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Ternary Complexes of Cd(II) and Gd(III) Involving Biologically Important Ligands

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ABSTRACT: Ternary complexes of metal M [M = Cd(II) and Gd(III)] with A (A = Malonic Acid) and B (B = Nitrotriacetic Acid and Iminodiacetic Acid), are investigated potentiometrically. Ligands A and B bind to metal ion M simultaneously to form 1:1:1 MAB mixed ligand complex in various equilibria. Experiments are performed in aqueous medium at three different temperatures (20ºC±1, 30ºC±1 and 40ºC±1) and at three ionic strengths (μ = 0.05M, 0.10M and 0.15M) in order to calculate thermodynamic stability constants and other thermodynamic parameters. SCOGS (stability constant of generalized species) computer program is used to obtain the speciation of various species formed in a particular equilibrium. The value of ΔG° and ΔH° are negative whereas ΔS° is positive in some systems while negative for others. The relative stability of ternary complexes as compared to binary species are expressed in term of Δ log K, values of ΔlogK suggest that the formation of ternary complexes are favorable. The stability of Gd(III) complexes are found to be greater than that of Cd(II) complexes.

Keywords: Malonic acid, ternary complexes, speciation, SCOGS.

INTRODUCTION

Development in the field of coordination chemistry is closely related to the study of mixed ligand complexes. The study of mixed ligand complexes is of extreme importance because it helps to predict general and probable form of existence of element in solution. This makes possible to understand the mechanism and kinetics in analytical reactions and open new prospects for development of selective and sensitive method for determination and separation. Further mixed ligand complexes have received much attention because of the fact that the biochemical reactions often involve the formation of ternary species through a dynamic equilibrium. This fact has prompted several researches to investigate mixed equilibria involving biologically significant ligands. In recent past there has been considerable interest in the study of mixed ligand complexes by pH-metric method involving biologically significant ligands[1-16].

Malonic acid has received considerable attention owing to the fact that it can be metabolized to acetyl coenzyme-A and that it is involved in fatty acid synthesis, aromatic synthesis and mevalonate synthesis [17-18]. It is important intermediate in synthesis of vitamins B1 and B6, barbiturates, non-steroidal anti-inflammatory agents, other numerous pharmaceuticals, agrochemicals flavor and fragrance compounds [19].

Iminodiacetic acid, a well known aminodicarboxylic acid, is one of most widely used complexing agent in industries. The analogous of iminodiacetic acid are used in nuclear hepatology for non-invasive and quantitative evaluation of numerous hepatobiliary diseases related to bile formation and excretion [20]. The biological properties of complexes depend on the blood bilirubin level [21].

Nitrilotriacetic acid was tested for carcinogenicity by oral administration in the diet in mice and rats. It induced renal-cell adenocarcinomas in mice of each sex, renal-cell tumours in male rats and transitional-cell and squamous-cell carcinomas of the urinary bladder, hepatocellular adenomas and adrenal phaeochromocytomas in female rats [22].

The present paper deals with mixed ligand complexes of Cd(II) and Gd(III) involving A = Malonic acid (Mal) and B = [Nitrilotriacetic acid (Nta) and Iminodiacetic acid (Imda)]

EXPERIMENTAL

All the systems were investigated under equimolar concentration ratio. For each set of titration moles of alkali required per mole of ligand / metal. ‘a’ was determined and curves were obtained by plotting pH vs ‘a’.

Solution : All the reagents used were of highest purity Merck/Aldrich products. Solutions were prepared in doubly distilled CO_2-free water having pH ≈ 6.8. Solutions of metal and ligand (each 0.01M) were prepared by dissolving accurately weighed amounts in double distilled water. The solution of Nta was neutralized with one equivalent of alkali to make dibasic.

Instrument: An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass Body; range 0-14 pH unit; 0-100°C Automatic/Manual) with accuracy ±0.01 was employed for pH-measurement.

Experimental conditions: Various sets of titration mixtures were prepared and titrated against standard sodium hydroxide solution (0.10M) at three different ionic strengths (μ = 0.05M, 0.10M and 0.15M) maintained by adding different concentration of $NaNO_3$ solution to each titration mixture at temperatures 20°C±1 , 30ºC±1 and 40ºC±1.Temperature was maintained by Siskin Julabo, thermostat model V-12B.

1. Acid titration: HNO_3 (2.0×10^{-3}M).
2. Ligand ‘A’ titration: HNO_3 (2.0×10^{-3}M) + Ligand ‘A’ (1.0×10^{-3}M).
3. Ligand ‘B’ titration: HNO_3 (2.0×10^{-3}M) + Ligand ‘B’ (1.0×10^{-3}M).
4. Metal(M)-Ligand ‘A’(1:1) titration: HNO_3 (2.0×10^{-3}M) + Ligand ‘A’ (1.0×10^{-3}M) + Metal nitrate (1.0×10^{-3}M).
5. Metal (M)-Ligand ‘B’(1:1) titration: HNO_3 (2.0×10^{-3}M) + Ligand ‘B’(1.0×10^{-3}M) + Metal nitrate (1.0×10^{-3}M).
6. Metal (M) - Ligand ‘A’ –Ligand ‘B’ (1:1:1) titration: HNO_3(2.0×10^{-3}M) + Ligand ‘A’(1.0×10^{-3}M) + Ligand ‘B’(1.0×10^{-3}M) + Metal nitrate (1.0×10^{-3}M).

Where, Ligand 'A' = Malonic acid(Mal) and **Ligand ‘B’** = Nitrilotriacetic acid(Nta) / Iminodiacetic acid(Imda)
and M = Cd(II) and Gd(III)

RESULTS AND DISCUSSION

The experimental data are used to obtain titration curves (pH vs ‘a’) where, a= moles of alkali added per mole of ligand/metal, and titration curves are given in (Figs. 1-4). The nature of ligand titration curves (curve 1 and 2) indicates that the deprotonation of all the ligands occurs in two distinct steps. Further, the deviation of metal – ligand curves (curve 3 and 4) from ligand curves suggests the formation of binary complexes. Curve 5 depicts the metal-ligand A- ligand B (1:1:1) titration of Cd(II)/Gd(III)-Mal-Imda/Nta ternary systems. The curve 5 in all the figs. is seen to be displaced to the right hand side of 1:1 (MA/MB) titration curves, thereby suggesting the formation of ternary complexes.

This is further supported by non-superimposible nature of theoretical composite curve in the region of ternary complex formation. The theoretical composite curve is obtained by plotting the theoretical addition of the values of ‘a’ corresponding to ligand titration curve of one ligand to the metal – ligand (1:1) titration curve of other ligand. Various equilibria and the corresponding equilibrium constants in binary and ternary metal-ligand systems are represented as follow:

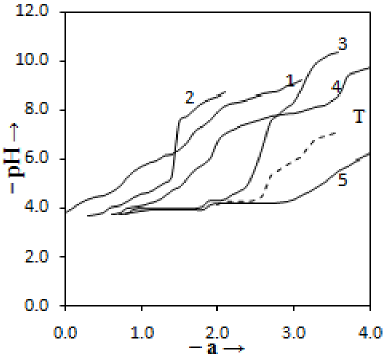


Fig. 1.

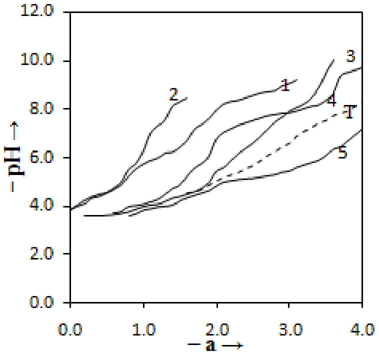


Fig. 2.

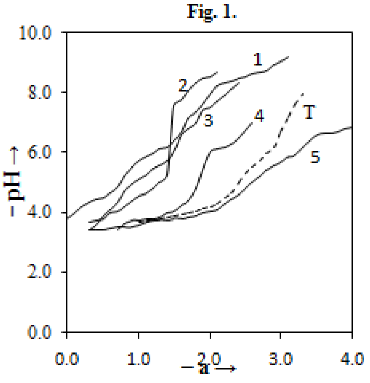


Fig. 3.

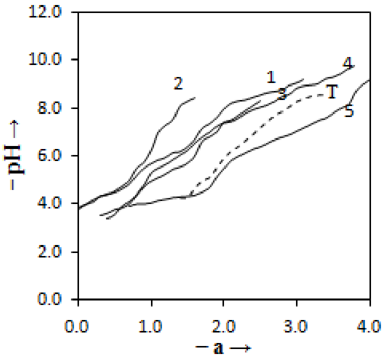


Fig. 4.

Fig. 1. pH vs 'a' curves for Gd(III)-Mal-Nta(1:1:1) system at 30ºC±1 [μ = 0.10M (NaNO3)]. **Fig. 2.** pH vs 'a' curves for Gd(III)-Mal-Imda(1:1:1) system at 30ºC±1 [μ = 0.10M (NaNO3)]. **Fig. 3.** pH vs 'a' curves for Cd((II) -Mal-Nta(1:1:1) system at 30ºC±1 [μ = 0.10M (NaNO3)].**Fig.4.** pH vs 'a' curves for Cd(II)-Mal- Imda(1:1:1) system at 30ºC±1 [μ = 0.10M (NaNO3)]

(Curve : 1 Ligand A (Mal) Titration Curve, Curve : 2 Ligand B (Nta/Imda) Titration Curve, Curve : 3 Metal-Ligand A (1:1) Titration Curve, Curve : 4 Metal-Ligand B (1:1) Titration Curve, Curve : 5 Mixed-Ligand (1:1:1) Titration Curve, Curve 'T' Theoreticle Composite Curve).

Proton-ligand system:

$$H_2A \xrightleftharpoons[\mathrm{p}K_1^{H}]{0 \le a \le 1} HA + H^+ \qquad \text{… (i)}$$

$$HA \xrightleftharpoons[\mathrm{p}K_2^{H}]{1 \le a \le 2} A + H^+ \qquad \text{… (ii)}$$

$$H_2B \xrightleftharpoons[\mathrm{p}K_1^{H}]{0 \le a \le 1} HB + H^+ \qquad \text{… (iii)}$$

$$HB \xrightleftharpoons[\mathrm{p}K_2^{H}]{1 \le a \le 2} B + H^+ \qquad \text{… (iv)}$$

Binary M-H_2A system:

$$M+H_2A \xrightleftharpoons[\log K_{MAH}^{H}]{0 \le a \le 1} MAH + H^+ \qquad \text{… (v)}$$

$$M+HA \xrightleftharpoons[\log K_{MAH}^{M}]{0 \le a \le 1} MAH \qquad \text{… (vi)}$$

$$MAH \xrightleftharpoons[\log K_{MA}^{H}]{1 \le a \le 2} MA + H^+ \qquad \text{… (vii)}$$

$$M+A \xrightleftharpoons[\log K_{MA}^{M}]{0 \le a \le 2} MA \qquad \text{… (viii)}$$

Binary M-H_2B system:

$$M+H_2B \xrightleftharpoons[\log K_{MBH}^{H}]{0 \le a \le 1} MBH + H^+ \qquad \text{… (ix)}$$

$$M+HB \xrightleftharpoons[\log K_{MBH}^{M}]{0 \le a \le 1} MBH \qquad \text{… (x)}$$

… (xi)

$$\mathrm{MBH} \underset{\log K^{\mathrm{H}}_{\mathrm{MB}}}{\overset{1\le a\le 2}{\rightleftharpoons}} \mathrm{MB} + \mathrm{H}^{+}$$

$$\mathrm{M+B} \underset{\log K^{\mathrm{M}}_{\mathrm{MB}}}{\overset{0\le a\le 2}{\rightleftharpoons}} \mathrm{MB} \qquad \text{---- (xii)}$$

Ternary M-H_2A-H_2B system:

$$\mathrm{M+H_2A+H_2B} \underset{\log K^{\mathrm{H}}_{\mathrm{MABH2}}}{\overset{0\le a\le 2}{\rightleftharpoons}} \mathrm{MABH_2} + 2\mathrm{H}^{+} \qquad \text{---- (xiii)}$$

$$\mathrm{M+HA+HB} \underset{\log K^{\mathrm{M}}_{\mathrm{MABH2}}}{\overset{0\le a\le 2}{\rightleftharpoons}} \mathrm{MABH_2} \qquad \text{---- (xiv)}$$

---- (xv)

$$\mathrm{MABH_2} \underset{\log K^{\mathrm{H}}_{\mathrm{MABH}}}{\overset{2\le a\le 3}{\rightleftharpoons}} \mathrm{MABH} + \mathrm{H}^{+}$$

---- (xvi)

$$\mathrm{M+A+HB} \underset{\log K^{\mathrm{M}}_{\mathrm{MABH}}}{\overset{0\le a\le 3}{\rightleftharpoons}} \mathrm{MABH}$$

---- (xvii)

$$\mathrm{MABH} \underset{\log K^{\mathrm{H}}_{\mathrm{MAB}}}{\overset{3\le a\le 4}{\rightleftharpoons}} \mathrm{MAB} + \mathrm{H}^{+}$$

---- (xviii)

$$\mathrm{M+A+B} \underset{\log K^{\mathrm{M}}_{\mathrm{MAB}}}{\overset{0\le a\le 4}{\rightleftharpoons}} \mathrm{MAB}$$

(Charges have been omitted for the sake of simplicity).

Treatment based on the algebraic method of Chaberek and Martell [23-24] as modified by Dey *et al.* [25] has been used in the present work for the calculation of various constants in proton-ligand and in binary and ternary metal-ligand systems. Another approach for the calculation of stability constant involving simultaneous equilibrium was developed and reported in literature by S. Ramamoorthy and M. Santappa [26-27]. These approaches have been used for the determination of stability constants of ternary systems formed through simultaneous equilibria. The stability constants obtained at various ionic strengths were extrapolated to zero ionic strength in order to obtain thermodynamic stability constants. These values are given in (Tables 1-4).

Table 1: Thermodynamic protonation constant of ligands.

Parameters	Mal			Parameters	Nta			Imda		
	20°C	30°C	40°C		20°C	30°C	40°C	20°C	30°C	40°C
$\log \beta_1^{HA}$	6.73	6.50	6.30	$\log \beta_1^{HB}$	9.98	9.83	9.48	9.02	8.65	8.35
$\log \beta_2^{H2A}$	9.89	9.80	9.60	$\log \beta_2^{H2B}$	12.96	12.82	12.70	12.00	11.35	11.15

$$\log \beta_1^{HA} = pK_2^H \qquad \log \beta_2^{H2A} = pK_1^H + pK_2^H$$

The values of the thermodynamic stability constants $\log K^{\mu\to 0}$ were used to determine the standard free energy change ($\Delta G°$) for the complexation reaction from Van't Hoff isotherm:

$$\Delta G° = -2.303RT \log K^{\mu\to 0} \quad \text{----- (xix)}$$

The Gibb's Helmholtz equation ($\Delta G° = \Delta H° - T\Delta S°$) and Van't Hoff equation can be put in the following form:

$$\log K^{\mu\to 0} = \frac{-\Delta H°}{2.303R}\,\frac{1}{T} + \frac{\Delta S°}{2.303R} \quad \text{----- (xx)}$$

The standard enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been determined by linear least square fit method by plotting a graph between $\frac{1}{T}$ vs $\log K^{\mu\to 0}$ using equation (xviii). In the above equation (xviii):

$$\text{Slope} = \frac{-\Delta H°}{2.303R} \quad \text{and} \quad \text{Intercept} = \frac{\Delta S°}{2.303R}$$

The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are presented in (Table 3 and 4). The negative values of $\Delta G°$ in each case indicate that the complexation is spontaneous. The negative enthalpy changes ($\Delta H°$) for the complexation suggest that all the complexation reaction are exothermic, favorable at lower temperature and the metal ligand binding process is enthalpy driven and metal-ligand bond are fairly strong. The positive value of $\Delta S°$ for some metal complexes indicate that the formation of these complexes was entropy favored, while negative $\Delta S°$ values for some metal complexes suggesting a highly solvated metal complexes [28-29].

The stability of mixed ligand complexes formed over their corresponding binary complexes was evaluated by calculating the parameter ΔlogK according to the following equation and values of ΔlogK for ternary complexes are given in (Table 5).

Table 2: Thermodynamic formation constants of binary complexes.

Parameters	Gd(III)-Mal			Cd(II)-Mal		
	20°C	30°C	40°C	20°C	30°C	40°C
log K^{M}_{MAH}	4.95	4.85	4.65	4.38	4.31	4.27
logK^{H}_{MAH}	-4.12	-4.07	-4.00	-5.62	-5.56	-5.50
logK^{H}_{MA}	-5.48	-5.37	-5.32	-6.32	-6.20	-6.10
log β_{MAH}	11.90	11.78	11.64	10.95	10.90	10.85
log β_{MA}	6.85	6.77	6.65	5.62	5.53	5.45
	Gd(III)-Nta			Cd(II)-Nta		
log K^{M}_{MAH}	3.00	2.70	2.56	2.55	2.50	2.28
logK^{H}_{MAH}	-4.12	-4.06	-3.98	-6.62	-6.54	-6.50
logK^{H}_{MA}	-4.77	-4.64	-4.35	-7.30	-7.25	-6.88
log β_{MAH}	12.62	12.20	11.67	12.20	12.10	11.85
log β_{MA}	8.17	8.02	7.95	7.10	6.97	6.90
	Gd(III)-Imda			Cd(II)-Imda		
log K^{M}_{MAH}	2.72	2.65	2.54	2.70	2.55	2.40
logK^{H}_{MAH}	-3.24	-3.18	-3.10	-3.90	-3.86	-3.80
logK^{H}_{MA}	-3.75	-3.30	-3.42	-4.70	-4.55	-4.38
log β_{MAH}	11.85	11.50	11.25	11.52	11.30	11.08
log β_{MA}	4.55	4.50	4.46	4.45	4.27	3.95

log β_{MAH} = logK^{M}_{MAH} + log $\beta_1{}^{HA}$

log β_{MA} = logK^{M}_{MA}

log β_{MBH} = logK^{M}_{MBH} + log $\beta_1{}^{HB}$

log β_{MB} = logK^{M}_{MB}

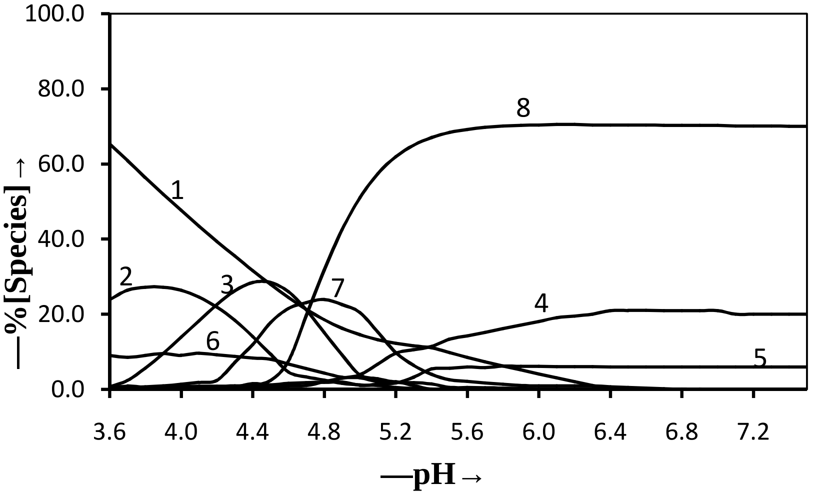
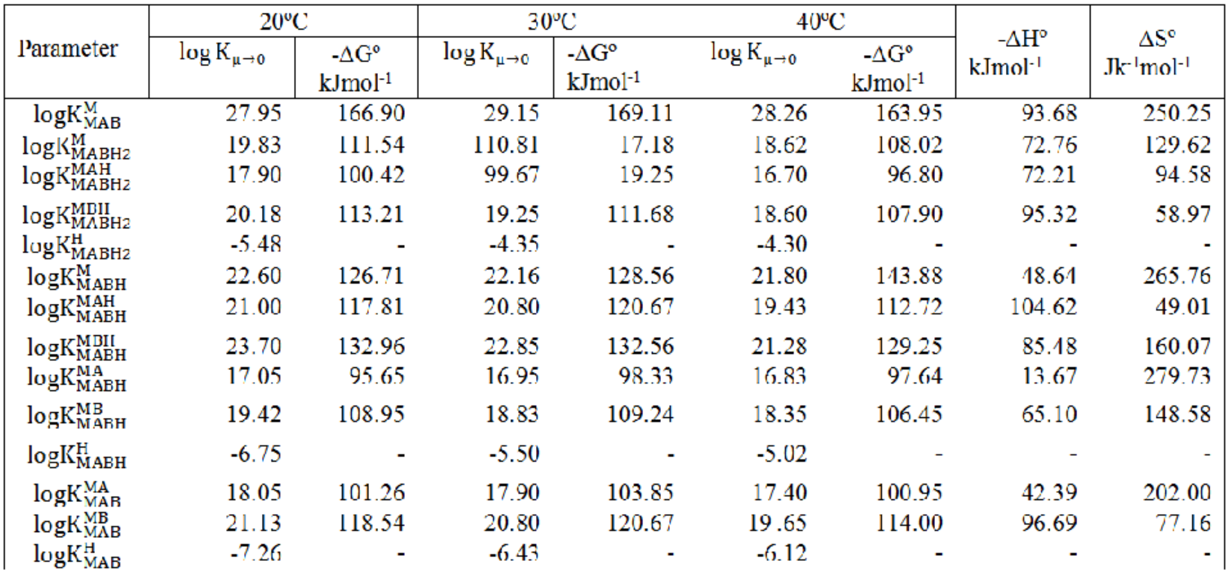


Fig. 5. Speciation Curves for Gd(III)-Mal-Nta (1:1:1) System at 30°C±1 [(μ=0.10M(NaNO$_3$)].

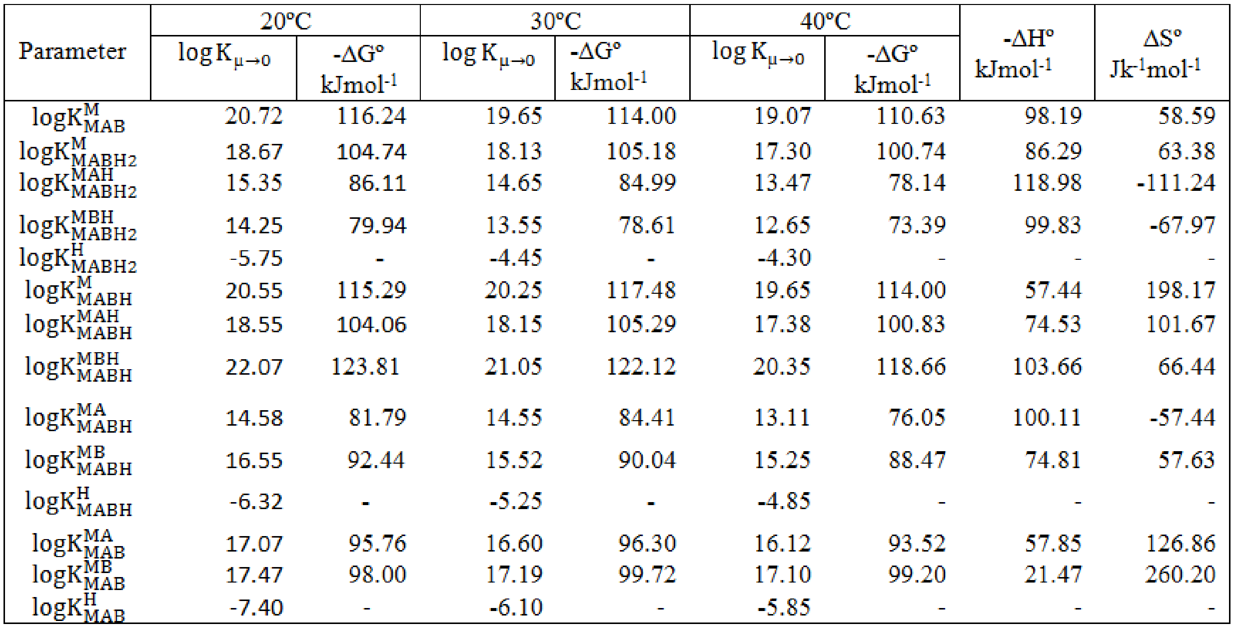
Table 3: Thermodynamic formation constants and thermodynamic parameters.

Gd(III)-Mal-Nta



Parameter	20°C		30°C		40°C		-ΔH° kJmol⁻¹	ΔS° Jk⁻¹mol⁻¹
	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹		
$\log K^{M}_{MAB}$	27.95	166.90	29.15	169.11	28.26	163.95	93.68	250.25
$\log K^{M}_{MABH2}$	19.83	111.54	110.81	17.18	18.62	108.02	72.76	129.62
$\log K^{MAH}_{MABH2}$	17.90	100.42	99.67	19.25	16.70	96.80	72.21	94.58
$\log K^{MBH}_{MABH2}$	20.18	113.21	19.25	111.68	18.60	107.90	95.32	58.97
$\log K^{H}_{MABH2}$	-5.48	-	-4.35	-	-4.30	-	-	-
$\log K^{M}_{MABH}$	22.60	126.71	22.16	128.56	21.80	143.88	48.64	265.76
$\log K^{MAH}_{MABH}$	21.00	117.81	20.80	120.67	19.43	112.72	104.62	49.01
$\log K^{MBH}_{MABH}$	23.70	132.96	22.85	132.56	21.28	129.25	85.48	160.07
$\log K^{MA}_{MABH}$	17.05	95.65	16.95	98.33	16.83	97.64	13.67	279.73
$\log K^{MB}_{MABH}$	19.42	108.95	18.83	109.24	18.35	106.45	65.10	148.58
$\log K^{H}_{MABH}$	-6.75	-	-5.50	-	-5.02	-	-	-
$\log K^{MA}_{MAB}$	18.05	101.26	17.90	103.85	17.40	100.95	42.39	202.00
$\log K^{MB}_{MAB}$	21.13	118.54	20.80	120.67	19.65	114.00	96.69	77.16
$\log K^{H}_{MAB}$	-7.26	-	-6.43	-	-6.12	-	-	-

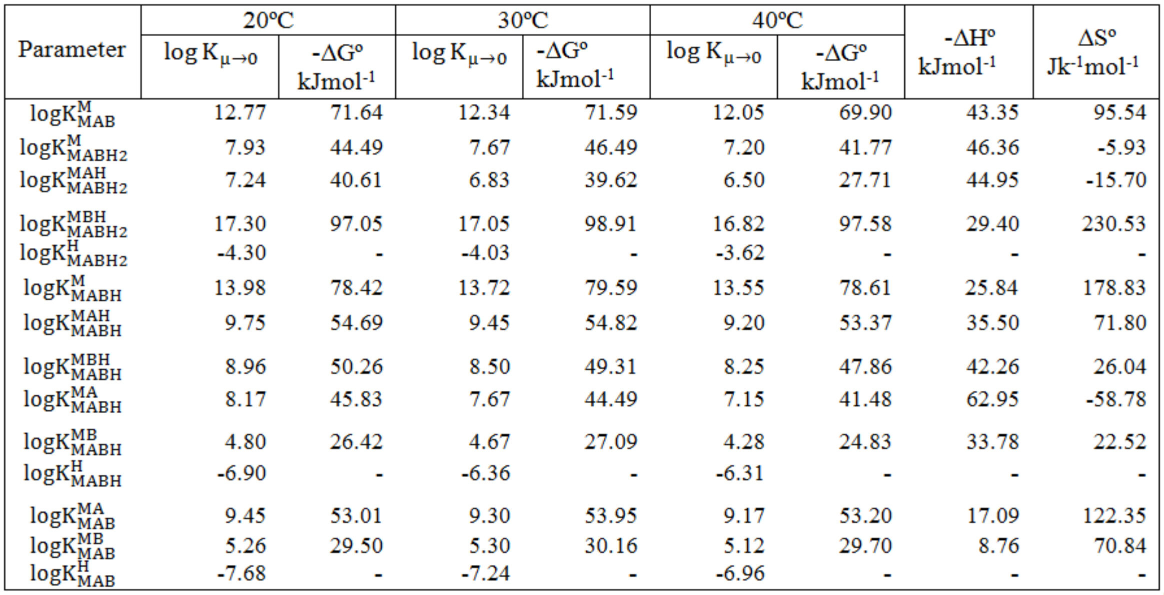
Gd(III)-Mal-Imda



Parameter	20°C		30°C		40°C		-ΔH° kJmol⁻¹	ΔS° Jk⁻¹mol⁻¹
	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹	$\log K_{\mu\to 0}$	-ΔG° kJmol⁻¹		
$\log K^{M}_{MAB}$	20.72	116.24	19.65	114.00	19.07	110.63	98.19	58.59
$\log K^{M}_{MABH2}$	18.67	104.74	18.13	105.18	17.30	100.74	86.29	63.38
$\log K^{MAH}_{MABH2}$	15.35	86.11	14.65	84.99	13.47	78.14	118.98	-111.24
$\log K^{MBH}_{MABH2}$	14.25	79.94	13.55	78.61	12.65	73.39	99.83	-67.97
$\log K^{H}_{MABH2}$	-5.75	-	-4.45	-	-4.30	-	-	-
$\log K^{M}_{MABH}$	20.55	115.29	20.25	117.48	19.65	114.00	57.44	198.17
$\log K^{MAH}_{MABH}$	18.55	104.06	18.15	105.29	17.38	100.83	74.53	101.67
$\log K^{MBH}_{MABH}$	22.07	123.81	21.05	122.12	20.35	118.66	103.66	66.44
$\log K^{MA}_{MABH}$	14.58	81.79	14.55	84.41	13.11	76.05	100.11	-57.44
$\log K^{MB}_{MABH}$	16.55	92.44	15.52	90.04	15.25	88.47	74.81	57.63
$\log K^{H}_{MABH}$	-6.32	-	-5.25	-	-4.85	-	-	-
$\log K^{MA}_{MAB}$	17.07	95.76	16.60	96.30	16.12	93.52	57.85	126.86
$\log K^{MB}_{MAB}$	17.47	98.00	17.19	99.72	17.10	99.20	21.47	260.20
$\log K^{H}_{MAB}$	-7.40	-	-6.10	-	-5.85	-	-	-

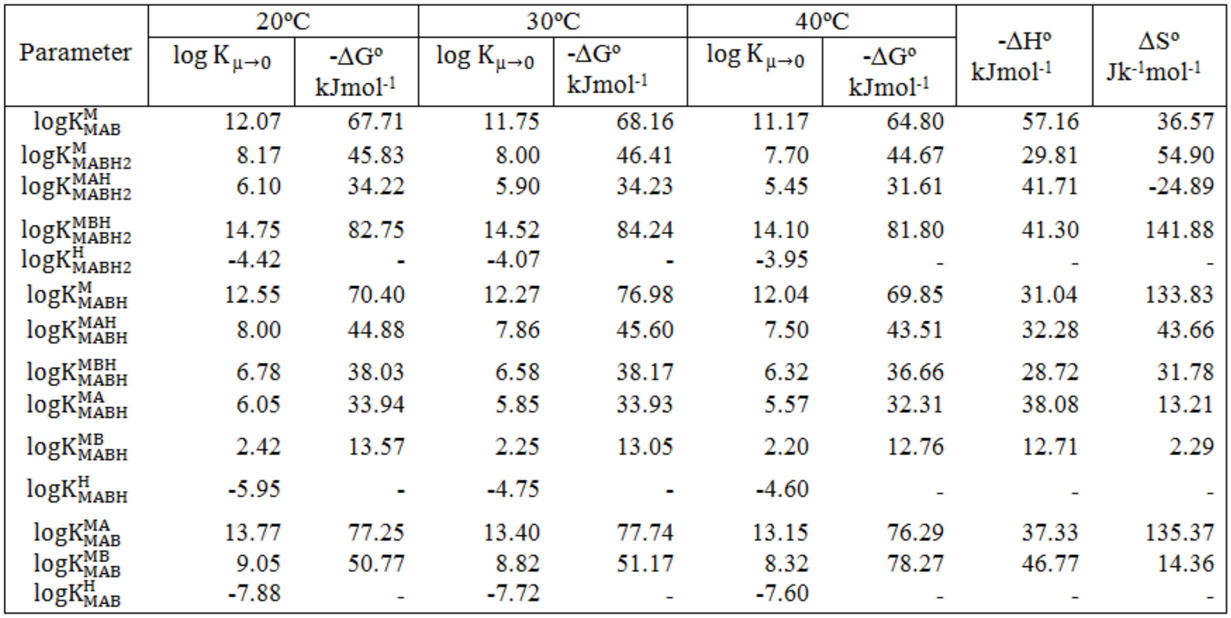
Table 4: Thermodynamic formation constants and thermodynamic parameters.

Cd(II)-Mal-Nta



Parameter	20°C		30°C		40°C		$-\Delta H^o$ kJmol^{-1}	ΔS^o Jk^{-1}mol^{-1}
	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}		
$\log K^{M}_{MAB}$	12.77	71.64	12.34	71.59	12.05	69.90	43.35	95.54
$\log K^{M}_{MABH2}$	7.93	44.49	7.67	46.49	7.20	41.77	46.36	-5.93
$\log K^{MAH}_{MABH2}$	7.24	40.61	6.83	39.62	6.50	27.71	44.95	-15.70
$\log K^{MBH}_{MABH2}$	17.30	97.05	17.05	98.91	16.82	97.58	29.40	230.53
$\log K^{H}_{MABH2}$	-4.30	-	-4.03	-	-3.62	-	-	-
$\log K^{M}_{MABH}$	13.98	78.42	13.72	79.59	13.55	78.61	25.84	178.83
$\log K^{MAH}_{MABH}$	9.75	54.69	9.45	54.82	9.20	53.37	35.50	71.80
$\log K^{MBH}_{MABH}$	8.96	50.26	8.50	49.31	8.25	47.86	42.26	26.04
$\log K^{MA}_{MABH}$	8.17	45.83	7.67	44.49	7.15	41.48	62.95	-58.78
$\log K^{MB}_{MABH}$	4.80	26.42	4.67	27.09	4.28	24.83	33.78	22.52
$\log K^{H}_{MABH}$	-6.90	-	-6.36	-	-6.31	-	-	-
$\log K^{MA}_{MAB}$	9.45	53.01	9.30	53.95	9.17	53.20	17.09	122.35
$\log K^{MB}_{MAB}$	5.26	29.50	5.30	30.16	5.12	29.70	8.76	70.84
$\log K^{H}_{MAB}$	-7.68	-	-7.24	-	-6.96	-	-	-

Cd(II)- Mal-Imda



Parameter	20°C		30°C		40°C		$-\Delta H^o$ kJmol^{-1}	ΔS^o Jk^{-1}mol^{-1}
	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}		
$\log K^{M}_{MAB}$	12.07	67.71	11.75	68.16	11.17	64.80	57.16	36.57
$\log K^{M}_{MABH2}$	8.17	45.83	8.00	46.41	7.70	44.67	29.81	54.90
$\log K^{MAH}_{MABH2}$	6.10	34.22	5.90	34.23	5.45	31.61	41.71	-24.89
$\log K^{MBH}_{MABH2}$	14.75	82.75	14.52	84.24	14.10	81.80	41.30	141.88
$\log K^{H}_{MABH2}$	-4.42	-	-4.07	-	-3.95	-	-	-
$\log K^{M}_{MABH}$	12.55	70.40	12.27	76.98	12.04	69.85	31.04	133.83
$\log K^{MAH}_{MABH}$	8.00	44.88	7.86	45.60	7.50	43.51	32.28	43.66
$\log K^{MBH}_{MABH}$	6.78	38.03	6.58	38.17	6.32	36.66	28.72	31.78
$\log K^{MA}_{MABH}$	6.05	33.94	5.85	33.93	5.57	32.31	38.08	13.21
$\log K^{MB}_{MABH}$	2.42	13.57	2.25	13.05	2.20	12.76	12.71	2.29
$\log K^{H}_{MABH}$	-5.95	-	-4.75	-	-4.60	-	-	-
$\log K^{MA}_{MAB}$	13.77	77.25	13.40	77.74	13.15	76.29	37.33	135.37
$\log K^{MB}_{MAB}$	9.05	50.77	8.82	51.17	8.32	78.27	46.77	14.36
$\log K^{H}_{MAB}$	-7.88	-	-7.72	-	-7.60	-	-	-

$\Delta \log K_{MABH2} = \log \beta_{MABH2} - (\log \beta_{MAH} + \log \beta_{MBH})$ -- - (xxi)

$\Delta \log K_{MABH} = \log \beta_{MABH} - (\log \beta_{MA} + \log \beta_{MBH})$ ---(xxii)

$\Delta \log K_{MAB} = \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB})$ --(xxiii)

In general, if mixed ligand complexes are most stable than their corresponding binary complexes, the value of ΔlogK is positive [30-32]. Values given in table 4 clearly reveal that all mixed ligand complexes formed are more stable than their corresponding binary complexes. Speciation curves are obtained for various systems by using SCOGS computer program [33-35]. Speciation curves for Cd(II)-Mal-Imda/Nta and Gd(III)-Mal- Imda/Nta systems are shown in (Figs. 5-8) respectively. These curves follow the same trend.

Mixed ligand complexes of $MABH_2$, MABH and MAB have been assumed in different equilibria. Speciation curves show that formation of MAH and MBH i.e. binary protonated complexes take place up to pH≈4.0 and then the concentration of free metal and protonated species starts decreasing continuously. The formation of non-protonated binary complexes comes into existence and its concentration increases constantly in higher pH range.

However, the concentration of binary protonated/nonprotonated species is less than 25% in all the systems. Formation of ternary species takes place by simultaneous coordination of the two ligands. Formation of $MABH_2$ and MABH species are evident, but is confined up to pH≈4.5 and its percentage remain less than 35%. Nonprotonated ternary complexes MAB also come into existence and its concentration increases appreciably. It is observed that the percentage of MAB species is maximum ≈<75% in all the systems investigated in the present work. Hence it is concluded the MAB ternary species is the most prominent species formed in mixed ligand equilibria.

The high thermodynamic stability of ternary complexes can be attributed to the fact that the electron densities of the metal-ligand bond in ternary systems are redistributed to increase the polarity and hence, mixed ligand complexes are not easily hydrolysed. This is supported by earlier investigation [36].

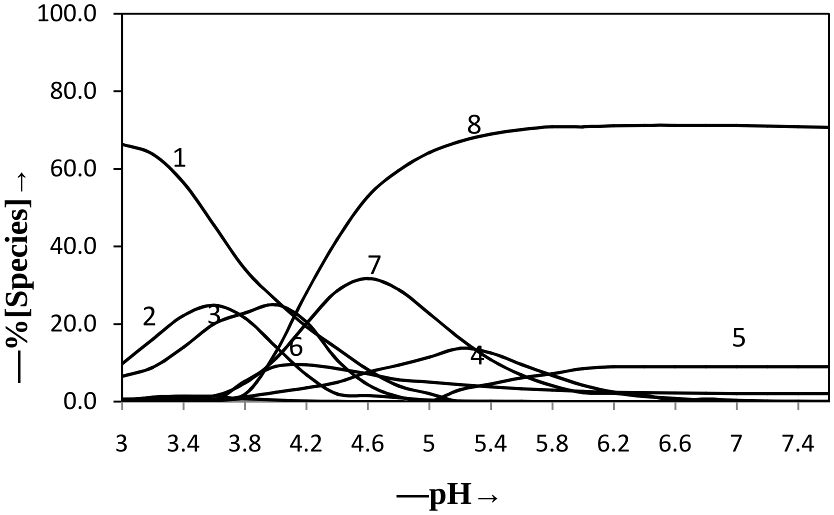


Fig. 6. Speciation Curves for Gd(III)-Mal-Imda (1:1:1) System at 30°C±1 [(μ=0.10M($NaNO_3$)]. Where, Curve 1: [M]; 2 [MAH]; 3[MA]; 4 [MBH]; 5 [MB]; 6 [$MABH_2$]; 7 [MABH]; 8 [MAB]

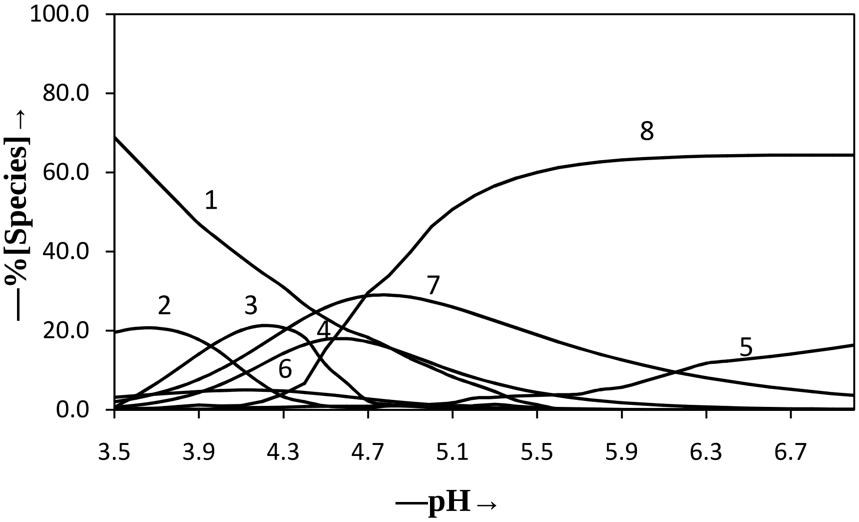


Fig. 7. Speciation Curves for Cd(II)-Mal-Nta(1:1:1) System at 30°C±1 [(μ=0.10M(NaNO$_3$)]

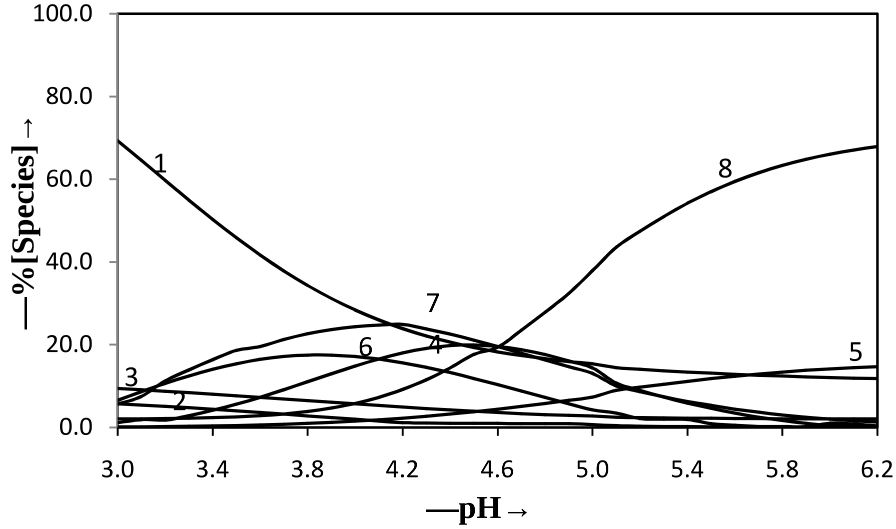


Fig. 8. Speciation Curves for Cd(II)-Mal-Imda(1:1:1) System at 30°C±1 [(μ=0.10M(NaNO$_3$)].
(Where, Curve 1: [M]; 2 [MAH]; 3[MA]; 4 [MBH]; 5 [MB]; 6 [MABH$_2$]; 7 [MABH]; 8 [MAB]).

CONCLUSION

The metal ions Cd(II) and Gd(III) form binary (1:1) and ternary (1:1:1) metal-ligand complexes with malonic acid and nitrilotriacetic acid/iminodiacetic acid.

The Gd(III) complexes are more stable than Cd(II) complexes, this can be explained on the basis of high charge of Gd(III) ion. The positive ΔlogK values indicate that the ternary metal- ligand complexes are more stable than binary complexes (Table 5).

The metal-ligand stability constant logK decrease with an increase in temperature and ionic strengths. The negative value of change in enthalpy (ΔH°) for the complexation suggests that all the reactions are exothermic, favorable at lower temperature. The negative change in free energy (ΔG°) values indicates that both dissociation of the ligand and complexation process are spontaneous. The negative change in entropy (ΔS°) values indicate a highly solvated metal complex while positive ΔS° value for some metal complexes indicate that the formation of these complexes are entropically favored.

Table 5 : Value of Δlog K for ternary complexes.

	20°C		30°C		40°C	
	$\log\beta^{\mu\to 0}$	Δlog K	$\log\beta^{\mu\to 0}$	Δlog K	$\log\beta^{\mu\to 0}$	Δlog K
Parameters	Gd(III)-Mal-Nta					
$\log\beta_{MABH2}$	36.54	12.02	35.43	11.45	34.40	11.09
$\log\beta_{MABH}$	32.58	13.11	31.99	13.02	31.30	12.96
$\log\beta_{MAB}$	29.75	15.03	29.15	14.36	28.26	13.66
	Gd(III)-Mal-Imda					
$\log\beta_{MABH2}$	34.42	10.67	33.38	10.01	31.95	9.06
$\log\beta_{MABH}$	29.57	10.87	28.90	10.63	28.00	10.01
$\log\beta_{MAB}$	20.72	9.32	19.65	8.38	19.07	7.59
	Cd(II)-Mal-Nta					
$\log\beta_{MABH2}$	24.90	1.75	24.62	1.62	24.22	1.60
$\log\beta_{MABH}$	23.73	5.91	23.60	5.97	23.27	5.97
$\log\beta_{MAB}$	15.05	2.33	14.57	2.03	14.33	1.98
	Cd(II)-Mal-Imda					
$\log\beta_{MABH2}$	24.92	2.45	23.15	0.95	22.35	0.42
$\log\beta_{MABH}$	21.57	4.43	20.92	4.09	20.39	3.86
$\log\beta_{MAB}$	12.01	1.94	11.65	1.85	11.30	1.79

$$\log\beta_{MABH2} = \log K^{M}_{MABH2} + \log\beta_1^{HA} + \log\beta_1^{HB}$$

$$\log\beta_{MABH} = \log K^{M}_{MABH} + \log\beta_1^{HB}$$

$$\log\beta_{MAB} = \log K^{M}_{MAB}$$

REFERENCES

[1]. S. Sharma, D. Dalwadi, and M. Neog, *J. Serb. Chem. Soc.*, **75**(1), 75-82 (2010).

[2]. J. Sanchiz, P. Esparza, S. Dominguez, F. Brito and A. Mederos, *Inorganica Chimica Acta*, **(29)**, 158-165(1999).

[3]. S.D. Dhage, M.B. Swami, *IOSR J. Applied Chem*., **2**(6), 36-38 (2012).

[4]. P. Harman, J. Kotek, V. Kubicek and I. Lukes, *Dalton Transaction*, 3027-3147 (2008).

[5]. S. Arzik, E.M. Ayan, and A.S. Celebi, *Turk. J. Chem.*, **32**, 721-729 (2008).

[6]. M. Alzahadi and A.A. Ei Sherif, *J. Solution Chem.*, **41**, 1759-1776(2012).

[7]. A. Branchi, L. Calaki, F. Corana, S. Fontana, P.Losi, A. Macchi, L. Paleari and B. Valtancoli, *Coordination Chem. Reviews,* **204**, 309-393 (2000).

[8]. M. Aljahdali, A.A. Ei-Sherif, M.M. Shoukry, S.E. Mohamed, *J. Solution Chem.* **42**, 1028-1050 (2013).
[9]. E.M. Khery, M.M. Shoukry, N.N. Khalil and M.M.A. Mohamed, *Trans. Metal Chem.*, **21**, 176-180 (1996).
[10]. M.M. Shoukry, M.R. Shehata and M.M.A. Mohamed, *Mikrochimica Acta*, **129**, 107-113 (1998)
[11]. VS. Katkar, Int. Res. J. Sci. and Eng., **1(2)**, 41-46 (2013).
[12]. P. Praveen Singh et. al. *J. Indian Chem. Soc.*, **86**, 83-86 (2009).
[13]. A.B. Patil and T.H. Mhaske, *Asian J. Chem.*, **14**(1), 125-129 (2002).
[14]. G.V. Mane, G. Devrao Kolhatkar, L.P. Shinde, *J. Chem. and Pharma. Res.* **4**(2),1022-1027 (2012).
[15]. H. Gazala Mohamed, Ben Hander, *Rec. J. Chem. Sci.*, **2**(3), 12.20 (2012).
[16]. K. Kumar, D.K. Dwivedi, *Int. J. Innovative Res. in Sci. Eng. and Tech.*, **3**, 14711-14718 (2014).
[17]. De. Vallis, L.M. Shannon, J.Y. Lew, *Plant Physiol*, **38**,686-690 (1963).
[18]. D.K. Stumpf, R.H. Burris, *Physiol*, **68**, 992-995 (1981).
[19]. O.F. Goulart, Hans-Yargen Schafer, *J. Braz. Chem. Soc.*, **10**, 235-341 (1999).
[20]. G. Galli, C.L. Maini, Technetium in Chemistry and Nuclear Medicine 2, Cortina International, Verona, Raven Press, New York, 309 (1986).
[21]. J.S. Briboric, M.S. Jovanovic, G. Popovic, V. Kapetanovic and S. Viladimirov, *J. Serb. Chem. Soc.*, **71**(1), 55-65 (2006).
[22]. Nitrilotriaccetic Acid and its Salt, *IRAC Monograph*, 73 (1990).
[23]. S. Chaberek and A.E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).
[24]. S. Chaberek and A.E. Martell, *J. Am. Chem. Soc.*, **77**, 1477, (1955).
[25]. R. Nayan and A.K. Dey, *Indian J. Chem.*, **14**(A), 892 (1976).
[26]. S. Ramamoorthy and M. Santappa *Indian J. Chem.*, **9**, 381 (1971).
[27]. S. Ramamoorthy and M. Santappa *J. Inorg. Nucl. Chem.*, **33**, 1775 (1971).
[28]. D.T. Promila and R. Lonibala, J. Chem. Eng. Data., **55**, 1166, (2010).
[29]. S.V. Singh Thakur, M. Farooqui and S.D. Naikwade, *J. Chem. Bio and Phy. Sci.*, **4**(1), 1-7, (2014).
[30]. H. Sigel, Cordination Chemistry, Pergamon Press, Oxford, UK (1980).
[31]. R. Thanavalen, G. Manikandan, G. Ramalingam and V. Thanikachalan, *Pelagia Res. Library*, **2**(4), 90-98 (2011).
[32]. A.M.D.S. Chandrathilaka, O.A. Ileperuma and C.V. Hettiarachchi, *J. Natn. Sci. Foundation Srilanka*, **41**(4), 337-344 (2013).
[33]. I.G. Sayce, *Talanta*, **15**, 1397 (1968).
[34]. I.G. Sayce, *Talanta*, **18**, 653 (1971).
[35]. I.G. Sayce, and V.S. Sharma, *Talanta*, **19**, 831 (1972).
[36]. M.T. El-Haty, A.H. Amrallah, R-A Mohmoud and A.A. Ibrahim, *Talanta*, **42**, 1711-1717 (1995).