2.1 Introduction:

The formation of complexes, in the aqueous solutions is a matter of great importance not only in inorganic but also in analytical, biochemistry and other scientific and industrial fields.[1-14] Metal ions can induce toxicity in humans and plants. Classic examples being heavy metal poisons such as cadmium, mercury and lead etc. Even essential metal ions can be toxic when present in excess or beyond certain threshold concentration. One way for treatment of metal toxicity involves chelation therapy, in which metal-specific chelating agents are administered as drugs to complex and facilitate excretion of unwanted excess element from the organism. Hence, chemical speciation study of toxic metal ion complexes is important for an understanding of their distribution, mobility, bioavailability, toxicity and for setting environmental quality standards.[15-19]

Cadmium and gadolinium are toxic elements and have negative health effects in human populations. Cadmium causes iron deficiency by binding to cysteine, glutamate, aspartate, and histidine ligands.[20] **Cadmium** inhibits enzymes that participate in bilirubine conjunction.[21] It increases urine Ca^{2+} excretion which can cause severe bone pathology.[22] The possible effects of long term low-level exposure to cadmium are of concern because it is readily distributed to tissues of liver and kidney, which are the main target organs in acute and chronic cadmium exposure.[23-24] Other tissues involved in cadmium toxicity include the testis, heart, bone, eye, and brain.[25]

Gadolinium ion is highly toxic and in order to reduce its toxicity, gadolinium ion must be transformed into complex with an organic molecule.[26-28] Several Gd(III) complexes are the active constituents of pharmaceuticals, employed as contrast agents in clinical MRI diagnostics.

The first human MRI study employing a Gd(III) complex was reported in 1984 by Carr et al., who made use of the $[Gd(DTPA)]^{2-}$ (DTPA= diethylentriaminepentacetic acid) complex to identify the presence of cerebral tumors.[29] This complex is the only contrast agent available for many years until a few other aminopolycarboxylic complexes were recognized to be of practical use in clinical diagnostics.[20-40]

It can be witnessed from the chemical literature that considerable data is available on equilibrium studies involving Cd(II) and Gd(III) in simple systems. However much attention is not given to equilibrium studies involving these metals in mixed systems where multiple equilibria exist. Hence it was considered worthwhile to investigate several hitherto unreported mixed systems involving Cd(II) and Gd(III) with malonic acid and aminopolycarboxylic acids (NTA and IMDA). The choice of the ligands is induced from the fact that these ligands have great significance in biological and industrial fields. Some significant aspects of the selected ligands and their complexes are described here under.

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.[41-42] It is important intermediate in synthesis of vitamins B1, B6, barbiturates, non-steroidal anti-inflammatory agents, other numerous pharmaceuticals, agrochemicals flavor and fragrance compounds.[43] Malonic acid (propanedioic acid) is an important difunctional carboxylic acid in geological systems. It is one of the most abundant of this class of acids in soils, and has received considerable attention because of its effect on nutrient availability. Its importance may not be limited to near-surface environments. Concentrations of malonate in excess of 2500 $mg\text{-}L^{-1}$ have been reported in basinal brines; thus, malonate may be an important species in the transport of aluminum and other metals in sedimentary

basins. Malonic acid is important to geochemical and industrial processes because its anion forms strong complexes with di- and trivalent metal cations. The thermodynamic behavior and activity-concentration relationships of malonic acid in all its forms must be understood in order to model geological or industrial systems, to use malonate species as pH buffers, or to measure the association constants of metal-malonate complexes.[44]

Survey of the existing literature reveals that very little work has been done on the mixed-ligand complexes of dibasic acids. Malonate complexes of Cu(II) metal ion have been reported.[45] Complex formation of iron (II) with oxalate, malonate, succinate and glutarate ion have been studied.[46] Recently potentiometric studies of speciation of Ni(II) complexes with oxalic and malonic acid in 1.0 mol dm^{-3} NaCl at 25°C is conducted and the results show that in nickel(II)-malonic acid system the complexes $[NiHL]^{+}$, [NiL], $[Ni(OH)L]^{-}$, and $[Ni(OH)_2L]^{2-}$ exist.[47] Rao et al. have published several papers on chemical speciation studies of malonic acid with some biologically important metal ions.[48-51]

Aminopolycarboxylic acids (APCAs) also known as complexones, are compounds that contain several carboxylate groups bound to one or more nitrogen atoms.[52-53] A significant chemical property of APCAs is their ability to form stable and water-soluble complexes with many metal ions. APCAs usually form metal chelates. The ring formation leads to a higher stability of the complex. Due to their metal-complexing capacities, APCAs occur in the environment mostly in the form of metal-complexes. Hence, the influence of metal speciation on various degradation processes is of utmost importance to understand the environmental behavior of these compounds. It is well known that the chelating properties of aminopolycarboxylates can be engineered by varying the groups linking

the nitrogen atoms so as to increase selectivity for a particular metal ion. This reagent provides a means of determining the metal content in intra-cellular fluid. Details concerning applications can be found in the individual articles and/or reference.[54-58]

Recent publications by several group of workers on equilibrium and speciation studies on aminopolycarboxylic acid with biologically important metal ions have furnished interesting results.[59-63]

Nitrilotriacetic acid is used as a chelating and sequestering agent, and as a builder in synthetic detergents.[64] It is also used as an eluting agent in the purification of rare earth elements,[65] as a boiler feed water additive, in water and textile treatment, in metal plating, cleaning in pulp and paper processing.[66] 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, squamous-cell carcinomas of the urinary bladder, hepatocellular adenomas and adrenal phaeochromocytomas in female rats.[67] The developmental and reproductive effects of nitrilotriacetic acid have been reviewed.[68] Addition of heavy metals such as mercury and cadmium did not change the response. Similarly, studies of reproductive toxicity did not indicate an effect on neonatal development. Ternary metal complexes of NTA are extensively used in medical, biological and environmental studies, as well as in water and soil treatment. Metal complexes are also used in dying and bleaching.[69-70]

Iminodiacetic acid is very suitable as an immobilized chelating agent, since a bidentate chelating moiety remains free after immobilization to which a matel ion can be coordinated. Various metal ions can be immobilized on the stationary phase via this immobilized chelating agent. Free coordination sites of the metal ions are used to bind different protein and peptides. Complexes play a key role in determining the affinity of the

radiopharmaceuticals for binding to hepatic transport proteins, the efficiency of their uptake by hepatocytes and the excretion rate. Increasing lipophilicity leads to a higher degree of resistance against the competitive effects of bilirubin.[71-74]

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

1. Cd(II) – Malonic acid – Nitrilotriacetic acid
2. Cd(II) – Malonic acid – Iminodiacetic acid
3. Gd(III) –Malonic acid – Nitrilotriacetic acid
4. Gd(III) – Malonic acid –Iminodiacetic acid

In addition to above ternary systems, the following binary systems have also been investigated under the same experimental conditions for comparison.

1. Cd(II)-Malonic acid
2. Cd(II)-Nitrilotriacetic acid
3. Cd(II)-Iminodiacetic acid
4. Gd(III)-Malonic acid
5. Gd(III)-Nitrilotriacetic acid
6. Gd(III)-Iminodiacetic acid

2.2. Experimental and computational methods:

All the reagents used were of highest purity Merck/Aldrich products. The experimental details regarding instrument and preparation of various sets of titration mixture are also explained in chapter-1

Each set of mixture was titrated potentiometrically against standard sodium hydroxide solution (0.10M). Experiments were performed at three different temperatures (20±1°C, 30±1°C and 40±1°C) and three ionic strengths (0.05M, 0.10M, 0.15M). Temperature was maintained by Siskin Julabo, thermostat model V-12B and ionic strength was maintained by sodium nitrate solution. All the binary and ternary systems were investigated under equimolar concentration ratio. For each set of experiment, pH was plotted against volume of titrant added and from these curves, moles of alkali required per mole of metal/ligand ('a') was determined. Then titration curves were obtained by plotting pH vs. 'a'. Representative titration curves are given in figs.1-4.

Treatment based on the algebraic method of Chaberek and Martell[75-76] as modified by Dey et al.[77] has been used in the present work for the calculation of various constants for proton-ligand and metal-ligand systems (binary and ternary). Formation constants of proton-ligand and metal-ligand complexes were evaluated and refined by SCOGS[78-80]. The values are recorded in tables 2.1-2.7. The speciation profiles for different systems investigated in the present work are shown as percent distribution curves in figs.5-8 and tables 2.10-2.13. The conditional stability constant values at three different ionic strengths were plotted against $\sqrt{?}$ and extrapolated to zero ionic strength to obtain thermodynamic stability constants. The value of ligational standard free energy change (ΔG°) is determined using Van't Hoff equation. The other thermodynamic parameters such as standard enthalpy change (ΔH°) and standard entropy change (ΔS°) have been obtained by least square fit method.[81] Regression analysis applied to it provides the means for objectively obtaining straight line and also for specifying the uncertainties associated with its subsequent use. A linear graph is obtained by plotting logK vs.

1/T. In this linear plot slope is equal to -ΔH°/2.303R and intercept is equal to ΔS°/2.303R. These thermodynamic parameters i.e. ΔG°, ΔH° and ΔS° are calculated and tabulated in tables 2.8-2.9.

2.3. Curves and tables:

Representative pH vs. '*a*' curves

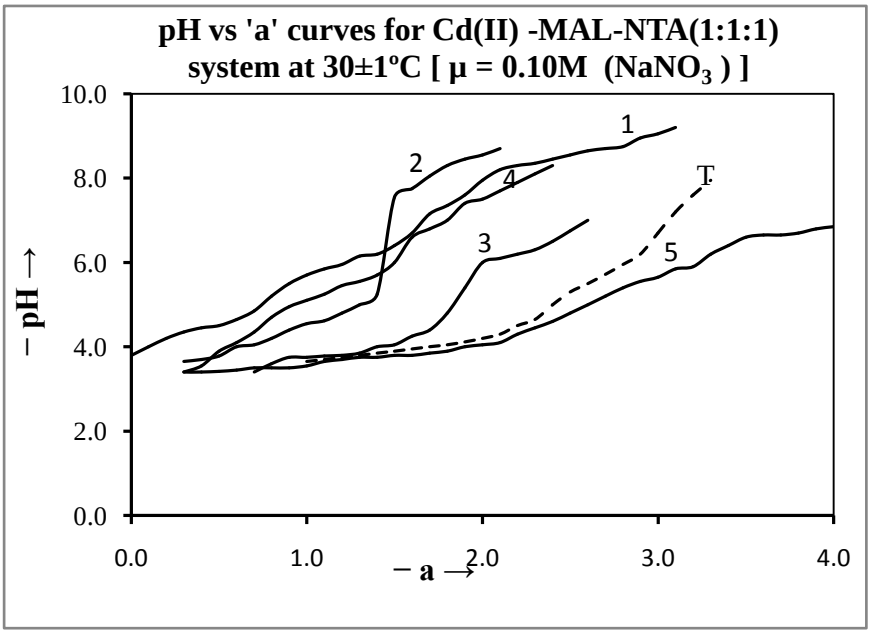

Fig. 1

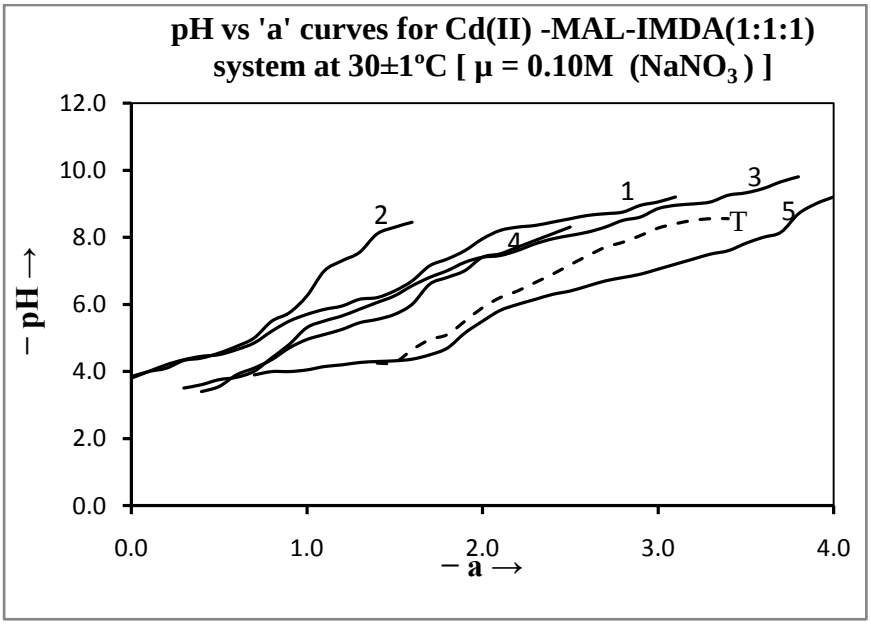

Fig. 2

Where- 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

Representative pH vs. '*a*' curves

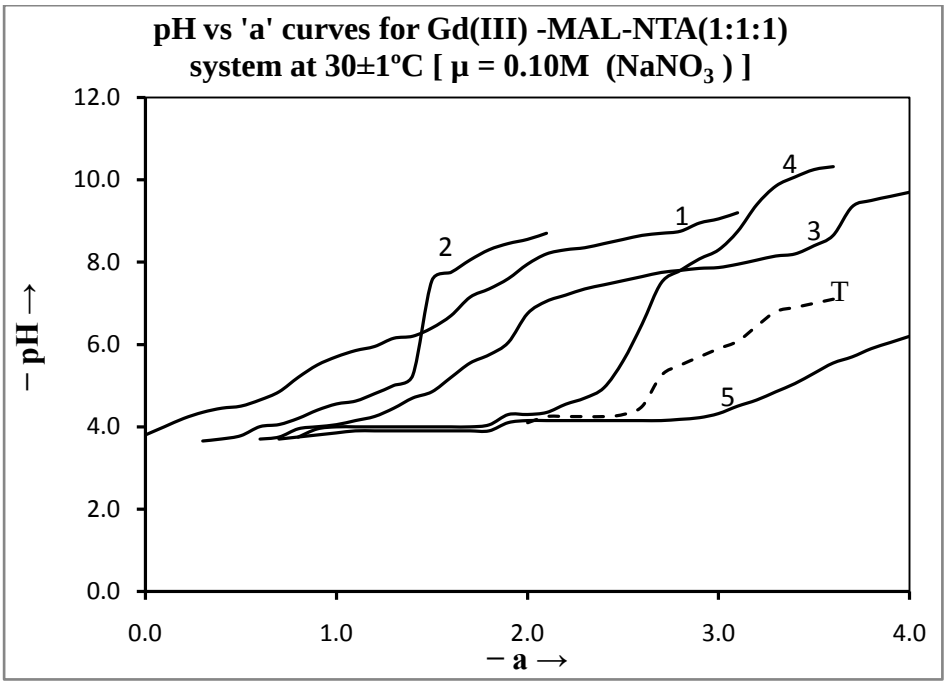

Fig. 3

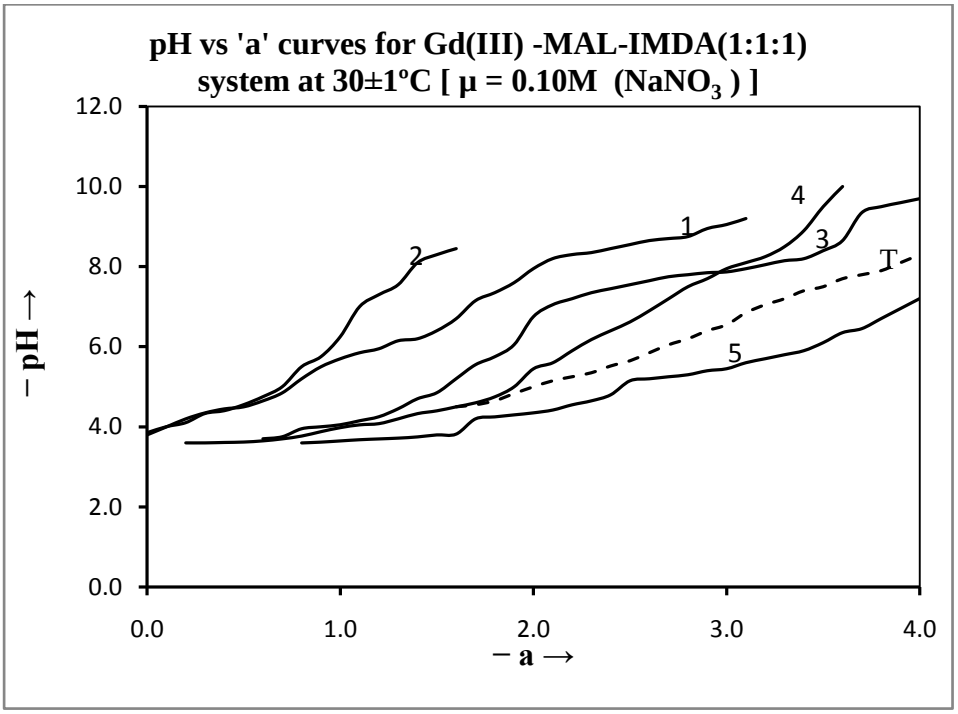

Fig. 4

Where- 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

Table: 2.1

Protonation constants of ligands

at different temperatures and ionic strengths

Parameters	20±1°C				30±1°C				40±1°C			
	0.05M	**0.10M**	**0.15 M**	**μ→0**	**0.05M**	**0.10M**	**0.15 M**	**μ→0**	**0.05M**	**0.10M**	**0.15 M**	**μ→0**
Malonic acid (MAL)												
$\log \beta_1^{HA}$	6.47	6.35	6.23	6.73	6.40	6.25	6.18	6.50	6.21	6.15	6.08	6.30
$\log \beta_2^{H2A}$	9.84	9.72	9.65	9.89	9.73	9.64	9.52	9.80	9.53	9.32	9.17	9.60
Nitrilotriacetic Acid (NTA)												
$\log \beta_1^{HB}$	9.99	9.96	9.92	10.10	9.70	9.64	9.60	9.83	9.28	9.23	9.20	9.48
$\log \beta_2^{H2B}$	13.20	13.14	13.10	13.45	12.88	12.84	12.80	12.92	12.30	12.25	12.20	12.54
Iminodiacetic Acid (IMDA)												
$\log \beta_1^{HB}$	8.90	8.85	8.80	9.02	8.45	8.40	8.35	8.65	8.15	8.10	8.05	8.35
$\log \beta_2^{H2B}$	11.88	11.82	11.78	12.00	11.26	11.22	11.18	11.35	11.06	11.00	10.95	11.15

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

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

Table: 2.2

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

Parameters	Cd(II)-Malonic Acid(MAL)											
	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
$\log K^{M}_{MBH}$	4.29	4.22	4.15	4.38	4.24	4.20	4.12	4.35	4.20	4.13	4.08	4.32
$\log K^{H}_{MBH}$	-5.35	-5.30	-5.24	-5.62	-5.27	-5.20	-5.16	-5.56	-5.12	-5.08	-5.04	-5.50
$\log K^{H}_{MB}$	-6.20	-6.14	-6.10	-6.32	-6.10	-6.01	-5.95	-6.20	-6.00	-5.93	-5.90	-6.10
$\log \beta_{MBH}$	11.89	11.84	11.79	11.95	11.84	11.78	11.71	11.90	11.76	11.64	11.59	11.85
$\log \beta_{MB}$	5.50	5.42	5.36	5.62	5.41	5.33	5.26	5.53	5.39	5.29	5.70	5.45
	Cd(II)-Nitrilotriacetic Acid(NTA)											
$\log K^{M}_{MBH}$	2.42	2.35	2.29	2.55	2.34	2.29	2.20	2.50	2.16	2.10	2.03	2.28
$\log K^{H}_{MBH}$	-6.44	-6.40	-6.34	-6.62	-6.32	-6.28	-6.20	-6.54	-6.23	-6.18	-6.11	-6.50
$\log K^{H}_{MB}$	-7.18	-7.10	-7.03	-7.30	-7.04	-6.99	-6.90	-7.25	-6.80	-6.74	-6.68	-6.88
$\log \beta_{MBH}$	12.15	12.10	12.02	12.30	11.96	11.89	11.80	12.10	11.78	11.82	11.78	11.85
$\log \beta_{MB}$	7.04	6.98	6.90	7.10	6.90	6.84	6.78	6.99	6.82	6.76	6.70	6.90
	Cd(II)-Iminodiacetic Acid(IMDA)											
$\log K^{M}_{MBH}$	2.62	2.58	2.50	2.75	2.34	2.29	2.20	2.55	2.22	2.15	2.08	2.49
$\log K^{H}_{MBH}$	-3.76	-3.70	-3.66	-3.90	-3.64	-3.60	-3.52	-3.86	-3.47	-3.41	-3.36	-3.80
$\log K^{H}_{MB}$	-4.60	-4.54	-4.50	-4.70	-4.45	- 4.38	-4.30	-4.55	-4.24	-4.18	-4.11	-4.38
$\log \beta_{MBH}$	8.45	8.40	8.35	11.52	8.18	8.10	8.02	11.30	8.02	7.95	7.90	11.08
$\log \beta_{MB}$	4.27	4.21	4.16	4.45	4.09	4.00	3.92	4.27	3.90	3.84	3.80	3.95

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

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

Table: 2.3

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

Parameters	Gd(III)- Malonic Acid(MAL)											
	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
$\log K^{M}_{MAH}$	4.65	4.58	4.43	4.95	4.60	4.54	4.49	4.85	4.45	4.36	4.25	4.65
$\log K^{H}_{MAH}$	-4.00	-3.94	-3.90	-4.12	-3.90	-3.86	-3.80	-4.07	-3.82	-3.78	-3.72	-4.00
$\log K^{H}_{MA}$	-5.32	-5.28	-5.24	-5.48	-5.24	-5.24	-5.16	-5.37	-5.18	-5.12	-5.08	-5.97
$\log \beta_{MAH}$	11.80	11.78	11.72	11.90	11.63	11.60	11.56	11.78	11.56	11.53	11.50	11.78
$\log \beta_{MA}$	6.62	6.56	6.46	6.85	6.54	6.48	6.38	6.77	6.42	6.38	6.24	6.77
	Gd(III)- Nitrilotriacetic Acid(NTA)											
$\log K^{M}_{MBH}$	2.83	2.78	2.70	3.00	2.48	2.40	2.31	2.70	2.38	2.30	2.24	2.56
$\log K^{H}_{MBH}$	-4.04	- 4.00	-3.94	-4.12	-3.94	-3.90	-3.84	-4.06	-3.80	-3.74	-3.70	-3.98
$\log K^{H}_{MB}$	-4.58	-4.50	-4.42	-4.77	-4.40	-4.32	-4.24	-4.64	-4.22	-4.15	-4.08	-4.35
$\log \beta_{MBH}$	12.54	12.45	12.38	12.62	12.02	11.95	11.90	12.20	11.89	11.82	11.66	11.67
$\log \beta_{MB}$	8.04	7.98	7.92	8.17	7.93	7.86	7.79	8.02	7.76	7.70	7.62	7.95
	Gd(III)- Iminodiacetic Acid(IMDA)											
$\log K^{M}_{MBH}$	2.53	2.54	2.46	2.72	2.49	2.43	2.38	2.65	2.42	2.34	2.38	2.54
$\log K^{H}_{MBH}$	-3.18	-3.14	-3.06	-3.24	-2.98	-2.94	-2.90	-3.18	-2.84	-2.80	-2.76	-3.10
$\log K^{H}_{MB}$	-3.56	-3.50	-3.42	-3.75	-3.21	-3.16	-3.08	-3.30	-3.34	-3.29	-3.21	-3.42
$\log \beta_{MBH}$	8.51	8.45	8.39	11.85	8.32	8.25	8.19	11.50	8.14	8.10	8.02	11.25
$\log \beta_{MB}$	4.43	4.39	4.30	4.55	4.34	4.28	4.20	4.50	4.40	4.36	4.26	4.46

Table: 2.4

Formation constants of (1:1:1) Cd(II)-MAL-NTA ternary systems 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
$\log K^{M}_{MAHBH}$	12.64	12.58	12.50	12.12	12.07	12.00	11.90	11.84	11.80
$\log K^{MAH}_{MAHBH}$	7.87	7.82	7.76	7.43	7.39	7.30	7.16	7.10	7.03
$\log K^{MBH}_{MAHBH}$	6.96	6.90	6.84	6.74	6.69	6.62	6.34	6.30	6.22
$\log K^{M}_{MAHB}$	17.20	17.14	17.10	17.00	16.94	16.90	16.75	16.70	16.55
$\log K^{M}_{MABH}$	14.92	14.86	14.80	14.60	14.52	14.48	14.30	14.20	14.11
$\log K^{MAH}_{MABH}$	9.68	9.62	9.58	9.38	9.32	9.28	9.10	9.02	8.96
$\log K^{MBH}_{MABH}$	8.90	8.83	8.77	8.34	8.29	8.23	8.16	8.10	8.02
$\log K^{MA}_{MABH}$	8.10	8.06	8.00	7.60	7.56	7.67	7.08	7.00	6.91
$\log K^{MB}_{MABH}$	4.69	4.64	4.59	4.57	4.45	4.50	4.21	4.15	4.11
$\log K^{MA}_{MAB}$	9.35	9.30	9.24	9.17	9.11	9.16	9.17	9.12	9.07
$\log K^{MB}_{MAB}$	5.20	5.15	5.10	5.10	5.05	5.10	5.02	4.94	4.88
$\log K^{H}_{MABH2}$	-4.25	-4.18	-4.10	-3.94	-3.90	-3.96	-3.52	-3.45	-3.38
$\log K^{H}_{MABH}$	-6.88	-6.82	-6.76	-6.30	-6.24	-6.30	-6.19	-6.12	-6.05
$\log K^{H}_{MAB}$	-7.54	-7.50	-7.44	-7.10	-7.04	-6.99	-6.84	-6.82	-6.78
$\log \beta_{MABH2}$	24.81	24.77	24.72	24.54	24.48	24.40	24.03	23.98	23.91
$\log \beta_{MABH}$	23.68	23.62	23.58	23.48	23.42	23.38	23.16	23.10	23.03
$\log \beta_{MAB}$	14.98	14.93	14.90	14.52	14.47	14.42	14.23	14.18	14.12

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

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

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

Table: 2.5

Formation constants of (1:1:1) Cd(II)-MAL-IMDA ternary systems 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
$logK^{M}_{MAHBH}$	11.92	11.85	11.80	11.56	11.52	11.78	11.06	11.00	10.94
$logK^{MAH}_{MAHBH}$	7.06	6.98	6.92	6.90	6.86	6.80	6.56	6.50	6.42
$logK^{MBH}_{MAHBH}$	5.99	5.94	5.90	5.78	5.70	5.63	5.31	5.28	5.20
$logK^{M}_{MAHB}$	14.62	14.56	14.50	14.32	14.28	14.20	14.00	13.94	13.90
$logK^{M}_{MABH}$	13.41	13.35	13.30	13.16	13.07	13.00	12.90	12.84	12.79
$logK^{MAH}_{MABH}$	7.92	7.88	7.82	7.69	7.61	7.56	7.38	7.30	7.23
$logK^{MBH}_{MABH}$	6.60	6.54	6.48	6.50	6.41	6.36	6.18	6.10	6.06
$logK^{MA}_{MABH}$	5.86	5.80	5.73	5.73	5.67	5.60	5.43	5.38	5.30
$logK^{MB}_{MABH}$	2.30	2.26	2.20	2.09	2.01	1.98	2.00	1.93	1.86
$logK^{MA}_{MAB}$	13.62	13.58	13.51	12.28	13.22	13.16	13.04	13.00	12.94
$logK^{MB}_{MAB}$	8.95	8.90	8.83	8.70	8.63	8.58	8.24	8.20	8.12
$logK^{H}_{MABH2}$	-4.32	-4.28	-4.22	-3.99	-3.94	-3.90	-3.86	-3.81	-3.78
$logK^{H}_{MABH}$	-5.83	-5.78	-5.70	-4.64	-4.60	-4.52	-4.46	-4.40	-4.33
$logK^{H}_{MAB}$	-7.64	-7.60	-7.55	-7.54	-7.50	-7.44	-7.48	-7.41	-7.37
$\log \beta_{MABH2}$	24.76	24.70	24.64	23.00	22.96	22.90	22.16	22.11	22.07
$\log \beta_{MABH}$	21.20	21.15	21.10	20.73	20.67	20.64	20.16	20.12	20.06
$\log \beta_{MAB}$	11.91	11.86	11.80	11.50	11.42	11.36	11.18	11.16	11.10

Table: 2.6

Formation constants of (1:1:1) Gd(III)-MAL-NTA 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
$\log K^{M}_{MAHBH}$	19.70	19.65	19.60	18.99	18.94	18.87	17.52	17.48	17.40
$\log K^{MAH}_{MAHBH}$	17.71	17.65	17.59	17.05	17.00	16.95	16.50	16.42	16.38
$\log K^{MBH}_{MAHBH}$	20.02	19.95	19.86	19.74	19.07	19.00	18.52	18.48	18.40
$\log K^{M}_{MAHB}$	24.90	24.83	24.78	24.70	24.64	24.59	24.50	24.44	24.38
$\log K^{M}_{MABH}$	22.52	22.46	22.38	22.10	22.03	21.97	21.70	21.65	21.60
$\log K^{MAH}_{MABH}$	20.86	20.80	20.72	20.66	20.60	20.54	19.31	19.26	19.21
$\log K^{MBH}_{MABH}$	23.62	23.56	23.50	22.72	22.67	22.60	21.22	21.18	21.13
$\log K^{MA}_{MABH}$	16.92	16.84	16.80	15.89	15.83	15.78	14.68	14.62	14.56
$\log K^{MB}_{MABH}$	19.22	19.10	19.00	18.71	18.65	18.59	17.30	17.26	17.21
$\log K^{MA}_{MAB}$	17.99	17.95	17.88	17.73	17.69	17.60	16.31	16.24	16.48
$\log K^{MB}_{MAB}$	20.93	20.89	20.83	20.66	20.62	20.58	19.54	19.48	19.43
$\log K^{H}_{MABH2}$	-5.32	-5.26	-5.20	-4.21	-4.15	-4.09	-3.99	-3.94	-3.90
$\log K^{H}_{MABH}$	-6.61	-6.55	-6.49	-5.30	-5.23	-5.16	-4.92	-4.86	-4.81
$\log K^{H}_{MAB}$	-7.10	-7.06	-7.00	-6.21	-6.17	-6.11	-5.90	-5.84	-5.80
$\log \beta_{MABH2}$	36.22	36.14	36.10	35.12	35.04	35.00	34.24	34.20	34.16
$\log \beta_{MABH}$	32.32	32.26	32.20	31.86	31.82	31.78	31.20	31.16	31.12
$\log \beta_{MAB}$	29.60	29.54	29.50	29.10	29.04	29.00	28.16	28.10	28.04

Table: 2.7

Formation constants of (1:1:1) Gd(III)-MAL-IMDA ternary systems 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
$\log K^{M}_{MAHBH}$	18.43	18.36	18.24	17.89	17.77	17.62	17.18	17.10	17.02
$\log K^{MAH}_{MAHBH}$	15.06	14.95	14.86	14.21	14.01	13.94	13.21	13.10	13.00
$\log K^{MBH}_{MAHBH}$	13.98	13.86	13.74	13.25	13.15	13.01	12.38	12.28	12.16
$\log K^{M}_{MAHB}$	20.24	20.10	20.00	19.97	19.85	19.74	19.34	19.20	19.08
$\log K^{M}_{MABH}$	21.34	21.28	21.20	21.11	21.07	21.00	20.96	20.90	20.82
$\log K^{MAH}_{MABH}$	18.32	18.20	18.04	17.68	17.50	17.36	17.12	17.00	16.88
$\log K^{MBH}_{MABH}$	21.76	21.64	21.52	20.70	20.53	20.20	20.19	20.10	12.02
$\log K^{MA}_{MABH}$	14.29	14.18	14.02	13.86	13.57	13.24	12.90	12.78	12.66
$\log K^{MB}_{MABH}$	16.38	16.25	16.05	15.26	15.12	15.02	15.03	14.94	14.84
$\log K^{MA}_{MAB}$	16.76	16.64	16.50	15.37	15.24	15.10	15.14	14.99	14.80
$\log K^{MB}_{MAB}$	17.24	17.12	17.02	16.70	16.61	16.54	16.39	16.23	16.08
$\log K^{H}_{MABH2}$	-5.40	-5.25	-4.90	-4.26	-4.14	-4.01	-4.10	- 4.00	-3.90
$\log K^{H}_{MABH}$	-6.04	-6.00	-5.95	-5.08	-5.00	-4.96	-4.72	-4.67	-4.60
$\log K^{H}_{MAB}$	-7.10	-6.98	-6.86	-5.92	-5.78	-5.65	-5.36	-5.16	-5.06
$\log \beta_{MABH2}$	34.38	34.26	34.14	33.18	33.15	33.08	31.60	31.45	31.32
$\log \beta_{MABH}$	29.14	27.04	26.96	26.68	26.64	26.60	26.58	26.51	26.48
$\log \beta_{MAB}$	20.42	20.30	20.16	20.36	19.24	19.10	18.78	18.64	18.52

Table: 2.8

Thermodynamic formation constants and thermodynamic parameters.

Cd(II)-MAL-NTA

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

Cd(II)-MAL-IMDA

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

Table: 2.9

Thermodynamic formation constants and thermodynamic parameters.

Gd(III)-MAL-NTA

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}		
$\log K^{M}_{MAB}$	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	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}		
$\log K^{M}_{MAB}$	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	-	-	-

Representative Speciation Curves

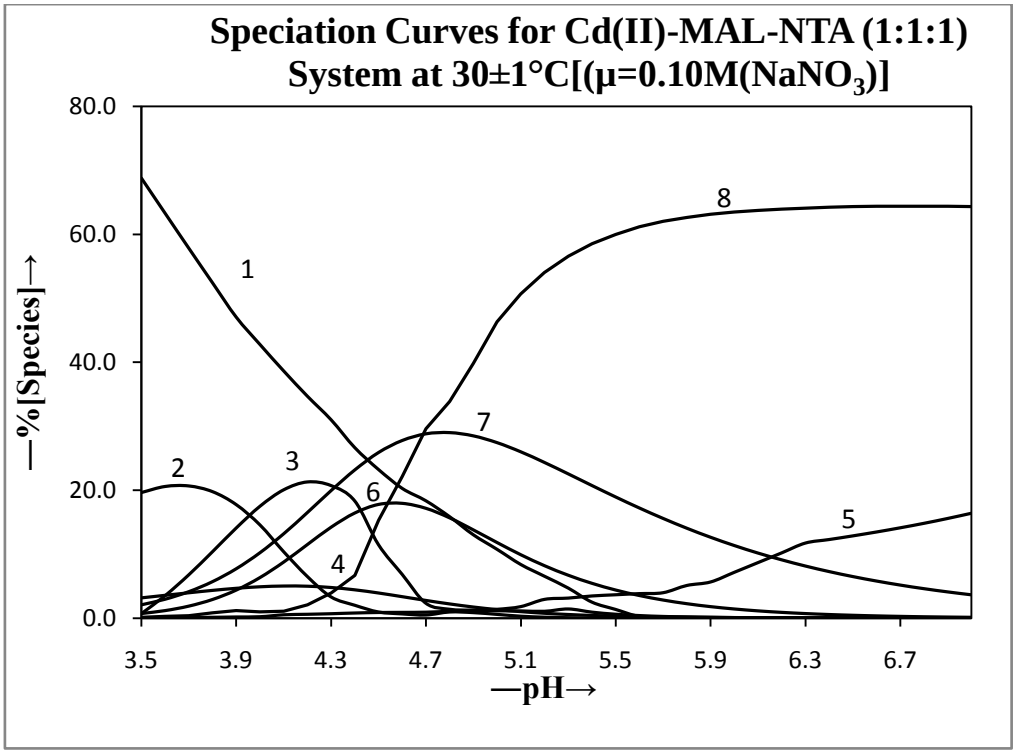

Fig. 5

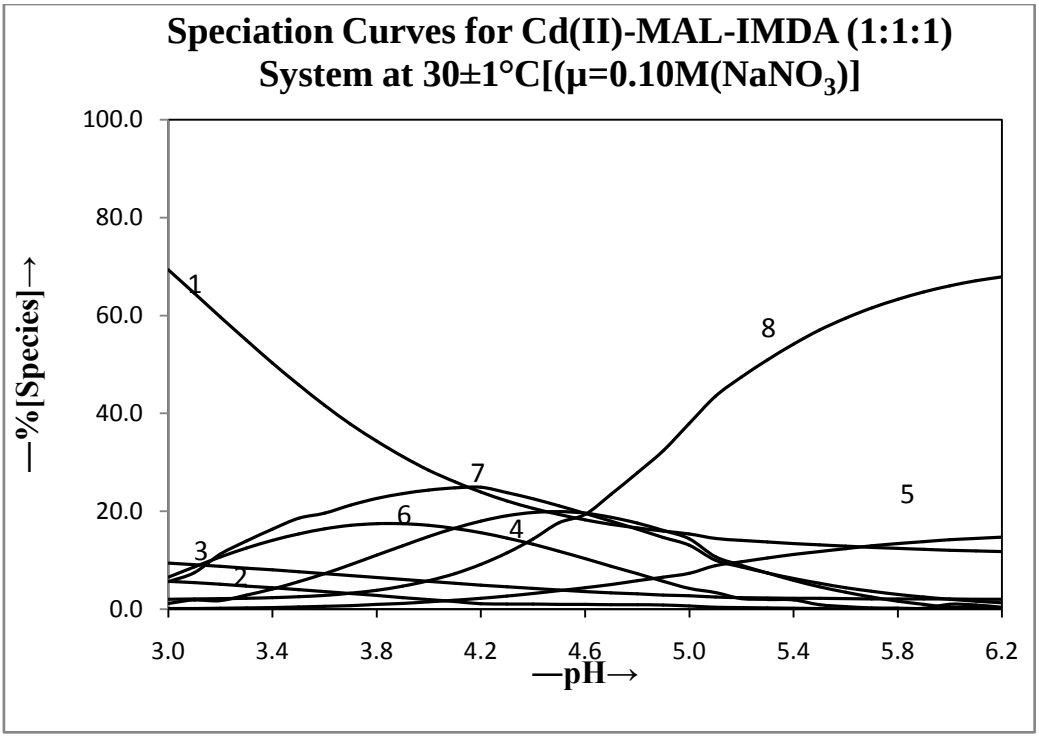

Fig. 6

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

Table: 2.10

Experimental values and concentration of different species for Cd(II)-MAL-NTA (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	3.5	1.02	68.79	19.65	0.68	3.15	0.00	2.08	0.73	0.15
2	3.6	1.08	63.29	20.60	3.49	3.55	0.10	2.95	1.19	0.31
3	3.7	1.14	57.82	20.68	6.76	3.95	0.12	4.13	1.90	0.41
4	3.8	1.17	52.41	19.79	10.38	4.33	0.15	5.70	2.93	0.85
5	3.9	1.26	47.04	17.76	14.09	4.65	0.20	7.72	4.40	1.20
6	4.0	1.38	42.77	14.59	17.49	4.89	0.24	10.22	6.36	1.00
7	4.1	1.54	38.63	10.40	20.07	5.01	0.54	13.18	8.78	1.10
8	4.2	1.64	34.68	6.52	21.30	4.98	0.62	16.50	11.52	2.09
9	4.3	1.76	30.99	3.33	20.73	4.78	0.71	19.93	14.23	3.97
10	4.4	1.84	26.63	2.03	18.31	4.41	0.82	23.16	16.45	6.68
11	4.5	1.86	23.21	0.98	11.46	3.92	0.90	25.88	17.79	15.33
12	4.6	2.08	20.26	0.68	6.81	3.34	0.92	27.76	17.96	22.17
13	4.7	2.14	18.32	0.51	2.29	2.75	0.95	28.80	17.18	29.60
14	4.8	2.19	15.83	0.98	1.36	2.20	1.10	28.99	15.69	33.90
15	4.9	2.24	13.00	0.88	1.20	1.72	1.25	28.48	13.81	39.81
16	5.0	2.28	10.73	0.61	1.12	1.31	1.40	27.42	11.83	46.35
17	5.1	2.31	8.36	0.32	1.10	0.99	1.82	25.99	9.93	50.69
18	5.2	2.34	6.52	0.17	1.04	0.73	2.95	24.32	8.21	54.04
19	5.3	2.37	4.67	0.09	1.40	0.54	3.15	22.54	6.72	56.59
20	5.4	2.40	2.47	0.04	0.91	0.39	3.48	20.72	5.46	58.54
21	5.5	2.43	1.33	0.02	0.58	0.29	3.67	18.93	4.41	60.02
22	5.6	2.44	0.23	0.01	0.37	0.21	3.85	17.21	3.55	61.19
23	5.7	2.46	0.16	0.01	0.24	0.15	3.99	15.58	2.85	62.06
24	5.8	2.52	0.11	0.00	0.15	0.11	5.12	14.05	2.28	62.66
25	5.9	2.56	0.08	0.00	0.10	0.08	5.66	12.64	1.82	63.14
26	6.0	2.60	0.06	0.00	0.06	0.05	7.17	11.30	1.45	63.49
27	6.1	2.64	0.04	0.00	0.04	0.04	8.69	10.10	1.15	63.75
28	6.2	2.67	0.03	0.00	0.02	0.03	10.21	9.10	0.92	63.96
29	6.3	2.70	0.02	0.00	0.02	0.02	11.74	8.14	0.73	64.11
30	6.4	2.72	0.01	0.00	0.01	0.01	12.29	7.27	0.58	64.24
31	6.5	2.74	0.01	0.00	0.01	0.01	12.86	6.49	0.46	64.33
32	6.6	2.76	0.01	0.00	0.00	0.01	13.47	5.79	0.37	64.39
33	6.7	2.80	0.01	0.00	0.00	0.00	14.12	5.16	0.29	64.40
34	6.8	2.84	0.00	0.00	0.00	0.00	14.82	4.60	0.23	64.39
35	6.9	2.86	0.00	0.00	0.00	0.00	15.58	4.09	0.18	64.40
36	7.0	2.90	0.00	0.00	0.00	0.00	16.39	3.64	0.15	64.37

Table : 2.11

Experimental values and concentration of different species for Cd(II)-MAL-IMDA (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	3.0	1.16	69.31	9.41	5.71	0.09	1.13	6.55	5.59	2.05
2	3.1	1.18	64.54	9.08	5.40	0.13	1.86	8.64	7.45	2.08
3	3.2	1.20	59.72	8.74	5.08	0.18	1.75	10.63	11.24	2.13
4	3.3	1.24	54.93	8.38	4.73	0.25	2.84	12.45	13.90	2.22
5	3.4	1.28	50.28	8.01	4.37	0.33	4.12	14.06	16.37	2.35
6	3.5	1.36	45.82	7.63	3.98	0.44	5.60	15.37	18.59	2.54
7	3.6	1.38	41.65	7.25	3.59	0.57	7.27	16.41	19.58	2.83
8	3.7	1.42	37.80	6.86	3.19	0.74	9.09	17.11	21.25	3.25
9	3.8	1.46	34.30	6.47	2.78	0.94	11.01	17.46	22.61	3.85
10	3.9	1.53	31.17	6.07	2.36	1.19	12.94	17.45	23.62	4.68
11	4.0	1.57	28.40	5.68	1.94	1.48	14.82	17.13	24.34	5.79
12	4.1	1.62	25.99	5.30	1.53	1.82	16.54	16.50	24.75	7.26
13	4.2	1.66	23.90	4.92	1.11	2.22	17.99	15.62	24.90	9.15
14	4.3	1.70	22.12	4.56	1.05	2.67	19.09	14.52	23.82	11.49
15	4.4	1.74	20.61	4.21	1.01	3.18	19.75	13.24	22.54	14.32
16	4.5	1.78	19.33	3.89	1.00	3.75	19.91	11.83	21.11	17.62
17	4.6	1.82	18.25	3.60	0.95	4.38	19.58	10.33	19.57	19.37
18	4.7	1.88	17.34	3.33	0.93	5.06	18.77	8.78	17.95	23.47
19	4.8	1.90	16.57	3.10	0.90	5.78	17.58	7.23	16.31	27.86
20	4.9	1.94	15.91	2.89	0.86	6.54	16.08	5.70	14.66	32.38
21	5.0	1.98	15.35	2.72	0.67	7.33	14.37	4.21	13.04	37.90
22	5.1	2.08	14.42	2.46	0.39	8.92	10.73	3.42	10.01	43.50
23	5.2	2.12	14.04	2.37	0.30	9.69	8.98	2.16	8.65	47.41
24	5.3	2.18	13.70	2.29	0.22	10.44	7.35	1.98	7.40	50.96
25	5.4	2.22	13.39	2.23	0.16	11.14	5.88	1.91	6.27	54.17
26	5.5	2.26	13.10	2.18	0.12	11.79	4.57	0.92	5.27	57.01
27	5.6	2.34	12.85	2.14	0.08	12.38	3.44	0.53	4.40	59.44
28	5.7	2.40	12.62	2.11	0.06	12.92	2.47	0.23	3.64	61.55
29	5.8	2.50	12.41	2.09	0.04	13.38	1.65	0.20	3.00	63.30
30	5.9	2.56	12.22	2.07	0.03	13.79	0.96	0.18	2.46	64.82
31	6.0	2.64	12.05	2.05	0.02	14.15	0.40	1.00	2.00	66.07
32	6.1	2.74	11.91	2.04	0.01	14.45	0.30	0.82	1.62	67.08
33	6.2	2.84	11.78	2.03	0.01	14.70	0.21	0.39	1.31	67.89

Representative Speciation Curves

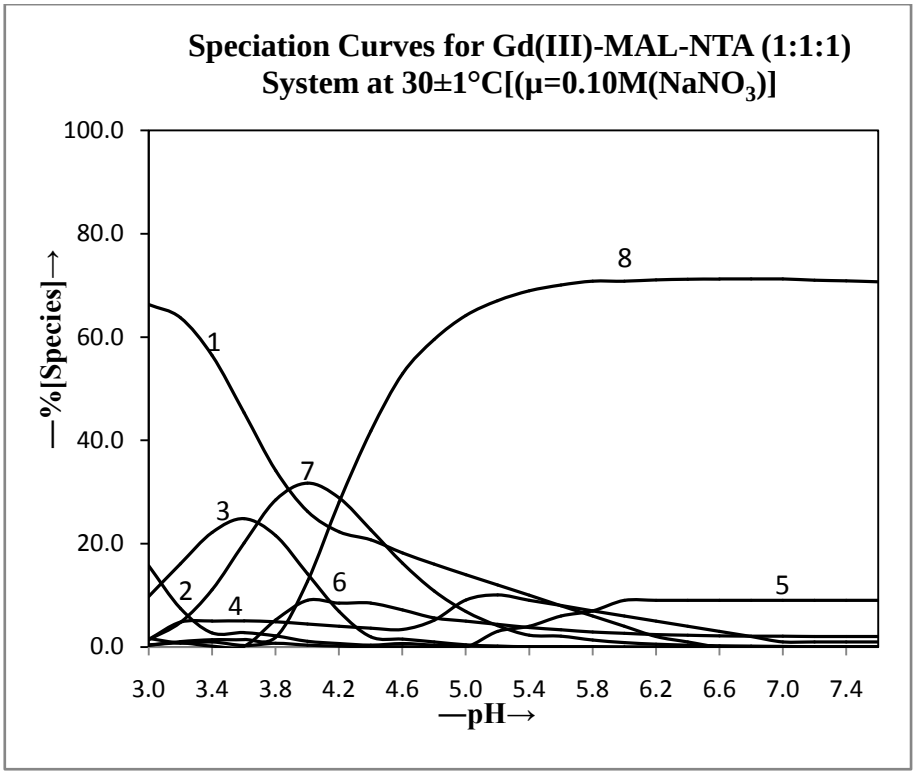

Fig. 7

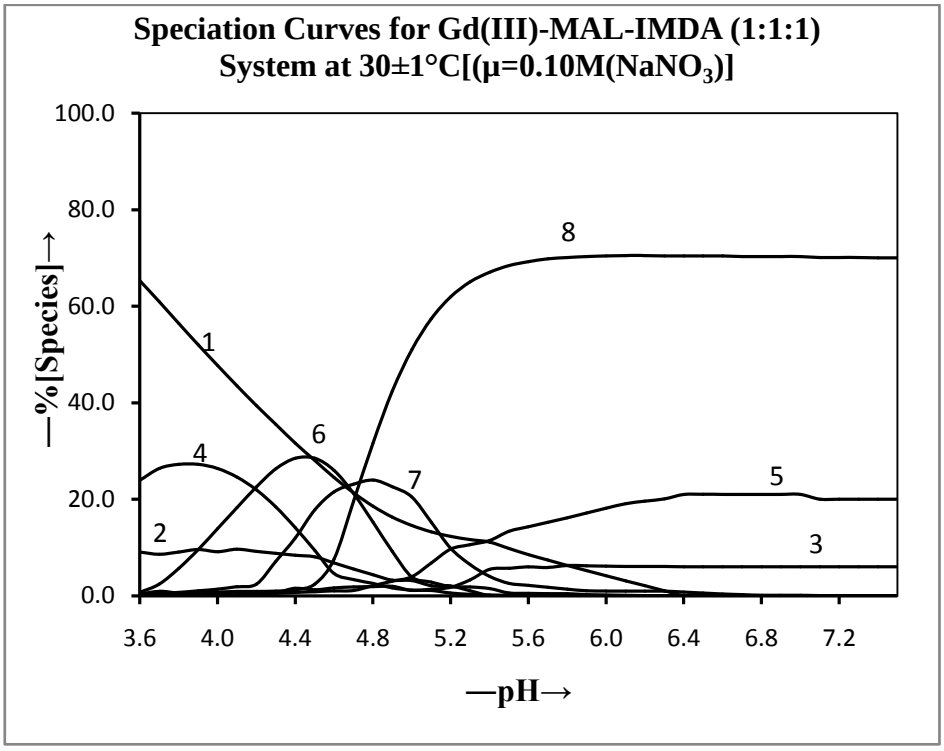

Fig. 8

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

Table: 2.12

Experimental values and concentration of different species for Gd(III)-MAL-NTA (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	3.6	1.06	65.30	9.09	23.90	0.34	0.03	0.36	0.70	0.08
2	3.7	1.10	60.90	8.59	26.40	0.92	0.04	0.52	2.40	0.08
3	3.8	1.18	56.40	9.09	27.20	0.52	0.07	0.73	5.70	0.35
4	3.9	1.21	52.00	9.59	27.20	0.10	0.11	1.01	9.60	0.69
5	4.0	1.24	47.70	9.11	26.40	0.65	0.17	1.39	13.90	0.75
6	4.1	1.50	43.50	9.64	24.60	0.10	0.25	1.87	18.30	0.89
7	4.2	1.56	39.40	9.20	21.90	0.44	0.36	2.46	22.60	0.92
8	4.3	1.62	35.50	8.79	18.40	0.61	0.51	7.17	26.30	0.98
9	4.4	1.66	31.60	8.41	14.10	1.56	0.68	11.97	28.50	1.25
10	4.5	1.70	28.00	8.07	9.40	1.24	0.86	17.79	28.50	2.45
11	4.6	1.72	24.50	6.78	4.60	1.66	1.01	21.54	26.00	7.60
12	4.7	1.76	21.30	5.55	3.34	1.85	1.10	23.12	21.20	19.60
13	4.8	1.82	18.56	4.36	2.54	1.92	2.11	23.98	15.20	31.70
14	4.9	1.84	16.31	3.23	1.63	1.97	3.05	22.59	9.20	42.40
15	5.0	1.85	14.56	3.15	1.20	1.11	3.94	20.49	3.90	51.00
16	5.1	1.86	13.25	2.09	1.09	1.37	6.81	15.24	2.85	57.40
17	5.2	1.90	12.30	2.05	0.58	1.77	9.68	9.87	1.89	61.90
18	5.3	1.92	11.62	1.03	0.30	3.31	10.56	6.45	1.85	65.00
19	5.4	1.96	11.13	0.02	0.15	5.46	11.45	4.01	1.48	67.00
20	5.5	1.97	9.79	0.01	0.08	5.69	13.36	2.58	0.59	68.40
21	5.6	2.03	8.53	0.01	0.04	6.00	14.29	2.15	0.51	69.20
22	5.7	2.06	7.39	0.00	0.02	5.86	15.23	1.75	0.44	69.80
23	5.8	2.10	6.27	0.00	0.01	6.26	16.19	1.38	0.41	70.10
24	5.9	2.14	5.19	0.00	0.01	6.18	17.15	1.04	0.26	70.30
25	6.0	2.18	4.14	0.00	0.00	6.13	18.12	1.00	0.16	70.40
26	6.1	2.22	3.10	0.00	0.00	6.09	19.09	0.99	0.10	70.50
27	6.2	2.26	2.07	0.00	0.00	6.07	19.57	0.97	0.06	70.50
28	6.3	2.31	1.05	0.00	0.00	6.05	20.06	0.95	0.04	70.40
29	6.4	2.34	0.03	0.00	0.00	6.03	21.00	0.74	0.03	70.40
30	6.5	2.37	0.02	0.00	0.00	6.02	21.04	0.55	0.02	70.40
31	6.6	2.40	0.02	0.00	0.00	6.02	21.03	0.38	0.01	70.40
32	6.7	2.42	0.01	0.00	0.00	6.01	21.02	0.23	0.01	70.30
33	6.8	2.46	0.01	0.00	0.00	6.01	21.02	0.10	0.00	70.30
34	6.9	2.48	0.01	0.00	0.00	6.01	21.01	0.09	0.00	70.30
35	7.0	2.48	0.00	0.00	0.00	6.00	21.01	0.08	0.00	70.30
36	7.1	2.55	0.00	0.00	0.00	6.00	20.01	0.07	0.00	70.10
37	7.2	2.57	0.00	0.00	0.00	6.00	20.01	0.06	0.00	70.10

Table: 2.13

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

PH	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[$MABH_2$]	[MABH]	[MAB]
3.0	0.28	66.29	9.75	1.48	15.71	1.62	0.41	1.43	0.27
3.2	0.45	63.76	16.10	4.79	7.46	0.77	0.78	4.77	1.03
3.4	0.61	56.42	22.19	5.02	2.72	0.97	0.19	11.06	1.40
3.6	0.76	45.37	24.82	5.06	2.79	0.27	0.16	20.10	1.43
3.8	0.92	34.12	21.54	4.86	2.13	0.72	5.23	28.51	1.89
4.0	1.06	26.23	14.17	4.47	1.11	0.36	9.04	31.71	12.70
4.2	1.18	22.26	6.88	4.03	0.66	0.16	8.47	28.84	28.06
4.4	1.30	20.72	1.95	3.65	0.33	0.06	8.49	22.69	41.78
4.6	1.41	18.21	1.52	3.38	0.66	0.02	7.16	16.22	52.91
4.8	1.71	16.06	0.98	5.21	0.33	0.01	5.62	10.80	59.53
5.0	1.75	14.01	0.41	9.11	0.17	0.00	5.00	6.86	64.17
5.2	1.85	12.00	0.17	10.05	0.09	3.00	4.37	4.12	67.05
5.4	1.90	10.00	0.07	9.03	0.05	4.00	3.79	2.30	68.93
5.6	1.95	8.00	0.03	8.01	0.03	6.00	3.30	2.11	70.09
5.8	1.98	6.00	0.01	7.01	0.01	7.00	2.92	1.34	70.83
6.0	2.26	4.00	0.00	6.00	0.01	9.00	2.62	0.85	70.82
6.2	2.29	2.00	0.00	5.00	0.01	9.00	2.42	0.53	71.08
6.4	2.33	1.00	0.00	4.00	0.00	9.00	2.27	0.34	71.21
6.6	2.39	0.00	0.00	3.00	0.00	9.00	2.18	0.21	71.22
6.8	2.43	0.00	0.00	2.00	0.00	9.00	2.11	0.13	71.23
7.0	2.46	0.00	0.00	1.00	0.00	9.00	2.07	0.08	71.23
7.2	2.61	0.00	0.00	1.00	0.00	9.00	2.05	0.05	70.99
7.4	2.68	0.00	0.00	1.00	0.00	9.00	2.03	0.03	70.88
7.6	2.78	0.00	0.00	1.00	0.00	9.00	2.02	0.02	70.71

Table: 2.14.

Value of Δlog K for ternary complexes.

	20°C		30°C		40°C	
	$\log\beta^{\mu\rightarrow 0}$	Δlog K	$\log\beta^{\mu\rightarrow 0}$	Δlog K	$\log\beta^{\mu\rightarrow 0}$	Δlog K
Parameters	**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
	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

2.4 Results and discussion:

The various equilibria corresponding to proton – ligand, metal – ligand and mixed ligand complexing systems are interpreted by carefully examining the titration curves and speciation curves obtained for various systems.

For illustration the potentiometric titration curves (pH vs. 'a') for Cd(II)/Gd(III) – ligand'A' – ligand'B' (1:1:1) systems are shown in figs. 1 to 4. These systems follow the same trend. The curves 1to 5 in figs 1 to 4 represent the following:

Curves 1 and 2 represent the ligand A and ligand B titration curve respectively. Curves 3 and 4 correspond to the metal-ligand A and metal-ligand B titration curves respectively. Whereas curve 5 depicts the metal-ligand A- ligand B (1:1:1) titration of ternary systems. Curve 'T' is theoretical composite curve, which 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.

The nature of ligand titration curves (curve 1and 2) indicate that the deprotonation of all the ligands occur in two distinct steps. Further, the deviation of metal–ligand curves (curves 3 and 4) from ligand curves suggests the formation of binary complexes. 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 which shows that the metal ion interacts with both the ligand simultaneously. A weak inflection at *'a'* = 2.0 indicates the formation of biprotonated ($MABH_2$) ternary complex upto pH ≈4.0 and above this monoprotonated (MABH)

ternary complex is formed by dissociation of proton from biprotonated ($MABH_2$) species. Thereafter nonprotonated (MAB) ternary complex is formed by dissociation of proton from monoprotonated (MABH) species in the pH range 5.0 to 8.0 and a≈4.0. Alternatively formation of MAB can be possible as given in eqn. 18. Various equilibria and the corresponding equilibrium constants in binary and ternary metal-ligand systems are represented as follow:

Proton-ligand system:

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

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

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

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

Binary M-H_2A 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-H_2B system:

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

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

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

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

Ternary M-H_2A-H_2B system:

$$M+H_2A+H_2B \underset{\log K^{H}_{MABH\ 2}}{\overset{0\le a\le 2}{\rightleftharpoons}} MABH_2 + 2H^{+} \qquad \text{---- (13)}$$

$$M+HA+HB \underset{\log K^{M}_{MABH\ 2}}{\overset{0\le a\le 2}{\rightleftharpoons}} MABH_2 \qquad \text{---- (14)}$$

$$MABH_2 \underset{\log K^{H}_{MABH}}{\overset{2\le a\le 3}{\rightleftharpoons}} MABH + H^{+} \qquad \text{---- (15)}$$

$$M+A+HB \underset{\log K^{M}_{MABH}}{\overset{0\le a\le 3}{\rightleftharpoons}} MABH \qquad \text{---- (16)}$$

$$MABH \underset{\log K^{H}_{MAB}}{\overset{3\le a\le 4}{\rightleftharpoons}} MAB + H^{+} \qquad \text{---- (17)}$$

$$M+A+B \underset{\log K^{M}_{MAB}}{\overset{0\le a\le 4}{\rightleftharpoons}} MAB \qquad \text{---- (18)}$$

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

Speciation curves are obtained for various systems which are presented in figs. 5-8. Speciation curves of all the systems under investigation are seen to follow the same trend. The formation of mixed ligand species $MABH_2$, MABH and MAB have been considered in different equilibria. It is seen that the formation of MAH and MBH occurs 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 comes into existence at pH≈4.5 and its concentration increases appreciably. It is observed that the percentage of MAB species reaches up to ≈<75(pH≈7.0) 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 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 2.14.

$$\Delta \log K_{MABH2} = \log \beta_{MABH2} - (\log \beta_{MAH} + \log \beta_{MBH}) \quad \text{------ (19)}$$

$$\Delta \log K_{MABH} = \log \beta_{MABH} - (\log \beta_{MA} + \log \beta_{MBH}) \quad \text{------(20)}$$

$$\Delta \log K_{MAB} = \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB}) \quad \text{------(21)}$$

In general, if mixed ligand complexes are most stable than their corresponding binary complexes, the value of ΔlogK is positive.[82-84] Values given in table 2.14 clearly reveal that all mixed ligand complexes formed are more stable than their corresponding binary complexes.

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.[85] Formation of ternary complex is not an absolute phenomenon but it depends on the formation of binary complex. The difference in the stability constants of binary and ternary species is used to predict the more favourable formation amongst the two and is represented as Δlog K. Δlog K indicates the difference between the tendency of a ligand to bind with the metal ion already bonded to another ligand and tendency of the ligand to bind with free metal ion.

The positive ΔlogK values also demonstrate the higher stability for ternary species over its binary analogues in the present studies. The results are in agreement with earlier investigation.[86] The thermodynamic stabilities of binary and ternary complexes of NTA (potentially tetradentate ligand) is found to be greater than IMDA (potentially tridentate ligand). This is in accordance to be expected trend.

The thermodynamic stability constants for various binary and ternary complex species with respect to metal ions is Gd(III)>Cd(II). This can be explained on the basis of high charge and higher coordination number of Gd(III) ion.

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 and 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[87-88] while positive ΔS° value for some metal complexes indicate that the formation of these complexes are entropically favoured.

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