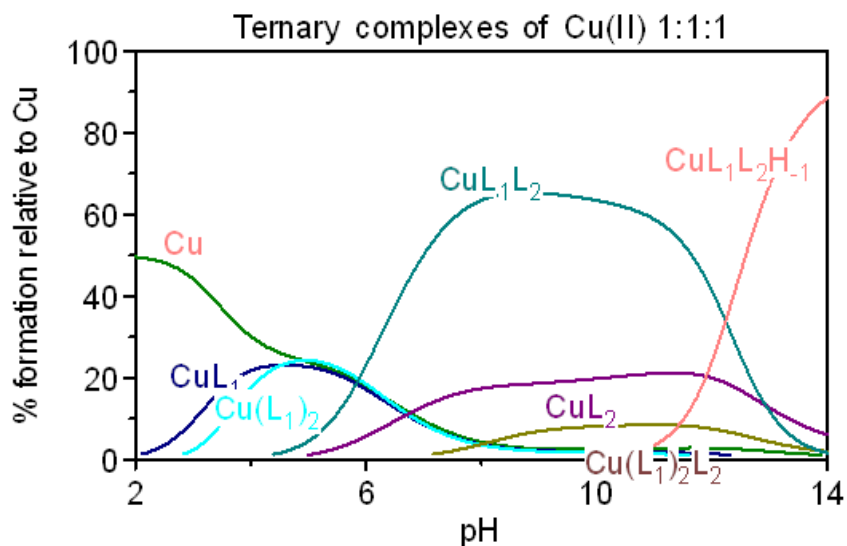


Figure 3 Species distribution curves as function of pH calculated for binary Cu(II)-O- phenylene- Salicylic acid systems in ratio of 1:1:1 at $30 \pm 0.1^\circ\text{C}$, $\mu = 0.2 \text{ mol}\cdot\text{L}^{-1}$ (NaClO_4). Cu- Opd = ML_1 , Cu- Opd₂ = $\text{M}(\text{L}_1)_2$, Cu- Salicylic acid = ML_2 , Cu- Sal₂ = $\text{M}(\text{L}_2)_2$, Cu- Opd - Salicylic acid = $\text{Cu L}_1\text{L}_2$ and $\text{Cu L}_1\text{L}_2\cdot\text{H}_{-1}$ = $\text{M L}_1\text{L}_2(\text{OH})$.

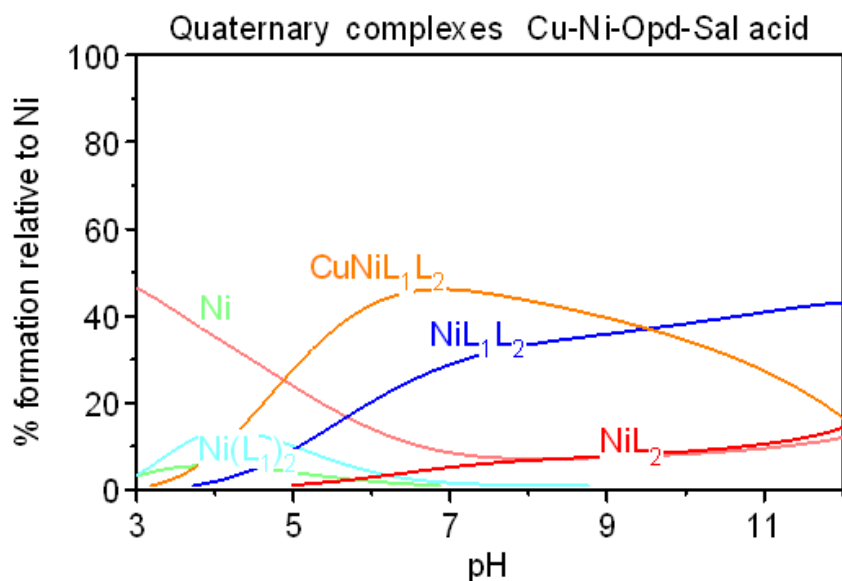


Figure 4 Species distribution curves as function of pH calculated for Heteronuclear Quaternary Cu(II)- Ni(II)-O phenylene- Salicylic acid systems in ratio of 1:1:1:1 at $30 \pm 0.1^\circ\text{C}$, $\mu = 0.2 \text{ mol}\cdot\text{L}^{-1}$ (NaClO_4). Cu- Opd = ML_1 , Cu- Opd₂ = $\text{M}(\text{L}_1)_2$, Cu- Salicylic acid = ML_2 , Cu- Sal₂ = $\text{M}(\text{L}_2)_2$, $\text{Cu L}_1\text{L}_2\cdot\text{H}_{-1}$ = $\text{M L}_1\text{L}_2(\text{OH})$ and $\text{CuNiL}_1\text{L}_2\cdot\text{H}_{-1}$ = $\text{M}_1\text{M}_2\text{L}_1\text{L}_2(\text{OH})$.

During complexation equilibrium for quaternary systems, the most probable and expected species are L_1H_1 , L_1H_2 , L_2H_1 , L_2H_2 , M^1L_1 , M^2L_1 , M^1L_2 , M^2L_2 , $\text{M}^1\text{L}_1\text{L}_2$, $\text{M}^2\text{L}_1\text{L}_2$ and $\text{M}^1\text{M}^2\text{L}_1\text{L}_2$. Likewise metal hydroxo species are also expected to be present in the form $\text{ML}_1(\text{OH})$, $\text{ML}_2(\text{OH})$, $\text{M}^1\text{L}_1\text{L}_2(\text{OH})$ in the pH range of 9–12. Such species are observed in speciation plots shown in **figures 2–4** depending on the nature of systems selected.

In hetero nuclear quaternary complexes of type $(\text{M}^1)^{2+} : (\text{M}^2)^{2+} : \text{L}_1 : \text{L}_2$ (1:1:1:1) appreciable concentration $\text{M}^1\text{M}^2\text{L}_1\text{L}_2$ species is observed. Some other species like M^1L_1 , M^2L_2 , $\text{M}^1(\text{L}_2)_2$, $\text{M}^2(\text{L}_2)_2$, $\text{M}^1\text{L}_1(\text{OH})$, $\text{M}^1\text{L}_2(\text{OH})$, $\text{M}^1\text{L}_1\text{L}_2(\text{OH})$, are

also observed in the range 3–11. $M^1M^2L_1L_2$ has maximum ~50% at pH ~7. Their formation can be explained by the following equilibrium.



Determination of stability constants at different temperatures has been used in the evaluation of thermodynamic parameters involved in the formation of these metal complexes. The enthalpy (ΔH) changes reflect the energy changes with the intermolecular bonding whereas free energy factor (ΔG) gives the magnitude of stability of complexation equilibrium. The values of overall change in the free energy (ΔG), Enthalpy (ΔH) and the Entropy (ΔS) for the complexation reaction of metal ions and ligands are reported in the **Tables 3–4**. The enthalpy (ΔH) changes have been calculated from linear plots of $\log K$ vs $1/T$ according to equation of isobaric reaction.

$$\frac{d(\log \frac{K_1}{K_2})}{d(1/T)} = \frac{-\Delta H}{4.57} \quad (1)$$

The significance of the thermodynamic quantities can be known by considering the well known thermodynamic relationship.

$$-2.303RT \log K = \Delta G - \Delta H = T\Delta S \quad (2)$$

The data shows that the dissociation constant of the ligands and their stability constants with metal ions decrease with increase in the temperature, indicating that formation equilibria are exothermic in nature. For all the binary complexes studied, the negative ΔH and the negative ΔS values obtained indicate that the both enthalpy and entropy factors are favoring the complex formation. The decrease in the $\log k$ values with increase in the temperature shows that the reactions are exothermic. The entropy changes could be due to the displacement of water molecules from hydration shells of interacting ions which accompanies the essentially electrostatic interaction between positively charged metal ions and donor pair of nitrogen of O-pda and/ or O-O interactions with salicylic acid.

Table 3 Stability constants and Thermodynamic parameters (ΔG , ΔH , ΔS) for ternary complexes ($M^1L_1L_2$ or $M^2L_1L_2$) where L_1 is O- phenylene diamine and L_2 is Salicylic acid

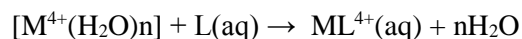
Metal ion	log β			ΔG K.Cal.mole ⁻¹	ΔH K.Cal.mole ⁻¹	ΔS K.Cal.mole ⁻¹
	30°C	40°C	50°C	313 K	313 K	313 K
Cd	11.28	11.20	11.10	-67.10	-16.90	-160.6
Cu	10.90	10.78	10.56	-64.60	-31.00	-104.9
Ni	10.11	10.05	09.98	-60.20	-12.00	-153.5
Co	09.49	09.37	09.27	-56.20	-20.60	-113.5

Table 4 Stability constants and Thermodynamic parameters (ΔG , ΔH , ΔS) for Quaternary ($M^1M^2L_1L_2$) complexes

Metal ion	log β			ΔG K.Cal.mole ⁻¹	ΔH K.Cal.mole ⁻¹	ΔS K.Cal.mole ⁻¹
	30°C	40°C	50°C	313 K	313 K	313 K
Cd-Cu	13.89	13.58	13.40	-81.40	-46.10	-112.00
Cd-Ni	12.76	12.47	12.20	-74.80	-52.50	-71.00
Cd-Co	11.24	11.10	10.87	-66.50	-34.60	-102.00
Cd-Cu	13.89	13.58	13.40	-81.40	-46.10	-112.00

This is also evident from negative values of the enthalpy (ΔH). The negative values of free energy (ΔG) indicate that these factors are major driving force for the spontaneity of ternary and quaternary complexes. The enthalpy changes accompanying the solution is the characteristic property of the heat of the reaction and measures energy difference between metal ligand (M-L) and the metal water [M-H₂O] coordination bonds. The results obtained in the present cases suggested that the metal – ligand bonds are fairly strong as evidenced by their negative enthalpy changes.

The entropy changes accompanying the formation of metal complexes can be related to number of reacting species in the system and changes in solvation of the reactant and product species. During the formation of metal complexes in the solution, the ligand species get coordinated to the solvated metal ions by displacing the water molecules from the aqua complex [M(H₂O)_n]⁴⁺ as shown by the following equation.



Thus, increase in number of particles in the system leading to increase in disorderliness of the system. Since entropy is a measure of extent of disorderliness of the system studied.

Conclusion

pH-metric studies on interaction of M(II) ion with two different ligands namely o-phenylenediamine and salicylic acid reveal that both ligands contains two dissociable sites in acidic medium. Species distribution curves and calculations using BESTFIT models show that when ML₁, and ML₂ type of binary complexes are studied, dominance of ML₂ type of complexes is observed. The stability of all the analogous binary and ternary complexes were in order of Cd > Cu > Ni > Co as anticipated by increasing charge/size ratio values. Data also suggest that o-phenylene diamine acts as primary ligand and coordinates with metal ions first in ternary and quaternary complexes. Thermodynamic studies have shown that the reactions for the formation of complexes are exothermic in nature and are favored by enthalpy change. The values of ΔS indicate that complexation reactions are entropically favored under present experimental conditions.

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