4.1. Introduction

Catecholamines play an important role in health and disease. The change of catecholamine level have been correlated with stress, heart disease, change in blood pressure, thyroid hormone level and various type of mental illness.[1-3] The metabolites are often the primary assay target because of their higher concentration and greater stability. Catecholamines are well known for their use in neurotransmission process and in the treatment of Parkinson disease.[4-13] In the present work, multiple equilibria involving tyrosine, dopa and dopm have been investigated. The choice of these ligands is due to their marked significance in the biological system.

Tyrosine is a precursor to neurotransmitters and increases plasma neurotransmitter levels.[14] Several studies have found tyrosine to be useful during conditions of stress, which helps to meet the reductions in stress hormone levels.[15] Tyrosine is synthesized in the body from phenylalanine and it is a direct precursor of adrenaline and thyroid hormones. Metabolic transformations of tyrosine require the presence of folic acid, niacin, vitamin c and copper. Its metabolic products include melanin, estrogen and encephalin. Tyrosine is used along with tryptophan to aid in the treatment of cocaine abuse and may also be useful in the control of anxiety or depression.[16-19] Tyrosine is created from phenylalanine by hydroxylation by the enzyme phenylalanine hydroxylase. Tyrosine is also ingested directly from dietary protein. Catecholamine-secreting cells use several reactions to convert tyrosine serially to dopa and then to dopamine. Depending on the cell type, dopamine may be further converted to norepinephrine or even further converted to epinephrine.[20]

Dopa is an ambidentate ligand which can bound to the metal ion via the (N,O) donor groups at physiological pH.[21] Dopamine is implicated in many neurological processes, including motivation, pleasure, cognition, memory, learning, and fine motor control, as well as a modulation of neuroendocrine signaling. Abnormal dopamine receptor signaling and dopaminergic nerve function is implicated in several neurological disorders [22–25]. **Dopamine** has pharmacologically appropriate effects in the management of low cardiac output associated with compromised renal function, such as severe congestive heart failure[26-27]. The neurotransmitters dopamine and dopa mediate the generation and growth of gold nano particles (Au-Nps). The plasmon absorption of the Au-Nps allows the quantitative colorimetric detection of the neurotransmitters [28].

Chemical literature reveals that the several important mixed systems involving catecholamines are carried by several groups of workers. Publications during last decade are noteworthy surveyed.[29-35] The protonation equilibria and complex forming properties of dopa and phenanthroline with certain transition metal ions are reported by Rao et al.[36-40]. There have been few reports on the detection of dopamine using the potentiometric approach.[41–46]

Heavy metals such as lead, cadmium and mercury are toxic substances which exert adverse effects on neurological, reproductive, renal and hematological systems in humans and animals. Organo- mercury and lead compounds exhibit toxic effect on the central nervous system.[47] Similarly cadmium exhibits various chronic and acute disorders like testicular atrophy, hypertension, damage to kidneys and bones, anemia and Itai-Itai.[48-52] The stability constants of the binary complexes of Pb(II), Cd(II) and Hg(II) have been determined using pH-metry.[53-61]. However, very few publications appear on the study of mixed ligand

systems.[62-66] Such studies are useful to biological and environmental problems. The importance of tyrosine, dopa and dopm in biological systems motivated to study the complex forming tendency of these ligands in mixed systems considering the most various possible equilibria.

The present chapter includes the experimental details and results obtained by the investigation of following mixed ligand systems:

1. Cd(II) –Malonic acid – Tyrosine (TYR)
2. Cd(II) –Malonic acid – 3,4-dihydroxyphenylalanine (DOPA)
3. Cd(II) –Malonic acid – Dopamine (DOPM)
4. Gd(III) –Malonic acid – Tyrosine (TYR)
5. Gd(III) –Malonic acid – 3,4-dihydroxyphenylalanine (DOPA)
6. Gd(III) –Malonic acid –Dopamine (DOPM)

In addition to these ternary systems, all the possible combinations of binary systems involving above metal ions and ligands have been investigated under the same experimental conditions.

1. Cd(II)-Malonic acid
2. Cd (II)-Tyrosine
3. Cd (II)-DOPA
4. Cd (II)-DOPM
5. Gd(III)-Malonic acid
6. Gd(III)-Tyrosine
7. Gd(III)-DOPA
8. Gd(III)-DOPM

4.2. Experimental and computational methods:

Computational and experimental details are same as describe in chapter-2. Solution were prepared using Merck /Aldrich grade reagents

and potentiometric titrations were performed under specified experimental conditions as described in the preceding chapters. The titration curves are presented in figs. 1-6. The metal-ligand binary and ternary equilibrium constants are given in tables 4.1-4.9. The percent distributions of various species are given in tables 4.13-4.18 and the speciation curves are given in figs. 7-12. The conditional stability constants at different temperature and different ionic strength are extrapolated to zero ionic strength in order to obtain the thermodynamic stability constants ($\log K^{\mu \rightarrow 0}$). This is further used to obtain other thermodynamic parameters i.e. standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) by the methods as described in the preceeding chapters. These values are given in tables 4.10 - 4.12.

4.3. Curves and tables:

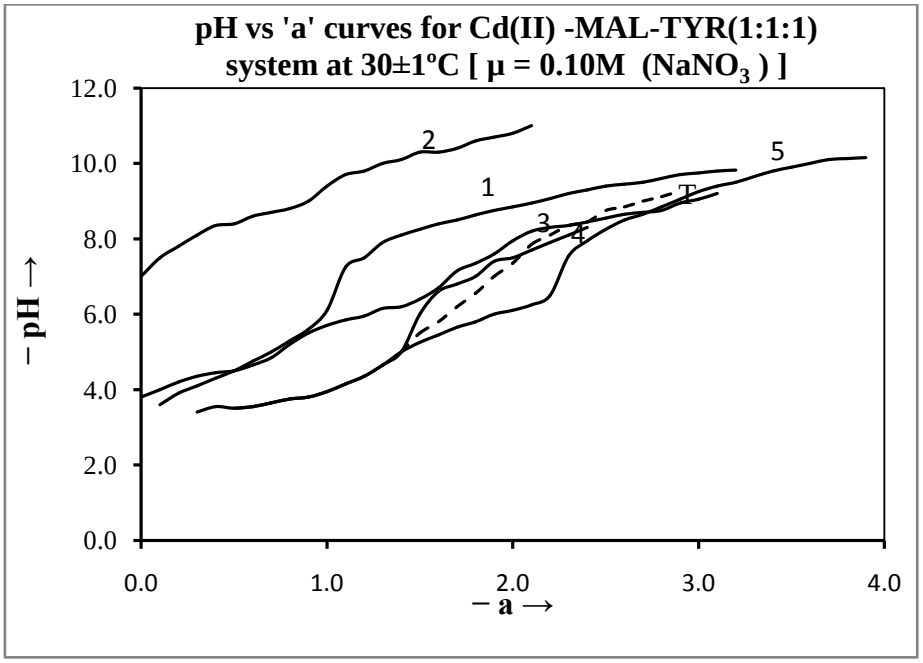

Fig. 1

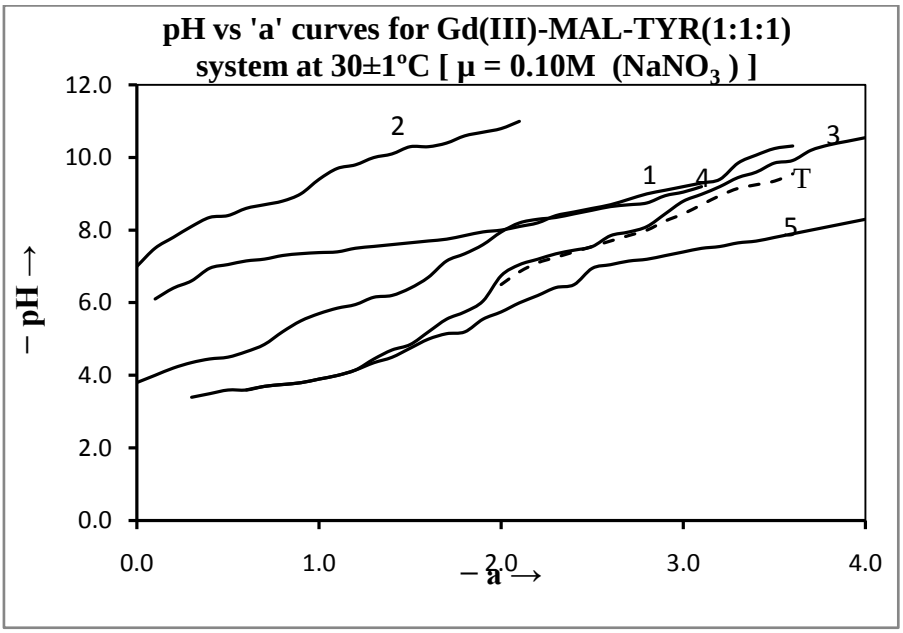

Fig. 2

Where- Curve : 1 Ligand A (MAL) Titration Curve
Curve : 2 Ligand B (TYR) 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

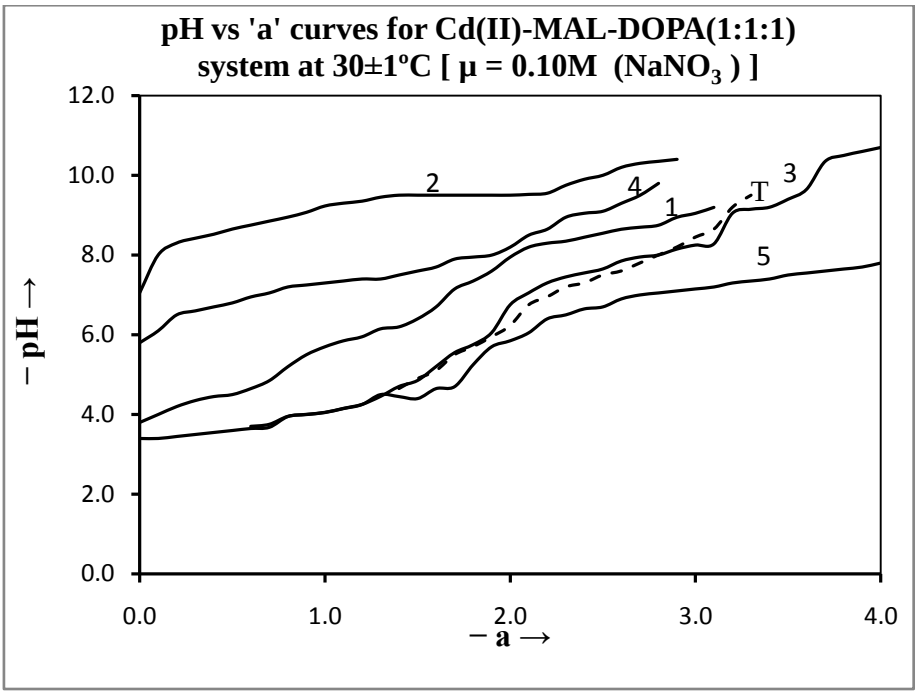

Fig. 3

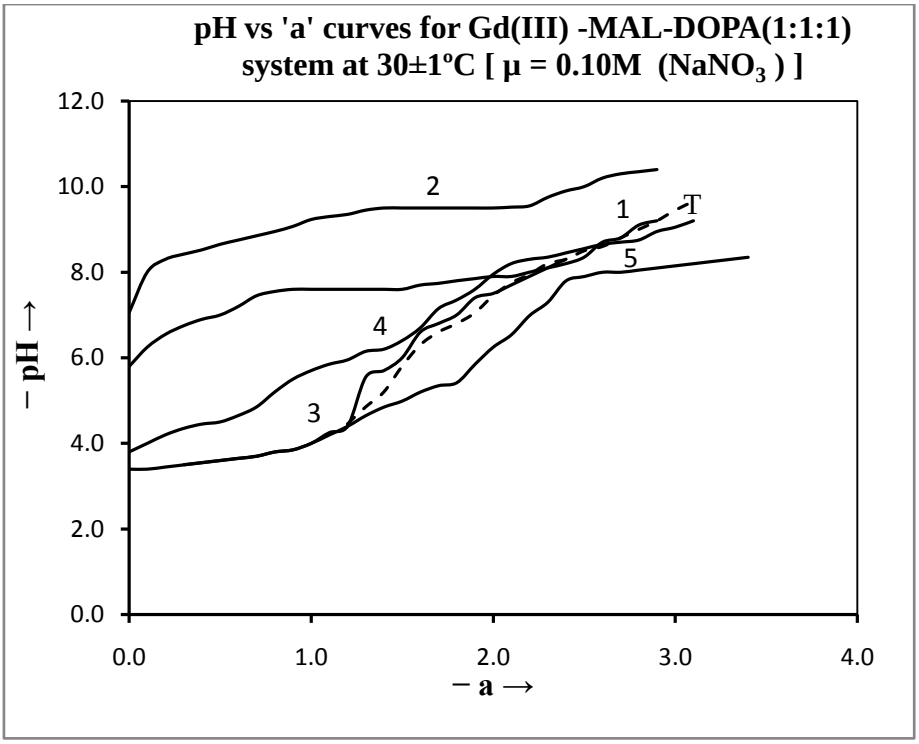

Fig. 4

Where- Curve : 1 Ligand A (MAL) Titration Curve
Curve : 2 Ligand B (DOPA) 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

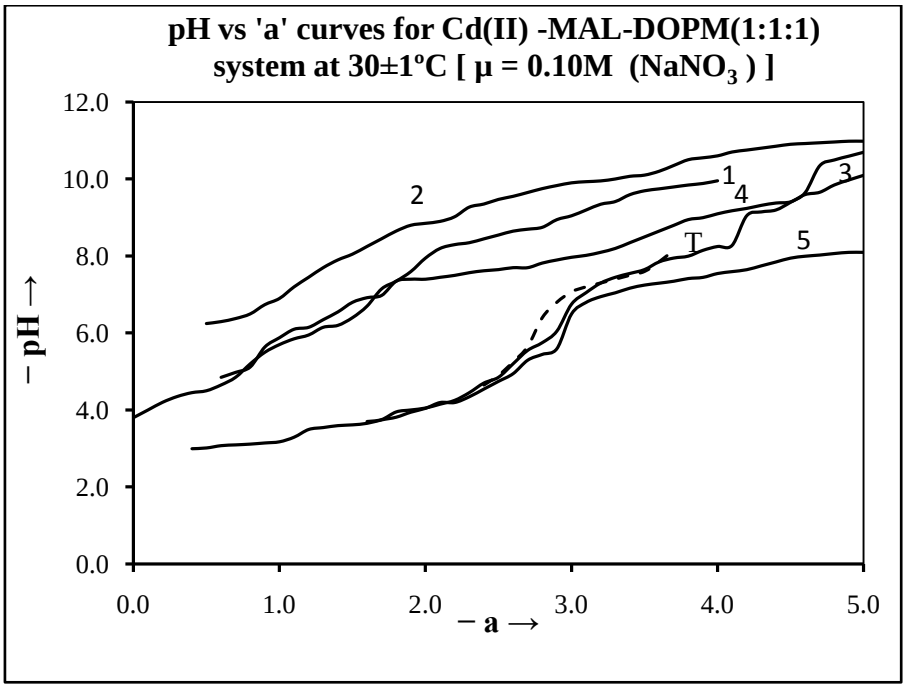

Fig. 5

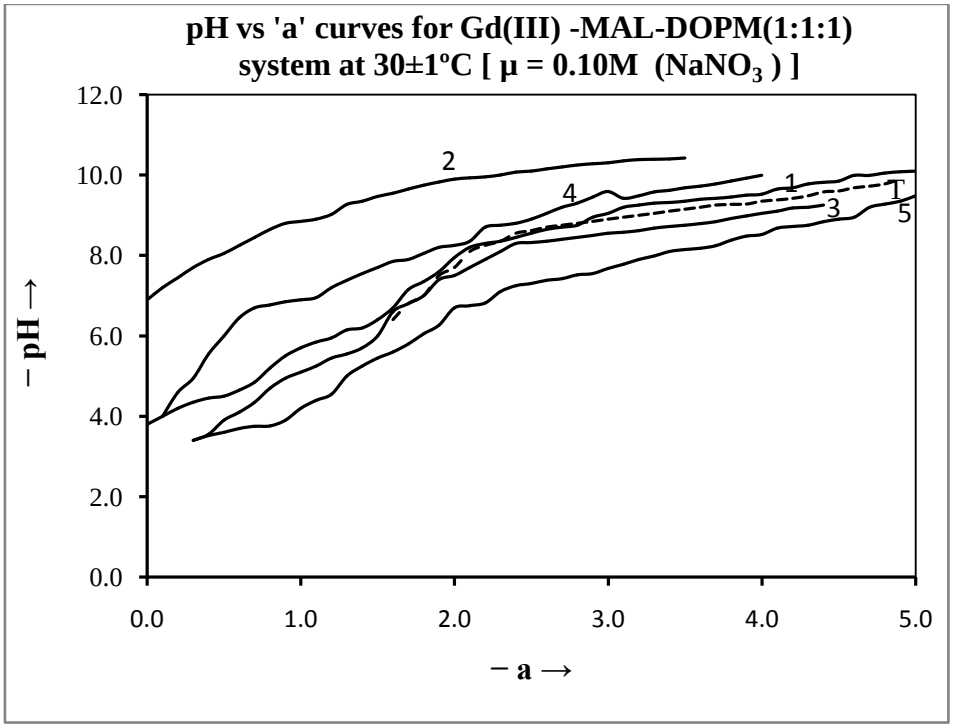

Fig. 6

Where- Curve : 1 Ligand A (MAL) Titration Curve
Curve : 2 Ligand B (DOPM) 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

Table: 4.1
Protonation constants of ligands at different temperatures and ionic strengths

Parameters	20±1°C				30±1°C				40±1°C			
	0.05M	**0.10M**	**0.15M**	**μ→0**	**0.05M**	**0.10M**	**0.15M**	**μ→0**	**0.05M**	**0.10M**	**0.15M**	**μ→0**
Tyrosine (TYR)												
log β_1^{HB}	9.80	9.72	9.65	10.10	9.75	9.61	9.50	10.00	9.63	9.54	9.46	9.92
log β_2^{H2B}	17.98	17.92	17.85	18.20	17.92	17.88	17.74	18.12	17.86	17.74	17.62	18.00
3,4-dihydroxyphenylalanine (DOPA)												
log β_1^{HB}	10.24	10.17	10.09	10.52	10.17	10.08	10.01	10.35	10.09	10.02	9.98	10.26
log β_2^{H2B}	19.86	19.78	19.70	20.10	19.78	19.70	19.62	20.02	19.70	19.62	19.53	19.96
log β_3^{H3B}	28.61	28.59	28.47	28.84	28.52	28.48	28.39	28.76	28.36	28.43	28.23	28.60
Dopamine (DOPM)												
log β_1^{HB}	12.58	12.45	12.30	12.76	12.04	11.98	11.94	12.24	11.58	11.40	11.32	12.86
log β_2^{H2B}	19.98	19.90	19.82	20.32	19.72	19.65	19.60	20.10	19.54	19.50	19.30	20.01
log β^{3H3B}	28.26	28.20	28.12	29.28	28.14	28.10	28.06	29.10	28.15	28.00	27.90	28.98

$\log \beta_1^{HA} = pK_2^H$

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

$\log \beta_1^{HB} = pK_3^H$

$\log \beta_2^{H2B} = pK_2^H + pK_3^H$

$\log \beta_3^{H3B} = pK_1^H + pK_2^H + pK_3^H$

Table: 4.2
Formation constants of (1: 1) binary systems at different temperatures and ionic strengths

Parameters	Cd(II)- Tyrosine											
	20±1°C				30±1°C				40±1°C			
	0.05M	0.10M	0.15M	μ→0	0.05M	0.10M	0.15M	μ→0	0.05M	0.10M	0.15M	μ→0
$\log K^{M}_{MBH}$	4.52	4.17	4.09	4.58	4.17	4.06	4.00	4.42	4.02	3.98	4.34	4.34
$\log K^{H}_{MBH}$	-6.28	-6.24	-6.20	-6.64	-6.22	-6.18	-6.10	-6.50	-6.18	-6.14	-6.12	-6.42
$\log K^{H}_{MB}$	-7.49	-7.42	-7.38	-7.84	-7.16	-7.06	-7.00	-7.80	-7.02	-6.98	-6.89	-7.42
$\log \beta_{MBH}$	13.92	13.87	13.81	14.25	13.89	13.68	13.80	14.20	13.78	13.69	13.60	14.10
$\log \beta_{MB}$	5.99	5.91	5.87	6.24	5.90	5.82	5.76	6.12	5.83	5.74	5.68	6.02
	Cd(II)- DOPA											
$\log K^{M}_{MH2B}$	4.58	4.51	4.46	4.80	4.50	4.47	4.41	4.72	4.42	4.36	4.30	4.65
$\log K^{H}_{MH2B}$	-6.00	-5.94	-5.90	-6.28	-5.72	-5.66	-5.60	-6.19	-5.55	-5.50	-5.44	-6.12
$\log \beta_{MH2B}$	24.72	24.66	24.56	24.96	24.70	24.65	24.60	24.90	24.54	24.49	24.38	24.84
	Cd(II)- DOPM											
$\log K^{M}_{MH2B}$	4.00	3.90	3.84	4.25	3.48	3.25	3.16	4.20	3.96	3.88	3.75	4.15
$\log K^{H}_{MH2B}$	-6.98	-6.90	-6.81	-7.15	-6.88	-6.79	-6.64	-7.18	-6.38	-6.20	6.00	-6.74
$\log K^{M}_{MHB}$	6.10	6.06	6.00	6.20	5.95	5.90	5.82	6.17	5.32	5.10	4.95	5.65
$\log K^{H}_{MHB}$	-7.00	-6.94	-6.90	-7.54	-6.83	-6.78	-6.72	-7.10	-6.64	-6.60	-6.52	-7.00
$\log K^{H}_{MB}$	-7.92	-7.81	-7.73	-8.26	-7.66	-7.59	-7.46	-8.00	-7.34	-7.10	-7.01	-7.68
$\log \beta_{MH2B}$	23.58	23.48	23.40	23.89	22.78	22.60	22.51	23.65	21.94	21.00	20.95	23.45
$\log \beta_{MHB}$	18.94	18.90	18.81	19.02	18.69	18.52	18.42	18.95	18.10	17.98	17.81	18.32
$\log \beta_{MB}$	12.10	11.98	11.80	12.45	11.56	11.42	11.34	11.95	10.82	10.56	10.31	11.03

$\log \beta_{MBH2} = \log K^{M}_{MBH\ 2} + \log \beta_2^{H2B}$

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

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

Table: 4.3

Formation constants of (1: 1) binary systems at different temperatures and ionic strengths

Parameters	Gd(III)- Tyrosine											
	20±1°C				30±1°C				40±1°C			
	0.05M	0.10M	0.15M	μ→0	0.05M	0.10M	0.15M	μ→0	0.05M	0.10M	0.15M	μ→0
$\log K^{M}_{MBH}$	4.52	4.42	4.33	4.70	4.41	4.31	4.24	4.52	4.33	4.23	4.16	4.46
$\log K^{H}_{MBH}$	-5.32	-5.26	-5.20	-5.85	-5.10	-5.06	-5.00	-5.29	-4.94	-4.90	-4.84	-5.71
$\log K^{H}_{MB}$	-7.85	-7.78	-7.72	-7.98	7.75	-7.70	-7.65	-7.83	-7.66	-7.63	-7.59	-7.75
$\log \beta_{MBH}$	14.25	14.15	14.08	14.40	14.20	14.15	14.00	14.35	14.02	13.92	13.82	14.15
$\log \beta_{MB}$	6.73	6.67	6.58	6.77	6.68	6.52	6.59	6.88	6.52	6.43	6.36	6.57
	Gd(III)- DOPA											
$\log K^{M}_{MH2B}$	4.78	4.70	4.61	4.90	4.70	4.62	4.54	4.85	4.59	4.52	4.46	4.75
$\log K^{H}_{MH2B}$	-6.80	-6.76	-6.71	-6.98	-6.20	-6.14	-6.10	-6.91	-6.06	-6.00	-5.93	-6.56
$\log \beta_{MH2B}$	24.90	24.82	24.67	24.96	24.82	24.78	24.59	24.85	24.73	24.64	24.51	24.78
	Gd(III)- DOPM											
$\log K^{M}_{MH2B}$	5.40	5.25	5.10	5.60	4.85	4.65	4.40	5.25	3.85	3.43	3.18	4.98
$\log K^{H}_{MH2B}$	-6.24	-6.20	-6.14	-6.42	-6.10	-6.05	-6.00	-.624	-5.23	-5.18	-5.10	-5.53
$\log K^{M}_{MHB}$	6.77	6.68	6.56	6.96	6.69	6.46	6.23	6.80	6.50	6.24	6.00	6.68
$\log K^{H}_{MHB}$	-7.68	-7.45	-7.12	-7.97	-7.50	-7.35	-7.26	-7.84	-6.56	-6.48	-6.34	-7.72
$\log K^{H}_{MB}$	-8.96	-8.90	-8.81	-9.06	-8.45	-8.36	-8.28	-8.60	-8.30	-8.20	-8.10	-8.45
$\log \beta_{MH2B}$	24.86	24.80	24.76	25.00	24.41	24.36	24.30	24.05	23.95	23.90	23.48	24.00
$\log \beta_{MHB}$	18.99	18.90	18.80	19.10	18.68	18.56	18.46	18.61	18.59	18.31	18.22	18.61
$\log \beta_{MB}$	17.60	17.50	17.40	17.88	16.90	16.70	16.50	17.81	16.53	16.42	16.34	17.75

Table: 4.4
Formation constants of (1:1:1) Cd(II)-MAL-TYR ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$\log K^{M}_{MAHBH}$	19.75	19.68	19.60	19.00	18.92	18.84	18.24	18.18	18.10
$\log K^{MAH}_{MAHBH}$	30.32	10.24	10.16	10.12	10.08	10.00	10.00	9.91	9.84
$\log K^{MBH}_{MAHBH}$	9.30	9.25	9.20	9.12	9.00	8.92	8.94	8.86	8.80
$\log K^{M}_{MAHB}$	23.48	23.06	23.00	22.78	22.70	22.62	22.16	22.10	22.01
$\log K^{M}_{MABH}$	20.28	20.20	20.12	19.18	19.10	19.04	19.02	18.97	18.90
$\log K^{MAH}_{MABH}$	11.39	11.30	11.22	11.20	11.11	11.02	11.15	11.10	11.05
$\log K^{MBH}_{MABH}$	9.98	9.92	9.84	9.45	9.36	9.30	9.29	9.23	9.20
$\log K^{MA}_{MABH}$	8.36	8.30	8.21	8.30	8.24	8.19	8.12	8.07	8.00
$\log K^{MB}_{MABH}$	3.94	3.90	3.82	3.84	3.80	3.72	3.74	3.70	3.63
$\log K^{MA}_{MAB}$	5.45	5.40	5.32	5.34	5.26	5.20	5.06	5.01	4.97
$\log K^{MB}_{MAB}$	5.26	5.19	5.12	5.01	4.92	4.86	4.83	4.78	4.72
$\log K^{H}_{MAHBH}$	-5.32	-5.24	-5.18	-5.10	-5.00	-4.65	-4.52	-4.45	-4.38
$\log K^{H}_{MABH}$	-6.88	- 6.80	-6.74	-6.42	-6.36	-6.30	-6.30	-6.24	-6.19
$\log K^{H}_{MAB}$	-8.29	- 8.23	- 8.18	-8.16	-8.10	-8.02	- 8.00	-7.92	-7.86
$\log \beta_{MABH2}$	36.59	36.50	36.42	35.98	35.92	35.83	35.12	35.06	35.00
$\log \beta_{MABH}$	30.12	30.08	30.00	29.72	29.70	29.61	29.31	29.26	29.20
$\log \beta_{MAB}$	18.23	18.16	18.10	17.89	17.80	17.71	17.16	17.11	17.06

$\log \beta_{MABH3} = \log K^{M}_{MABH\ 3} + \log \beta_1^{HA} + \log \beta_1^{H2B}$

$\log \beta_{MABH2} = \log K^{M}_{MABH\ 2} + \log \beta_1^{HA} + \log \beta_1^{HB}$

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

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

Table: 4.5

Formation constants of (1:1:1) Gd(III)-MAL-TYR ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$\log K^{M}_{MAHBH}$	26.70	26.64	26.60	25.02	24.97	24.92	24.06	24.00	23.95
$\log K^{MAH}_{MAHBH}$	18.40	18.34	18.30	18.04	17.98	17.95	16.10	16.05	16.00
$\log K^{MBH}_{MAHBH}$	15.30	15.25	15.20	14.68	14.64	14.60	13.98	13.92	13.88
$\log K^{M}_{MAHB}$	30.82	30.75	30.70	29.98	29.92	29.86	29.74	29.69	29.60
$\log K^{M}_{MABH}$	28.70	28.64	28.59	27.99	27.97	27.94	27.12	27.08	27.04
$\log K^{MAH}_{MABH}$	19.52	19.48	19.40	18.65	18.60	18.55	17.56	17.52	17.50
$\log K^{MBH}_{MABH}$	17.20	17.12	17.08	16.90	16.04	16.74	15.98	15.92	15.88
$\log K^{MA}_{MABH}$	16.00	15.95	15.90	15.80	15.74	15.68	15.20	15.14	15.08
$\log K^{MB}_{MABH}$	10.05	10.00	9.94	9.72	9.66	9.60	9.43	9.36	9.50
$\log K^{MA}_{MAB}$	8.60	8.60	8.53	8.24	8.16	8.10	8.00	7.95	7.88
$\log K^{MB}_{MAB}$	5.25	5.20	5.14	5.18	5.16	5.07	5.00	4.93	4.86
$\log K^{H}_{MAHBH}$	-6.42	-6.35	-6.22	-6.10	-6.04	-6.00	-5.20	-5.14	-5.08
$\log K^{H}_{MABH}$	-7.83	-7.76	-7.69	-7.56	-7.51	-7.42	-7.22	-7.16	-7.10
$\log K^{H}_{MAB}$	-8.10	-8.02	-7.94	-7.96	-7.90	-7.84	-7.33	-7.29	-7.20
$\log \beta_{MABH2}$	43.20	43.18	43.16	42.34	42.28	42.22	41.48	41.42	41.40
$\log \beta_{MABH}$	38.46	38.42	38.46	37.82	37.78	37.73	36.68	36.63	36.60
$\log \beta_{MAB}$	20.18	20.14	20.10	19.54	19.49	19.44	19.50	19.45	19.40

Table: 4.6

Formation constants of (1:1:1) Cd(II)-MAL-DOPA ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$\log K^{M}_{MAHBH}$	20.98	20.90	20.82	20.78	20.70	20.66	19.68	19.60	19.52
$\log \beta_{MABH2}$	38.25	38.20	38.16	37.90	37.86	37.80	37.80	37.70	37.62

Table :4.7

Formation constants of (1:1:1) Gd(III)-MAL-DOPA ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$\log K^{M}_{MAHBH}$	21.59	21.44	21.40	21.19	21.12	21.04	21.00	20.90	21.81
$\log \beta_{MABH2}$	39.00	38.96	38.90	38.58	38.50	38.42	38.45	38.40	38.33

Table :4.8
Formation constants of (1:1:1) Cd(II)-MAL-DOPM ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$logK^{M}_{MAHBH2}$	13.67	13.61	13.56	13.24	13.20	13.15	13.00	12.94	12.86
$logK^{MAH}_{MAHBH2}$	8.84	8.80	8.75	8.25	8.19	8.04	8.05	8.00	7.93
$logK^{MBH2}_{MAHBH2}$	9.67	9.62	9.58	9.15	9.10	9.06	8.90	8.84	8.78
$logK^{M}_{MABH2}$	15.16	15.12	15.08	15.00	14.94	14.88	14.90	14.86	14.80
$logK^{M}_{MAHBH}$	16.35	16.30	16.25	16.21	16.18	16.10	16.02	15.96	15.90
$logK^{MBH2}_{MABH2}$	11.69	11.63	11.59	11.25	11.20	11.16	11.00	10.94	10.88
$logK^{MAH}_{MAHBH}$	9.52	9.46	9.40	9.25	9.20	9.14	9.06	9.00	8.94
$logK^{MBH}_{MAHBH}$	10.38	10.31	10.26	10.00	9.92	9.86	9.90	9.86	9.80
$logK^{MA}_{MABH2}$	8.36	8.32	8.28	8.25	8.20	8.16	8.10	8.03	7.97
$logK^{M}_{MAHB}$	19.01	18.98	18.93	18.96	18.90	18.84	18.84	18.80	18.75
$logK^{M}_{MABH}$	13.82	13.78	13.73	13.70	13.65	13.59	13.54	13.46	13.40
$logK^{MAH}_{MAHB}$	11.29	11.23	11.19	11.10	11.06	11.00	11.02	10.97	10.90
$logK^{MBH}_{MABH}$	14.28	14.24	14.20	14.16	14.10	14.03	14.10	14.05	14.00
$logK^{MA}_{MABH}$	9.67	9.62	9.58	9.40	9.32	9.28	9.25	9.20	9.14
$logK^{MB}_{MAHB}$	9.56	9.50	9.46	9.35	9.30	9.24	9.20	9.16	9.10
$logK^{MA}_{MAB}$	8.34	8.30	8.26	8.28	8.20	8.14	8.10	8.04	7.98
$logK^{MB}_{MAB}$	19.36	19.32	19.26	19.30	19.24	19.20	19.10	19.05	19.00
$logK^{H}_{MAHBH2}$	-4.32	-4.25	-4.16	-4.05	-4.00	-3.96	-4.02	-3.96	-3.92
$logK^{H}_{MAHBH}$	-6.22	-6.10	-6.05	-5.94	-5.90	-5.82	-5.60	-5.52	-5.48
$logK^{H}_{MABH}$	-7.12	-7.07	-7.00	-7.05	-7.00	-6.96	-6.90	-6.87	-6.87
$logK^{H}_{MAB}$	-8.23	-8.20	-8.16	-8.00	-7.94	-7.88	-7.85	-7.81	-7.76
$\log \beta_{MABH3}$	40.34	40.30	40.26	40.20	40.16	40.10	40.08	40.02	47.06
$\log \beta_{MABH2}$	35.28	35.22	35.18	35.10	35.04	35.00	34.94	34.90	41.10
$\log \beta_{MABH}$	26.36	26.35	26.27	26.02	25.98	25.90	25.88	25.82	29.96
$\log \beta_{MAB}$	17.85	17.80	17.75	17.15	17.10	17.02	17.10	17.05	24.54

Table :4.9
Formation constants of (1:1:1)Gd(III)-MAL-DOPM ternary system at different temperatures and ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M	0.05M	0.10M	0.15M
$logK^{M}_{MAHBH2}$	20.40	20.34	20.30	19.98	19.94	19.90	19.87	19.83	19.79
$logK^{MAH}_{MAHBH2}$	14.78	14.74	14.70	14.72	14.67	14.62	14.50	14.54	14.50
$logK^{MBH2}_{MAHBH2}$	15.42	15.38	15.32	15.16	15.10	15.04	15.08	15.04	14.99
$logK^{M}_{MABH2}$	22.30	22.26	22.22	21.90	21.84	21.80	21.79	21.76	22.72
$logK^{M}_{MAHBH}$	22.06	22.00	21.94	21.20	21.16	21.12	21.14	22.10	21.04
$logK^{MBH2}_{MAH2B}$	16.14	16.08	16.04	15.98	15.94	15.90	15.88	15.84	15.80
$logK^{MAH}_{MAHBH}$	14.18	14.06	14.02	13.96	13.96	13.91	13.90	13.87	13.82
$logK^{MBH}_{MAHBH}$	15.62	15.56	15.51	15.50	15.46	15.41	15.44	15.38	15.32
$logK^{MA}_{MAH2B}$	13.12	13.04	13.00	13.04	12.99	12.94	12.96	12.90	12.84
$logK^{M}_{MAHB}$	20.19	20.16	20.14	20.02	19.96	19.91	19.94	19.90	19.88
$logK^{M}_{MABH}$	22.62	22.58	22.53	22.54	22.49	22.43	22.48	22.42	22.40
$logK^{MAH}_{MAHB}$	15.20	15.16	15.12	15.01	14.96	14.93	14.96	14.92	14.88
$logK^{MBH}_{MABH}$	19.28	19.20	19.12	19.00	18.94	18.87	18.60	18.52	18.47
$logK^{MA}_{MABH}$	14.04	13.94	13.90	13.92	13.88	13.84	13.88	13.83	13.80
$logK^{MB}_{MAHB}$	14.02	13.98	13.92	13.86	13.82	13.78	13.82	13.78	13.72
$logK^{MA}_{MAB}$	13.60	13.54	13.50	13.48	13.42	13.40	13.30	13.25	13.20
$logK^{MB}_{MAB}$	14.80	14.76	14.72	14.60	14.62	14.58	14.42	14.38	14.32
$logK^{H}_{MAHBH2}$	-4.98	-4.95	-4.90	-4.84	-4.88	-4.84	-4.68	-4.62	-4.58
$logK^{H}_{MAHBH}$	-6.21	-6.14	-6.01	-5.48	-5.40	-5.21	-5.14	-5.02	-4.93
$logK^{H}_{MABH}$	-7.64	-7.57	-7.53	-7.48	-7.42	-7.39	-7.30	-7.25	-7.20
$logK^{H}_{MAB}$	-8.18	-8.15	-8.10	-8.30	-8.26	-8.23	-8.14	-8.10	-8.04
$\log \beta_{MABH3}$	47.84	47.80	47.74	47.20	47.16	47.12	47.14	47.10	47.06
$\log \beta_{MABH2}$	42.30	42.24	42.20	41.30	41.24	41.20	41.18	41.14	41.10
$\log \beta_{MABH}$	31.60	31.53	31.50	30.22	30.17	30.12	30.04	30.00	29.96
$\log \beta_{MAB}$	24.94	24.89	24.86	24.80	24.74	24.70	24.68	24.60	24.54

Table: 4.10

Thermodynamic formation constants and thermodynamic parameters

Cd(II)-MAL-TYR

Parameter	20ºC		30ºC		40ºC		$-\Delta H^{o}$ kJmol^{-1}	ΔS^{o} Jk^{-1}mol^{-1}
	$\log K_{\mu\to 0}$	$-\Delta G^{o}$ kJmol^{-1}	$\log K_{\mu\to 0}$	$-\Delta G^{o}$ kJmol^{-1}	$\log K_{\mu\to 0}$	$-\Delta G^{o}$ kJmol^{-1}		
$\log K^{M}_{MAB}$	12.70	71.24	12.25	71.06	11.80	68.45	55.38	53.61
$\log K^{M}_{MAHBH}$	14.25	79.94	13.45	78.03	12.90	74.84	77.95	4.75
$\log K^{MAH}_{MAHBH}$	10.85	60.86	10.60	61.49	10.20	59.17	41.02	67.97
$\log K^{MBH}_{MAHBH}$	9.50	53.29	9.35	54.24	9.15	53.08	21.68	107.22
$\log K^{H}_{MAHBH}$	-5.67	-	-5.45	-	-4.87	-	-	-
$\log K^{M}_{MAHB}$	17.80	99.86	17.20	99.78	16.56	96.07	76.58	78.88
$\log K^{M}_{MABH}$	14.50	81.45	13.75	79.97	13.32	77.27	71.52	31.78
$\log K^{MAH}_{MABH}$	11.95	67.04	11.85	68.74	11.75	63.23	70.43	186.68
$\log K^{MBH}_{MABH}$	10.70	60.02	10.45	66.62	10.00	54.82	78.64	53.61
$\log K^{MA}_{MABH}$	8.65	48.52	8.50	49.31	8.35	48.44	18.46	102.43
$\log K^{MB}_{MABH}$	4.35	24.40	4.25	22.33	4.15	17.11	12.30	41.17
$\log K^{H}_{MABH}$	-7.10	-	-6.78	-	-6.54	-	-	-
$\log K^{MA}_{MAB}$	8.95	50.21	8.85	51.34	8.60	49.89	22.56	94.77
$\log K^{MB}_{MAB}$	5.70	31.77	5.55	32.19	5.30	30.14	25.30	22.92
$\log K^{H}_{MAB}$	-8.66	-	-8.52	-	-8.46	-	-	-

Gd(III)-MAL-TYR

Parameter	20ºC		30ºC		40ºC		$-\Delta H^{o}$ kJmol^{-1}	ΔS^{o} Jk^{-1}mol^{-1}
	$\log K_{\square\to 0}$	$-\Delta G^{o}$ kJmol^{-1}	$\log K_{\square\to 0}$	$-\Delta G^{o}$ kJmol^{-1}	$\log K_{\square\to 0}$	$-\Delta G^{o}$ kJmol^{-1}		
$\log K^{M}_{MAB}$	15.46	86.73	14.84	115.70	14.78	85.75	38.02	86.09
$\log K^{M}_{MAHBH}$	17.10	95.93	48.14	98.16	74.36	94.91	48.14	164.28
$\log K^{MAH}_{MAHBH}$	18.85	105.75	17.65	102.39	16.39	95.08	61.54	150.30
$\log K^{MBH}_{MAHBH}$	16.15	90.60	15.10	87.60	14.24	82.69	60.17	102.44
$\log K^{H}_{MAHBH}$	-6.75	-	-6.54	-	-5.84	-	-	-
$\log K^{M}_{MAHB}$	21.50	120.61	20.58	119.39	99.92	115.56	95.86	83.86
$\log K^{M}_{MABH}$	19.35	108.55	18.55	107.69	17.94	104.08	85.47	77.16
$\log K^{MAH}_{MABH}$	20.05	112.48	19.10	110.63	17.83	103.44	50.87	208.89
$\log K^{MBH}_{MABH}$	18.00	100.98	17.36	100.71	16.32	94.68	86.16	49.78
$\log K^{MA}_{MABH}$	16.95	95.09	16.25	94.27	15.44	87.57	69.06	87.11
$\log K^{MB}_{MABH}$	10.55	59.18	9.94	57.66	9.67	56.10	32.82	89.03
$\log K^{H}_{MABH}$	-8.15	-	-7.89	-	-7.78	-	-	-
$\log K^{MA}_{MAB}$	8.95	50.21	8.54	49.54	8.30	48.15	38.84	37.71
$\log K^{MB}_{MAB}$	5.48	30.74	5.37	31.15	5.34	30.40	14.90	53.99
$\log K^{H}_{MAB}$	-8.38	-	-8.20	-	-7.84	-	-	-

Table: 4.11

Thermodynamic formation constants and thermodynamic parameters

Cd(II)-MAL- DOPA								
Parameter	**20ºC**		**30ºC**		**40ºC**		**-ΔHº kJmol^{-1}**	**ΔSº Jk^{-1}mol^{-1}**
	log $K_{\mu\to0}$	**-ΔGº kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔGº kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔGº kJmol^{-1}**		
$logK^{M}_{MAHBH}$	18.20	102.10	18.10	105.00	17.85	103.55	22.36	271.88
Gd(III)-MAL- DOPA								
$logK^{H}_{MAHBH}$	18.70	203.31	18.59	107.85	18.22	105.70	31.31	251.97

Table: 4.12

Thermodynamic formation constants and thermodynamic parameters

Cd(II)-MAL-DOPM

Parameter	**20ºC**		**30ºC**		**40ºC**		**-ΔHº kJmol^{-1}**	**ΔSº Jk^{-1}mol^{-1}**
	log $K_{\mu\to0}$	**-ΔGº kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔGº kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔGº kJmol^{-1}**		
$logK^{M}_{MAB}$	16.13	90.49	15.48	89.90	15.34	88.99	45.43	190.51
$logK^{M}_{MAHBH2}$	13.99	78.48	13.67	79.30	13.42	77.85	34.60	149.16
$logK^{MAH}_{MAHBH2}$	9.15	51.33	8.98	50.35	8.40	48.73	44.86	20.87
$logK^{MBH2}_{MAHBH2}$	9.95	55.76	9.56	55.46	9.32	54.07	37.20	62.42
$logK^{H}_{MAHBH2}$	-4.32	-	-4.40	-	-4.28	-	-	-
$logK^{M}_{MAHBH}$	15.48	86.84	15.42	89.46	14.28	82.84	81.24	22.97
$logK^{M}_{MAHBH}$	16.63	93.29	16.61	96.36	16.39	95.08	16.13	264.04
$logK^{MBH2}_{MAHBH}$	11.92	66.87	11.64	67.53	11.46	66.48	31.73	121.77
$logK^{MAH}_{MAHBH}$	9.98	55.43	9.68	56.16	9.42	54.65	28.72	91.14
$logK^{MA}_{MAHBH}$	10.64	59.69	10.43	60.51	10.31	59.81	19.69	135.94
$logK^{H}_{MAHBH}$	-5.24	-	-6.82	-	-5.08	-	-	-
$logK^{M}_{MAHB}$	17.32	99.52	17.30	100.36	17.21	99.84	20.24	271.50
$logK^{M}_{MABH}$	12.12	67.99	12.08	70.08	11.96	69.38	10.39	196.83
$logK^{MAH}_{MABH}$	11.63	65.25	11.48	66.60	11.40	66.13	13.67	175.58
$logK^{MBH}_{MABH}$	14.64	82.13	14.57	84.52	14.51	84.18	7.93	253.12
$logK^{MA}_{MABH}$	9.91	55.59	9.88	56.44	9.68	56.15	15.31	138.05
$logK^{MB}_{MABH}$	8.46	49.14	8.30	49.89	8.21	49.54	12.85	123.30
$logK^{H}_{MABH}$	-6.24	-	-6.16	-	-6.04	-	-	-
$logK^{MA}_{MAB}$	8.76	14.14	8.66	50.24	8.56	49.39	16.41	111.82
$logK^{MB}_{MAB}$	7.79	43.70	7.72	44.78	7.45	43.22	22.29	73.71
$logK^{H}_{MAB}$	-8.66	-	-8.26	-	-8.10	-	-	-

Gd(III)-MAL-DOPM

Parameter	20°C		30°C		40°C		-ΔH° kJmol^{-1}	ΔS° Jk^{-1}mol^{-1}
	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}		
$logK^{M}_{MAB}$	21.05	118.03	20.95	121.54	20.90	121.02	8.88	372.41
$logK^{M}_{MAHBH2}$	18.58	104.23	18.07	104.83	17.97	104.25	34.73	235.12
$logK^{MAH}_{MAHBH2}$	14.94	83.87	14.90	86.44	14.75	85.57	12.44	243.93
$logK^{MBH2}_{MAHBH2}$	15.50	56.95	15.45	89.63	15.35	89.05	9.57	264.23
$logK^{H}_{MAHBH2}$	-4.98	-	-4.90	-	-4.81	-	-	-
$logK^{M}_{MAHBH}$	20.40	114.44	20.13	116.78	19.90	114.45	30.49	286.05
$logK^{M}_{MAHBH}$	20.30	113.88	19.30	110.98	19.25	111.68	58.12	185.72
$logK^{MBH2}_{MAHBH}$	16.25	91.16	16.05	93.11	15.95	92.53	17.77	249.87
$logK^{MAH}_{MAHBH}$	14.20	79.66	14.06	8.57	14.00	81.22	11.76	231.29
$logK^{MA}_{MAHBH}$	15.72	88.19	15.55	90.25	15.51	59.81	12.03	259.25
$logK^{H}_{MAHBH}$	-5.34	-	-5.12	-	-4.92	-	-	-
$logK^{M}_{MAHB}$	18.73	105.19	18.62	108.02	18.54	89.98	20.24	186.30
$logK^{M}_{MABH}$	14.40	80.78	14.10	81.80	14.02	107.56	21.88	199.89
$logK^{MAH}_{MABH}$	13.35	74.89	13.18	76.46	13.02	81.33	20.24	186.30
$logK^{MBH}_{MABH}$	24.28	140.86	24.20	140.39	24.10	139.81	11.21	426.59
$logK^{MA}_{MABH}$	19.45	109.11	19.12	110.93	18.95	108.78	43.35	224.21
$logK^{MB}_{MABH}$	14.12	79.32	13.98	81.10	13.93	80.75	11.76	229.76
$logK^{H}_{MABH}$	-7.89	-	-7.87	-	-7.76	-	-	-
$logK^{MA}_{MAB}$	14.10	79.10	13.95	80.93	13.90	80.65	11.62	229.75
$logK^{MB}_{MAB}$	10.70	60.02	10.59	61.43	10.41	60.39	18.32	142.45
$logK^{H}_{MAB}$	-8.96	-	-8.58	-	-8.39	-	-	-

Representative Speciation Curves

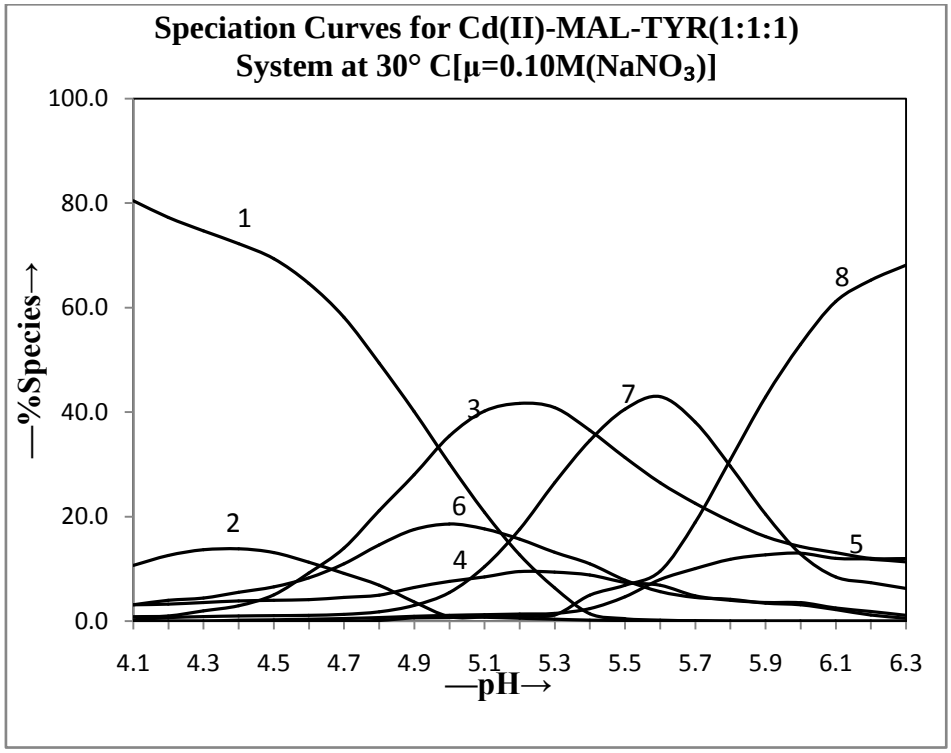

Fig. 7

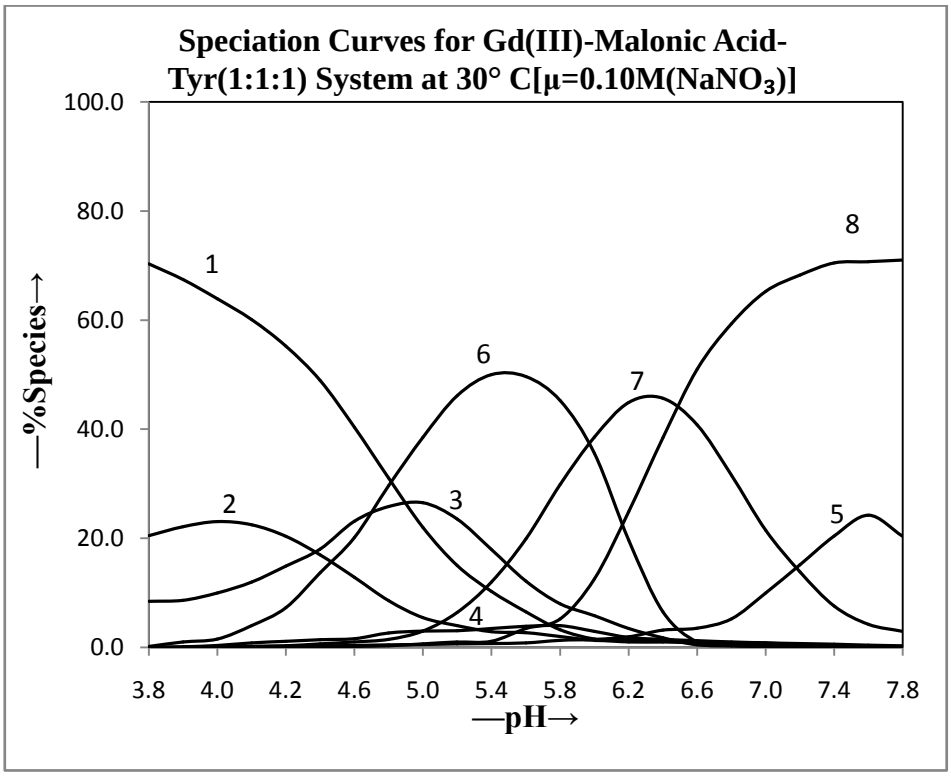

Fig. 8

Where, Curve 1: [M]; 2 [MAH]; 3[MA]; 4 [MBH]; 5 [MB]; 6 [$MABH_2$]; 7 [MABH]; 8 [MAB]

Table: 4.13

Experimental values and concentration of different species for Cd(II)-MAL-TYR (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	PH	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[$MABH_2$]	[MABH]	[MAB]
1	4.1	0.68	80.45	10.68	0.85	3.12	0.00	3.15	0.25	0.00
2	4.2	0.86	77.25	12.58	0.99	3.25	0.00	3.95	0.65	0.00
3	4.3	0.96	74.65	13.65	1.95	3.58	0.00	4.41	0.85	0.00
4	4.4	1.10	72.21	13.84	2.94	3.84	0.15	5.48	0.98	0.00
5	4.5	1.30	69.35	13.13	5.05	3.99	0.24	6.54	1.03	0.00
6	4.6	1.49	64.61	11.25	9.21	4.12	0.38	8.28	1.09	0.00
7	4.7	1.64	58.14	9.12	13.98	4.51	0.49	10.95	1.28	0.00
8	4.8	1.73	49.38	6.84	21.14	4.98	0.68	14.57	1.79	0.12
9	4.9	1.78	40.12	3.68	27.98	6.45	0.89	17.49	2.99	0.58
10	5.0	1.83	30.19	0.84	35.42	7.57	1.12	18.57	5.45	0.65
11	5.1	1.91	20.84	0.72	40.18	8.47	1.24	17.64	10.42	0.98
12	5.2	1.96	12.65	0.54	41.68	9.49	1.35	15.68	17.58	1.12
13	5.3	2.04	6.35	0.35	40.85	9.38	1.46	13.15	26.45	1.19
14	5.4	2.09	1.38	0.18	36.48	8.84	2.41	10.98	34.58	4.97
15	5.5	2.16	0.44	0.10	31.28	7.42	4.68	7.85	40.58	6.84
16	5.6	2.25	0.17	0.08	26.47	6.84	7.95	5.65	42.95	9.54
17	5.7	2.32	0.08	0.04	22.54	4.85	10.02	4.51	38.12	18.84
18	5.8	2.44	0.02	0.02	19.10	4.00	11.84	4.18	29.65	30.86
19	5.9	2.56	0.00	0.01	16.20	3.58	12.65	3.45	20.45	42.89
20	6.0	2.71	0.00	0.00	14.29	3.52	12.98	3.12	12.84	52.94
21	6.1	2.92	0.00	0.00	13.10	2.50	11.98	2.18	8.45	61.13
22	6.2	3.17	0.00	0.00	12.00	1.85	11.84	1.18	7.35	65.24
23	6.3	3.50	0.00	0.00	11.95	1.10	11.32	0.54	6.24	68.14

Table: 4.14

Experimental values and concentration of different species for Gd(III)-MAL-TYR (1:1:1) system at 30±1ºC [μ=0.10M($NaNO_3$)]

S.NO.	PH	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[$MABH_2$]	[MABH]	[MAB]
1	3.8	4.40	70.32	20.50	8.45	0.02	0.00	0.20	0.00	0.00
2	3.9	4.70	67.42	22.15	8.65	0.10	0.00	0.98	0.00	0.00
3	4.0	5.00	63.89	23.05	10.00	0.35	0.00	1.52	0.09	0.00
4	4.1	5.30	60.10	22.48	11.98	0.85	0.20	3.98	0.15	0.00
5	4.2	5.60	55.24	20.38	14.88	1.10	0.25	7.25	0.28	0.00
6	4.4	5.85	48.95	16.98	18.00	1.38	0.30	13.65	0.65	0.00
7	4.6	6.15	40.35	12.87	23.12	1.60	0.35	20.12	0.98	0.15
8	4.8	6.40	31.02	8.54	25.80	2.65	0.48	29.65	1.45	0.28
9	5.0	6.75	22.00	5.45	26.52	2.99	0.54	38.51	2.98	0.64
10	5.2	7.15	15.00	3.98	23.54	3.08	0.62	46.15	6.42	0.98
11	5.4	7.40	10.29	2.85	17.95	3.45	0.71	50.00	11.98	1.12
12	5.6	7.75	6.54	2.68	12.12	3.85	0.84	49.65	19.87	3.45
13	5.8	8.00	3.24	1.98	8.00	3.98	1.32	45.22	29.84	5.22
14	6.0	8.20	1.51	1.30	5.80	2.95	1.45	35.54	38.54	12.58
15	6.2	8.55	1.00	1.35	3.48	1.80	1.92	19.65	44.91	24.89
16	6.4	8.85	0.98	1.15	1.74	1.46	3.15	6.54	45.67	38.46
17	6.6	9.15	0.84	1.00	0.48	1.22	3.50	0.98	40.81	51.00
18	6.8	9.40	0.72	0.90	0.30	1.00	5.24	0.28	31.58	59.32
19	7.0	9.80	0.61	0.85	0.10	0.85	9.98	0.24	21.48	65.25
20	7.2	10.10	0.55	0.45	0.05	0.72	15.15	0.21	13.84	68.24
21	7.4	10.30	0.21	0.30	0.00	0.58	20.42	0.11	7.58	70.48
22	7.6	10.35	0.15	0.20	0.00	0.40	24.25	0.05	4.24	70.69
23	7.8	10.45	0.10	0.10	0.00	0.30	20.35	0.00	2.95	70.98

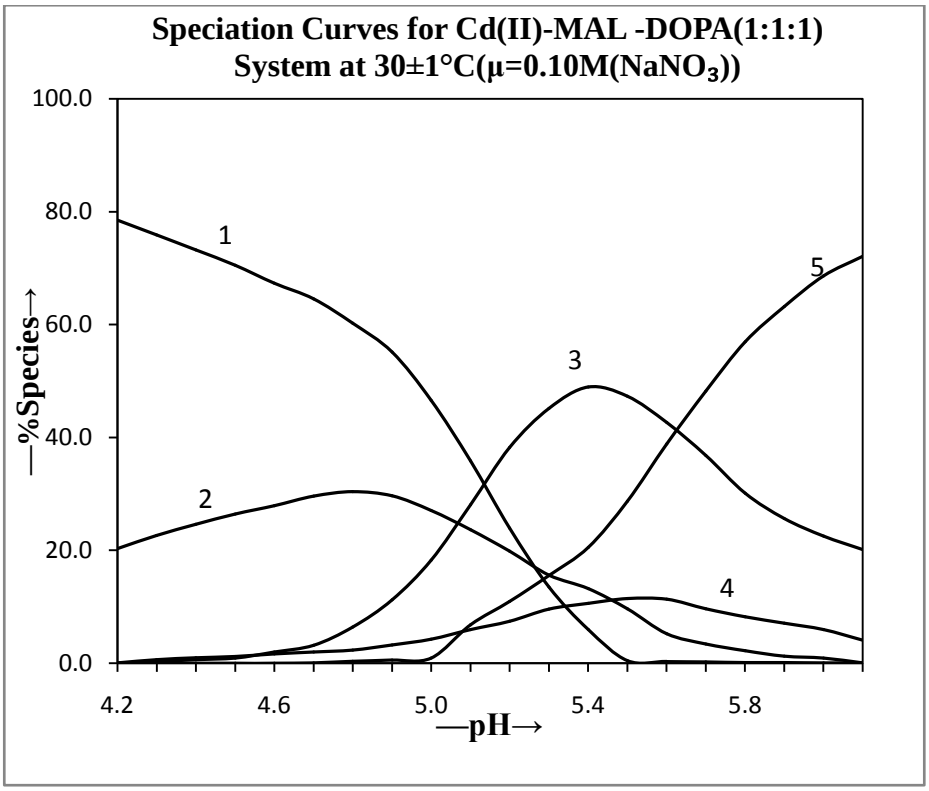

Fig. 9

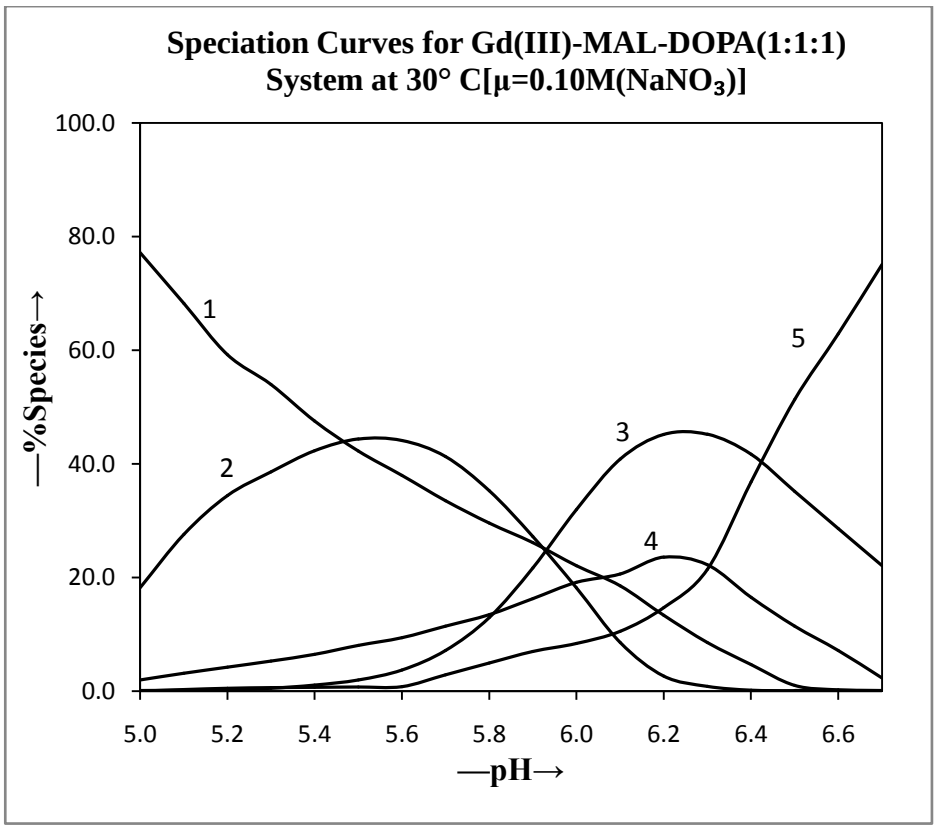

Fig. 10

Where, Curve 1: [M]; 2 [MAH]; 3[MA]; 4 [MBH_2]; 5 [$MABH_2$]

Table: 4.15

Experimental values and concentration of different species for Cd(II)-MAL-DOPA (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[$MABH_2$]
4.2	1.58	78.55	20.31	0.04	0.05	0.00
4.3	1.62	75.89	22.65	0.32	0.65	0.00
4.4	1.64	73.25	24.62	0.64	0.98	0.00
4.5	1.68	70.52	26.48	0.95	1.20	0.00
4.6	1.70	67.33	27.95	1.98	1.68	0.00
4.7	1.74	64.59	29.61	3.20	1.98	0.10
4.8	1.78	60.24	30.41	6.45	2.32	0.38
4.9	1.81	55.14	29.66	11.23	3.24	0.58
5.0	1.85	46.59	27.10	18.29	4.25	0.95
5.1	1.89	35.87	23.69	28.12	5.98	6.85
5.2	1.92	23.95	19.85	38.26	7.45	10.97
5.3	1.96	13.52	15.64	45.18	9.62	15.59
5.4	2.00	5.95	13.21	48.95	10.62	20.54
5.5	2.06	0.46	9.65	47.32	11.47	28.74
5.6	2.15	0.32	5.25	42.65	11.35	38.89
5.7	2.40	0.22	3.45	36.85	9.65	48.25
5.8	2.60	0.15	2.21	30.12	8.24	56.98
5.9	2.80	0.12	1.28	25.64	7.12	63.21
6.0	2.95	0.10	0.95	22.52	6.00	68.65
6.1	3.10	0.08	0.10	20.14	4.10	72.12

Table: 4.16

Experimental values and concentration of different species for Gd(III)-MAL-DOPA (1:1:1) system at 30±1ºC [μ=0.10M($NaNO_3$)]

pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[$MABH_2$]
5.0	1.02	77.20	18.24	0.13	2.01	0.02
5.1	1.03	68.24	27.62	0.18	3.17	0.30
5.2	1.04	59.21	34.45	0.29	4.22	0.54
5.3	1.05	53.98	38.58	0.54	5.31	0.62
5.4	1.07	47.54	42.32	1.10	6.48	0.71
5.5	1.09	42.27	44.38	1.99	8.08	0.75
5.6	1.11	38.00	44.14	3.75	9.42	0.81
5.7	1.14	33.54	41.29	7.18	11.46	2.92
5.8	1.18	29.57	35.28	12.95	13.49	4.98
5.9	1.20	26.14	27.25	21.68	16.32	7.01
6.0	1.24	22.11	18.19	31.98	19.15	8.40
6.1	1.28	18.57	8.59	40.84	20.65	10.58
6.2	1.32	13.35	2.69	45.21	23.60	14.72
6.3	1.38	8.59	0.89	45.22	22.26	21.45
6.4	1.43	4.69	0.21	41.70	16.50	36.87
6.5	1.52	1.04	0.12	35.19	11.47	51.35
6.6	1.60	0.27	0.18	28.61	7.20	62.89
6.7	1.70	0.01	0.14	22.10	2.32	75.10

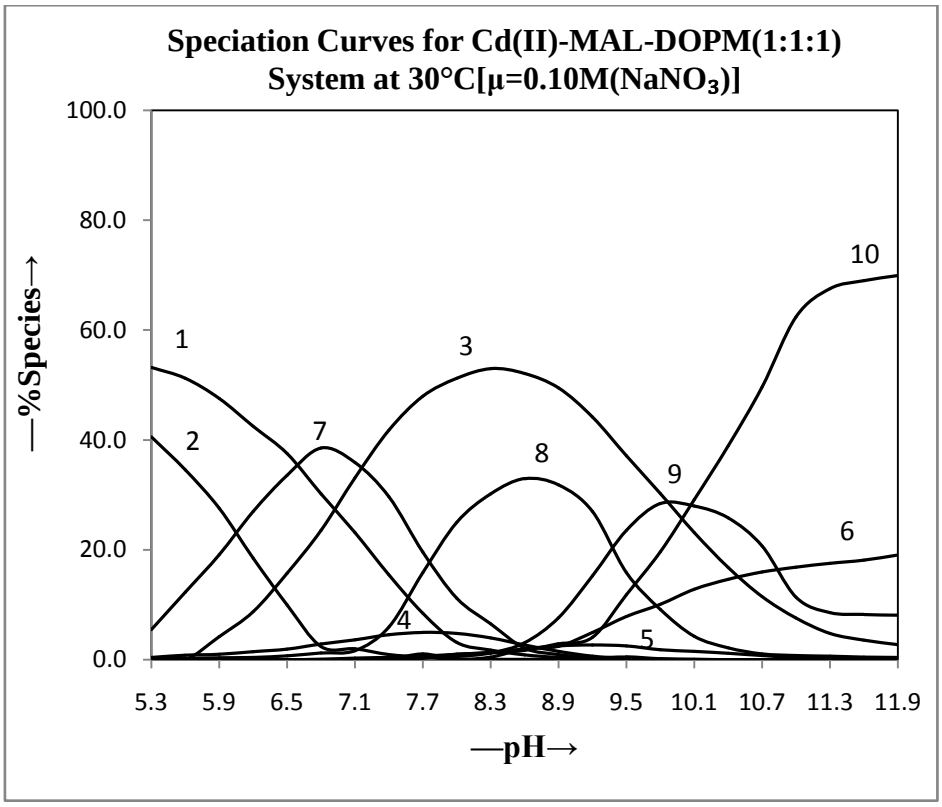

Fig. 11

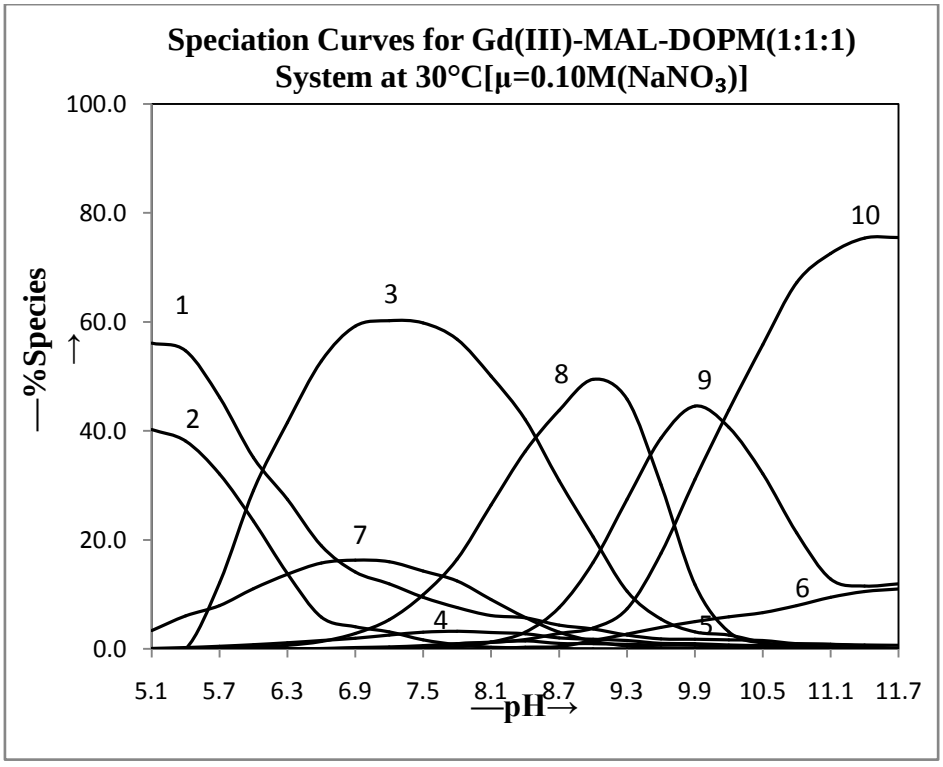

Fig. 12

Curve 1: [M]; 2 [MAH]; 3[MA]; 4 [MBH_2]; 5 [MBH]; 6 [MB]; 7 [$MABH_3$]; 8 [$MABH_2$]; 9 [MABH]; 10 [MAB]

Table: 4.17

Experimental values and concentration of different species for Cd(II)-MAL-DOPM (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[MBH]	[MB]	[$MABH_3$]	[$MABH_2$]	[MABH]	[MAB]
1	5.3	1.32	53.20	40.59	0.00	0.45	0.00	0.00	5.48	0.18	0.00	0.00
2	5.6	1.49	51.25	34.58	0.00	0.85	0.00	0.00	12.31	0.25	0.00	0.00
3	5.9	1.55	47.58	27.58	4.25	0.99	0.00	0.00	19.12	0.38	0.00	0.00
4	6.2	1.64	42.48	18.48	8.75	1.51	0.02	0.00	27.00	0.46	0.00	0.00
5	6.5	1.72	37.52	9.98	15.78	1.94	0.05	0.00	33.58	0.75	0.00	0.00
6	6.8	1.79	30.21	2.39	23.54	2.89	0.08	0.01	38.54	1.25	0.10	0.00
7	7.1	1.84	23.14	1.98	33.14	3.64	0.15	0.04	35.89	1.68	0.30	0.00
8	7.4	1.91	15.48	0.94	41.78	4.57	0.35	0.09	29.68	5.98	0.42	0.00
9	7.7	1.94	8.47	0.48	47.96	4.98	0.65	1.05	19.58	15.87	0.51	0.25
10	8.0	2.00	3.15	0.10	51.24	4.80	0.99	0.10	11.21	25.00	0.60	0.99
11	8.3	2.10	1.78	0.08	53.00	3.99	1.35	0.48	6.54	30.20	1.27	1.25
12	8.6	2.24	0.92	0.07	52.14	2.68	1.98	1.98	2.15	32.98	3.09	1.74
13	8.9	2.36	0.45	0.06	49.48	1.54	2.54	2.47	0.98	31.86	7.68	2.92
14	9.2	2.55	0.28	0.04	44.17	0.68	2.68	4.98	0.42	26.98	15.30	4.10
15	9.5	2.74	0.16	0.01	37.12	0.28	2.52	7.87	0.54	15.85	23.59	11.87
16	9.8	2.92	0.12	0.00	30.28	0.10	1.86	10.10	0.18	9.15	28.45	19.69
17	10.1	3.04	0.08	0.00	23.18	0.05	1.54	12.87	0.09	4.28	28.00	29.15
18	10.4	3.20	0.05	0.00	16.78	0.02	1.22	14.68	0.04	2.18	25.84	38.95
19	10.7	3.44	0.02	0.00	11.48	0.01	0.76	15.97	0.01	1.08	20.71	49.68
20	11.0	3.85	0.01	0.00	7.58	0.00	0.45	16.88	0.00	0.77	11.38	62.45
21	11.3	4.50	0.00	0.00	4.79	0.00	0.39	17.58	0.00	0.64	8.57	67.58
22	11.6	4.90	0.00	0.00	3.58	0.00	0.22	18.12	0.00	0.52	8.25	69.00
23	11.9	5.10	0.00	0.00	2.78	0.00	0.10	19.10	0.00	0.41	8.15	69.92

Table: 4.18

Experimental values and concentration of different species for Gd(II)-MAL-DOPM (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[MBH]	[MB]	[$MABH_3$]	[$MABH_2$]	[MABH]	[MAB]
1	5.1	1.10	56.12	40.25	0.00	0.10	0.00	0.00	3.40	0.08	0.00	0.00
2	5.4	1.30	54.71	38.15	0.00	0.28	0.00	0.00	6.08	0.10	0.00	0.00
3	5.7	1.49	46.21	32.12	12.15	0.48	0.00	0.00	7.98	0.15	0.00	0.00
4	6.0	1.64	35.12	23.47	29.12	0.78	0.00	0.00	11.10	0.38	0.00	0.00
5	6.3	1.73	27.45	13.85	41.58	1.12	0.00	0.00	13.69	0.67	0.00	0.00
6	6.6	1.78	18.92	5.87	52.85	1.54	0.10	0.00	15.78	1.38	0.00	0.00
7	6.9	1.83	14.14	4.08	59.25	1.98	0.25	0.00	16.28	2.84	0.15	0.00
8	7.2	1.91	11.98	3.15	60.25	2.57	0.38	0.00	16.00	5.39	0.18	0.00
9	7.5	1.96	9.47	1.67	59.85	3.10	0.62	0.00	14.28	9.98	0.25	0.28
10	7.8	2.04	7.58	0.78	56.87	3.25	0.98	0.04	12.48	16.48	0.38	0.98
11	8.1	2.09	6.14	0.34	50.10	3.00	1.24	0.09	9.08	26.42	1.25	1.18
12	8.4	2.16	5.70	0.18	42.12	2.78	1.48	0.32	5.79	36.28	3.08	1.75
13	8.7	2.25	4.35	0.06	30.85	2.05	1.00	0.45	3.10	43.82	7.60	2.87
14	9.0	2.32	3.65	0.04	20.58	1.78	0.98	1.54	1.42	49.48	15.92	3.85
15	9.3	2.44	2.54	0.01	10.58	1.54	0.84	2.76	0.54	45.85	27.48	7.38
16	9.6	2.56	1.85	0.00	5.47	1.05	0.75	3.98	0.18	30.18	38.69	17.51
17	9.9	2.71	1.78	0.00	3.12	0.98	0.68	5.04	0.09	11.84	44.58	31.12
18	10.2	2.92	1.68	0.00	2.58	0.74	0.55	5.92	0.04	3.15	40.68	43.85
19	10.5	3.17	1.57	0.00	1.20	0.62	0.42	6.69	0.01	1.10	32.15	55.87
20	10.8	3.50	0.98	0.00	0.23	0.54	0.35	7.99	0.00	0.98	21.28	67.27
21	11.1	3.67	0.84	0.00	0.10	0.33	0.22	9.50	0.00	0.84	12.82	72.57
22	11.4	3.74	0.50	0.00	0.00	0.10	0.18	10.55	0.00	0.72	11.54	75.42
23	11.7	3.85	0.00	0.00	0.00	0.00	0.10	11.00	0.00	0.66	11.98	75.52

Table: 4.19

Value of Δlog K for ternary complexes.

Parameters	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
	Cd(II)-MAL-TYR					
$\log\beta_{MABH2}$	30.90	5.70	30.20	5.10	29.69	4.74
$\log\beta_{MABH}$	24.20	4.33	24.10	4.37	23.84	7.29
$\log\beta_{MAB}$	12.70	0.84	12.25	0.60	11.80	0.33
	Gd(III)-MAL-TYR					
$\log\beta_{MABH2}$	33.60	7.15	32.54	6.19	31.84	5.71
$\log\beta_{MABH}$	29.20	7.95	28.14	7.02	26.16	6.46
$\log\beta_{MAB}$	15.46	1.73	14.84	1.30	14.78	0.18
	Cd(II)-MAL-DOPA					
$\log\beta_{MABH2}$	35.43	-0.34	35.20	-0.40	35.04	-0.44
	Gd(III)-MAL-DOPA					
$\log\beta_{MABH2}$	37.24	0.23	37.10	0.25	37.00	0.24
	Cd(II)-MAL-DOPM					
$\log\beta_{MABH3}$	41.84	7.24	41.63	6.84	40.30	6.00
$\log\beta_{MABH2}$	35.65	5.68	35.50	5.65	35.26	6.08
$\log\beta_{MABH}$	24.76	0.12	24.50	0.10	24.24	0.47
$\log\beta_{MAB}$	16.13	-1.94	15.48	-2.00	14.34	-2.14
	Gd(III)-MAL-DOPM					
$\log\beta_{MABH3}$	45.92	8.87	45.35	8.85	45.17	9.14
$\log\beta_{MABH2}$	40.40	9.25	39.39	8.59	39.27	8.68
$\log\beta_{MABH}$	31.77	5.82	31.32	5.82	31.17	5.91
$\log\beta_{MAB}$	27.05	0.45	26.95	0.38	26.90	0.55

4.4. 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. Titration curves are given in figs. 1-6. The ligand titration curve 1 show that the deprotonation of ligands A occurs in two distinct steps and curve 2 indicates that the liberation of proton up to pH≈8.0 showing the strong basic nature of ligand B. Further, the deviation of metal–ligand curves (curves 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- TYR/DOPA/DOPM ternary systems. Curve 5 in all the figs. is seen to be superimposed on 1:1 (MA) titration curve and theoretical composite curve 'T' up to pH ≈ 5.0 followed by inflections at a≈2.0 and a≈3.0. The theoretical composite curve is obtained by plotting the theoretical addition of the values of 'a' corresponding to ligand titration curve of ligand A to the metal – ligand (1:1) titration curve of ligand B. The observation leads to conclusion that the ligand A binds primarily with metal ion thereby forming MA complex. The displacement of curve 5 above the pH≈5 and a>2 from curve 3, 4 and 'T' indicates the liberation of extra protons from ligand B which coordinate to the MA complex. Hence in the mixed ligand equilibria, ligand A acts as primary ligand and ligand B as secondary. Various equilibria and the corresponding equilibrium constants for the investigated binary and ternary metal-ligand systems are represented as follow:

<u>M -Malonic acid - Tyrosine</u>

<u>Proton-ligand system:</u>

Malonic acid:

$$H_2A \underset{pK_1^H}{\overset{0 \le a \le 1}{\rightleftharpoons}} HA + H^+ \qquad \text{---- (1)}$$

$$HA \underset{pK_2^H}{\overset{1\le a\le 2}{\rightleftharpoons}} A + H^+ \quad \text{---- (2)}$$

Tyrosine:

$$H_2B \underset{pK_1^H}{\overset{0\le a\le 1}{\rightleftharpoons}} HB + H^+ \quad \text{------ (3)}$$

$$HB \underset{pK_2^H}{\overset{1\le a\le 2}{\rightleftharpoons}} B + H^+ \quad \text{---- (4)}$$

Binary M-Malonic acid system:

$$M+H_2A \underset{\log K_{MAH}^H}{\overset{0\le a\le 1}{\rightleftharpoons}} MAH + H^+ \quad \text{---- (5)}$$

$$M+HA \underset{\log K_{MAH}^M}{\overset{0\le a\le 1}{\rightleftharpoons}} MAH \quad \text{---- (6)}$$

$$MAH \underset{\log K_{MA}^H}{\overset{1\le a\le 2}{\rightleftharpoons}} MA + H^+ \quad \text{---- (7)}$$

$$M+A \underset{\log K_{MA}^M}{\overset{0\le a\le 2}{\rightleftharpoons}} MA \quad \text{---- (8)}$$

Binary M-Tyrosine system:

$$M+H_2B \underset{\log K_{MBH}^H}{\overset{0\le a\le 1}{\rightleftharpoons}} MBH + H^+ \quad \text{---- (9)}$$

$$M+HB \underset{\log K_{MBH}^M}{\overset{0\le a\le 1}{\rightleftharpoons}} MBH \quad \text{------(10)}$$

$$MBH \underset{\log K_{MB}^H}{\overset{1\le a\le 2}{\rightleftharpoons}} MB + H^+ \quad \text{------- (11)}$$

$$M+B \underset{\log K_{MB}^M}{\overset{0\le a\le 2}{\rightleftharpoons}} MB \quad \text{---- (12)}$$

Ternary M-Malonic acid-Tyrosine system:

Step-I:

$$M+H_2A \underset{\log K^{H}_{MAH}}{\overset{0\le a\le 1}{\rightleftharpoons}} MAH + H^+ \quad \text{---- (13)}$$

$$M+HA \underset{\log K^{M}_{MAH}}{\overset{0\le a\le 1}{\rightleftharpoons}} MAH \quad \text{---- (14)}$$

$$MAH \underset{\log K^{H}_{MA}}{\overset{1\le a\le 2}{\rightleftharpoons}} MA + H^+ \quad \text{---- (15)}$$

$$M+A \underset{\log K^{M}_{MA}}{\overset{0\le a\le 2}{\rightleftharpoons}} MA \quad \text{-------(16)}$$

Step-II:

$$MAH + HB \underset{\log K^{M}_{MABH\ 2}}{\overset{1\le a\le 2}{\rightleftharpoons}} MABH_2 \quad \text{---- (17)}$$

$$MABH_2 \underset{\log K^{H}_{MABH}}{\overset{2\le a\le 3}{\rightleftharpoons}} MABH + H^+ \quad \text{-----(18)}$$

$$MA+ HB \underset{\log K^{M}_{MABH}}{\overset{2\le a\le 3}{\rightleftharpoons}} MABH \quad \text{------ (19)}$$

$$MABH \underset{\log K^{H}_{MAB}}{\overset{3\le a\le 4}{\rightleftharpoons}} MAB + H^+ \quad \text{---------- (20)}$$

$$MA + B \underset{\log K^{H}_{MAB}}{\overset{2\le a\le 4}{\rightleftharpoons}} MAB \quad \text{---------- (21)}$$

M -Malonic acid - DOPA

Dopa

$$H_3B \underset{pK^{H}_{1}}{\overset{0\le a\le 1}{\rightleftharpoons}} H_2B + H^+ \quad \text{------- (22)}$$

$$H_2B \overset{1\le a\le 2}{\underset{pK_2^H}{\rightleftharpoons}} HB + H^+ \quad \text{---- (23)}$$

$$HB \overset{2\le a\le 3}{\underset{pK_3^H}{\rightleftharpoons}} B + H^+ \quad \text{---- (24)}$$

Binary M-DOPA system:

$$M+H_3B \overset{0\le a\le 1}{\underset{\log K^H_{MBH\,2}}{\rightleftharpoons}} MBH_2 + H^+ \quad \text{---- (25)}$$

$$M+H_2B \overset{0\le a\le 1}{\underset{\log K^M_{MBH\,2}}{\rightleftharpoons}} MBH_2 \quad \text{---- (26)}$$

Ternary M-Malonic acid-DOPA system:

Step-I: Same as represented in equation 13-16

Step-II

$$MA + H_2B \overset{2\le a\le 3}{\underset{\log K^M_{MA}}{\rightleftharpoons}} MABH_2 \quad \text{--------(27)}$$

M -Malonic acid – DOPM

Dopm

$$H_3B \overset{0\le a\le 1}{\underset{pK_1^H}{\rightleftharpoons}} H_2B + H^+ \quad \text{------- (28)}$$

$$H_2B \overset{1\le a\le 2}{\underset{pK_2^H}{\rightleftharpoons}} HB + H^+ \quad \text{---- (29)}$$

$$HB \overset{2\le a\le 3}{\underset{pK_3^H}{\rightleftharpoons}} B + H^+ \quad \text{---- (30)}$$

Binary M-DOPM system:

$$M+H_3B \underset{\log K^{H}_{MBH\ 2}}{\overset{0\le a\le 1}{\rightleftharpoons}} MBH_2 + H^+ \quad \text{---- (31)}$$

$$M+H_2B \underset{\log K^{M}_{MBH\ 2}}{\overset{0\le a\le 1}{\rightleftharpoons}} MBH_2 \quad \text{-------(32)}$$

$$MBH_2 \underset{\log K^{H}_{MBH}}{\overset{1\le a\le 2}{\rightleftharpoons}} MB + H^+ \quad \text{-------- (33)}$$

$$M+HB \underset{\log K^{M}_{MBH}}{\overset{0\le a\le 2}{\rightleftharpoons}} MBH \quad \text{---- (34)}$$

$$MBH \underset{\log K^{H}_{MB}}{\overset{2\le a\le 3}{\rightleftharpoons}} MB + H^+ \quad \text{--------- (35)}$$

$$M+B \underset{\log K^{M}_{MB}}{\overset{0\le a\le 3}{\rightleftharpoons}} MB \quad \text{---- (36)}$$

Ternary M-Malonic acid-DOPM system:

Step-I: Same as represented in equation 13-16

Step-II:

$$MAH + H_2B \underset{\log K^{M}_{MABH\ 3}}{\overset{1\le a\le 2}{\rightleftharpoons}} MABH_3 \quad \text{---- (37)}$$

$$MABH_3 \underset{\log K^{H}_{MABH\ 2}}{\overset{2\le a\le 3}{\rightleftharpoons}} MABH_2 + H^+ \quad \text{-----(38)}$$

$$MA + H_2B \underset{\log K^{M}_{MABH\ 2}}{\overset{2\le a\le 3}{\rightleftharpoons}} MABH_2 \quad \text{------ (39)}$$

$$MABH_2 \underset{\log K^{H}_{MABH}}{\overset{3\le a\le 4}{\rightleftharpoons}} MABH + H^+ \quad \text{------- (40)}$$

$$MA + HB \underset{\log K^{M}_{MABH}}{\overset{2\leq a \leq 4}{\rightleftharpoons}} MABH \qquad \text{---------- (41)}$$

$$MABH \underset{\log K^{H}_{MAB}}{\overset{4\leq a \leq 5}{\rightleftharpoons}} MAB + H^{+} \qquad \text{--------- (42)}$$

$$MA + B \underset{\log K^{M}_{MAB}}{\overset{2\leq a \leq 5}{\rightleftharpoons}} MAB \qquad \text{---------- (43)}$$

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

Where, Step-I: Interaction of metal M primary ligand A

Step -II: Interaction of MA species with secondary ligand B

Various approaches for the calculation of stability constant involving stepwise equilibria are reported in literature.[67-70] In the present work the treatment based on the algebraic method of Chaberek and Martell[71-72] as modified by Dey et al.[73] has been used for the calculation of various constants in proton-ligand and metal-ligand in binary and ternary systems. 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 4.1-4.9.

Speciation curves are obtained for various systems by using SCOGS computer program. [74-76] Speciation curves for Cd(II)/Gd(III)-MAL-TYR are shown in figs. 7-8, the trends observed are nearly same. It can be seen that the formation of MAH species occurs up to pH≈4.0 and then concentration of MAH and free metal decreases continuously. Thereafter MA species is formed by deprotonation of MAH complex. Simultaneously formation of protonated ternary species $MABH_2$ also comes into existence. However the concentration of these two species is less than 25% in both the systems. Deprotonation of $MABH_2$ species leads to the formation of MABH in pH range ≈ 5.0 to 6.5 and 2≤a≤3.

Thereafter the MAB species is formed by the coordination of ligand B to MA complex. Formation of MAB species commences at a≈2 and attains a maximum value of ≈70% at a≈4. MAB ternary complex is the predominant species in both the systems. Formation of MAB occurs through two alternative equilibria (Ref. eq. 20 and 21). The equation 20 represents the formation of MAB by deprotonation of MABH species, whereas equation 21 shows the formation of MAB by coordination of ligand B (deprotonated form) to MA species.

Figures 9 and 10 correspond to the Cd(II)/Gd(III)-MAL-DOPA systems. Nature of curves in these figs. shows that the two ligands coordinate in two distinct steps with metal ion above pH≈5.0. Mixed ligand complexes come into existence above pH≈6.5 in the form of $MABH_2$. Concentration of binary (MBH_2) and ternary ($MABH_2$) species increases up to pH≈7.0. After that, concentration of binary species decreases and ternary species increases. The percentage of $MABH_2$ species becomes maximum ≈70% at pH≈7.5. The equation 27 represents the formation of $MABH_2$ by coordination of H_2B species to MA complex.

All the systems involving dopa are confined below pH≈8.0 to avoid errors due formation of polymeric species at higher pH. Therefore dissociation of protonated species was not considered.

Figures 11 and 12 show the percent distribution curves of Cd(II)/Gd(III)-MAL-DOPM system. Trends observed in these figs. show the formation of non-protonated species [MA] as a major species up to pH≈6.5 which shows that all the protons in ternary complex species are attached to dopm site. After pH≈6.5, concentration of free metal M, MAH and MA species is decreased and $MABH_3$ is increased.

Speciation curves also show that in these systems above pH≈7.5 $MABH_2$ is formed by dissociation of $MABH_3$ as well as by combination of MA and H_2B species (Ref. eq. 38 and 39). MABH and MAB also seem to be formed in both the ways, i.e. by combination of ligand 'B' with MA and dissociation of higher protonated ternary complexes (Ref. Eq. 40-43).

According to Sigel[77], the relative stability of ternary complex MAB as compared to that of the binary complex MA can be quantitatively expressed in different ways. The most suitable comparison is in term of ΔlogK. This parameter can be calculated from the reaction of secondary ligand B either with MA or with free metal ion. According to the following equation and values of ΔlogK for ternary complexes are obtained and given in table 4.19.

$$\Delta\log K_{MAB} = \log K^{MA}_{MAB} - \log K^{M}_{MB} \qquad \text{----(44)}$$

The reaction represents the following overall equilibrium:

$$\Delta\log K_{MAB} = \log\beta_{MAB} - (\log\beta_{MA} + \log\beta_{MB}) \qquad \text{----(45)}$$

The magnitudes of ΔlogK are strongly influenced by statistical differences in the formation of complex as well as differences in bonding. In most of the systems values of ΔlogK are found to be positive which indicate that the ternary complexes are more stable than the binary complexes. This is perhaps due to the complete satisfaction of primary valency (oxidation number) and the secondary valency (coordination number) of metal cations, thereby leading to more stable complexes. The higher stability of ternary complexes of Gd(III) can be attributed to its higher coordination number as compared to Cd(II). The negative value in some ternary systems of Cd(II) can be attributed to the availablity of less number of coordination sites on binary complexes of Cd(II) thereby

decreasing the flexibility of secondary ligand B to coordinate with MA species. Further MA complex of Gd(III) bears mono-negative charge whereas that of Cd(II) bears di-negative charge. Hence the secondary ligand B has to face greater repulsion in the latter case, which in turn leads to negative value of ΔlogK.

The values of ΔG°, ΔH° and ΔS° are presented in table 4.10-4.15. The negative values of ΔG° in each case indicate that the complexation is spontaneous. The negative enthalpy changes (ΔH°) for the complexation suggest that all the complexation reaction are exothermic, favorable at lower temperature and the metal ligand binding process is enthalpy driven. This also indicates that metal-ligand bonds are fairly strong. The positive values of ΔS° indicate that the formations of these complexes are entropically favoured.

The protonation constants of the ligands involved in the present work show the following trend:

DOPM > DOPA > TYR > MAL

The stability of binary complexes also follows the same trend. In ternary systems malonic acid acts as primary ligand in all the systems. In the mixed systems involving tyrosine/dopa/dopm as secondary ligand, it is seen that most stable ternary complexes are formed with dopm. This is in agreement with the fact that dopm is most basic amongst the selected ligands. The binding of dopm to the metal may be assumed to be via the amino group and by bridging any one of the phenolato oxygen. In such mode it forms eight membered chelate ring which is considered to be sterically unfavorable due to large size. Alternatively, metal can bind to dopm with two phenolato oxygen and form five membered ring this type of binding is favorable.[78] Hence it is understood that dopm binds to the metal ion in pyrocatechol mode.

Comparing the stabilities of binary and ternary metal-ligand species of dopm and dopa it is seen that more stable complex are formed in former case. This is due to less steric hindrance and small size of dopm as compared to dopa. Dopa coordinates with metal ion in glycine like mode in lower pH range. This is in confirmation with the earlier reports which state that dopa behaves as ambidentate ligand changing its coordination mode depending on pH.[79-83] It is established that at higher pH dopa coordinates in pyrocatechol mode consequently leading to polymeric species.[84] In present investigation the complex formation is established only upto pH≈ 6.5 to 7.5. Hence polymeric species are not considered.

Tyrosine bears structural similarity to dopa, hence the stability constant values with these ligands are nearly same. This indicates that both the ligands coordinate with the metal in glycine like mode. However, the slightly lower values of equilibrium constants obtained in case of tyrosine as compared to dopa can be attributed due to their basicity difference.

The Gd(III) complexes are more stable than Cd(II) complexes. This can be explained on the basis of high charge and higher coordination number of Gd(III) ion. The metal-ligand stability constants logK decrease with an increase in temperature and ionic strengths. The negative value of both free energy ($\Delta G°$) and enthalpy ($\Delta H°$) and positive value of entropy ($\Delta S°$) confirms the favorable condition for complex formation.

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