5.1. Introduction:

In the preceding chapters of the thesis investigation based on multiple equilibria involving simple cations (Cd^{2+} and Gd^{3+}) and oxocations (UO_2^{2+} and VO^{2+}) with malonic acid and aminopolycarboxylic acids (NTA and IMDA) have been analysed and discussed. Further mixed ligand systems of Cd(II) and Gd(III) involving dopa, dopm and tyrosine as secondary ligands have been investigated and the results are presented in the last chapter. The choice for the selected metals/ligands and their significance is already been described in the preceding chapters.

Survey of literature reveals very few publication appear involving VO^{2+}/UO_2^{2+} and catecholamines or related ligands. Vanadium, occurring between Ca^{2+} and Zn^{2+} in the first transition-metal series, exhibits complex chemistry because of multiple oxidation states.[1–3] This factor has lead to confusion in identifying the antidiabetic agent, because vanadium compounds of oxidation states IV and V are both associated with insulin-enhancing activity but through different mechanisms. Furthermore, vanadyl (VO^{2+}) compounds, of oxidation state IV, under physiological conditions are subject to oxidation by a variety of oxidants, including molecular oxygen[4], and vanadate compounds, of oxidation state V are thought to undergo reduction to state IV in the cell.[4–6] For these reasons, the mechanisms by which vanadium compounds mediate antidiabetic effects in vivo are poorly described and incompletely understood.

Hesheng Ou et.al have studied the (VO^{2+}) chelates bis (acetylacetonato) oxovanadium (IV) [$VO(acac)_2$], bis (maltolato) oxovanadium (IV) [$VO(malto)_2$], and bis (1-Noxide- pyridine-2-thiolato) oxovanadium (IV) [$VO(OPT)_2$] and have compared their activity with insulin.[7]

Complexes of osmium, uranium, molybdenum, and tungsten with the catecholamines adrenaline, noradrenaline, dopamine, dopa, and

isoproterenol have been studied by Ahmed and coworkers.[8]The majority of the available data on the complexation of actinides are for 25°C.[9] Recent theoretical models have been used by few workers who have done work to predict the thermodynamic properties of aqueous species under geothermal conditions.[10-12] In order to understand the problem further, a reliable experimental data on the complexation of actinides in solution at different temperatures are needed. Hence it was decided to investigate binary and ternary systems of UO_2(II) and VO(II) with malonic acid and catecholamine (tyr, dopa, dopm) at three different temperatures in aqueous solution and obtain their thermodynamic stability constants and other thermodynamic parameters.

The various mixed ligand systems reported in the present chapter are:

A. Ternary metal-ligand systems-

1. UO_2(II) –Malonic acid – Tyrosine (TYR)
2. UO_2 (II) –Malonic acid – 3,4-dihydroxyphenylalanine (DOPA)
3. UO_2 (II) –Malonic acid – Dopamine (DOPM)
4. VO (II) –Malonic acid – Tyrosine (TYR)
5. VO (II) –Malonic acid – 3,4-dihydroxyphenylalanine (DOPA)
6. VO (II) –Malonic acid –Dopamine (DOPM)

B. Binary metal-ligand systems-

1. UO_2(II)-Malonic acid
2. UO_2(II)-Tyrosine
3. UO_2(II)-DOPA
4. UO_2(II)-DOPM
5. VO(II)-Malonic acid
6. VO (II)-Tyrosine
7. VO (II)-DOPA
8. VO(II)-DOPM

5.2. Experimental and computational methods:

Experimental and computational details are same as described in chapter-2. Solutions were prepared as described in previous chapters. The titration curves are presented in figs. 1-6. The prototonation constants of the ligands are tabulated in table 4.1 (chapter-4) and the metal-ligand binary and ternary equilibrium constants are given in tables 5.1-5.8. The percent distributions of various species are given in tables 5.12-5.17 and the speciation curves are presented in figs. 7-12. Thermodynamic stability constants are obtained by extrapolating the logK values to zero ionic strength ($\log K^{\mu\rightarrow 0}$). $\log K^{\mu\rightarrow 0}$ is used to obtain standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) by the methods as described in the previous chapters. These values are given in tables 5.9 – 5.11.

5.3 Curves and tables:

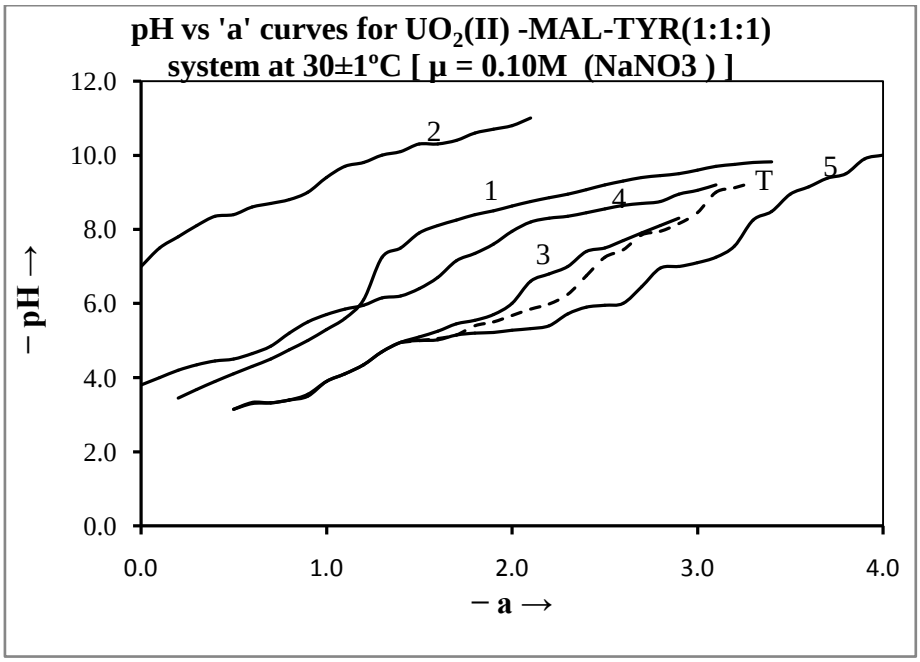

Fig. 1

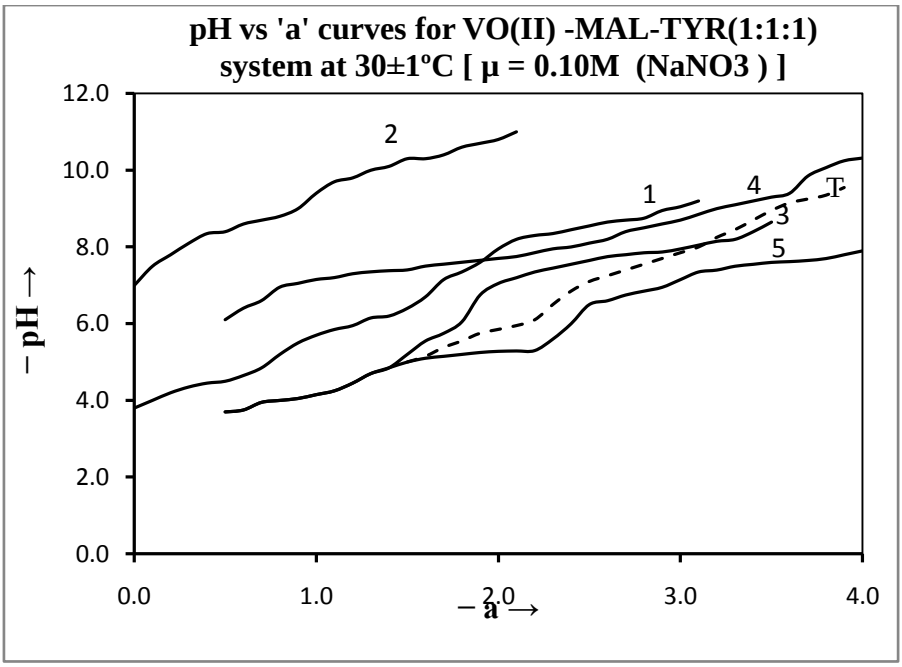

Fig. 2

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

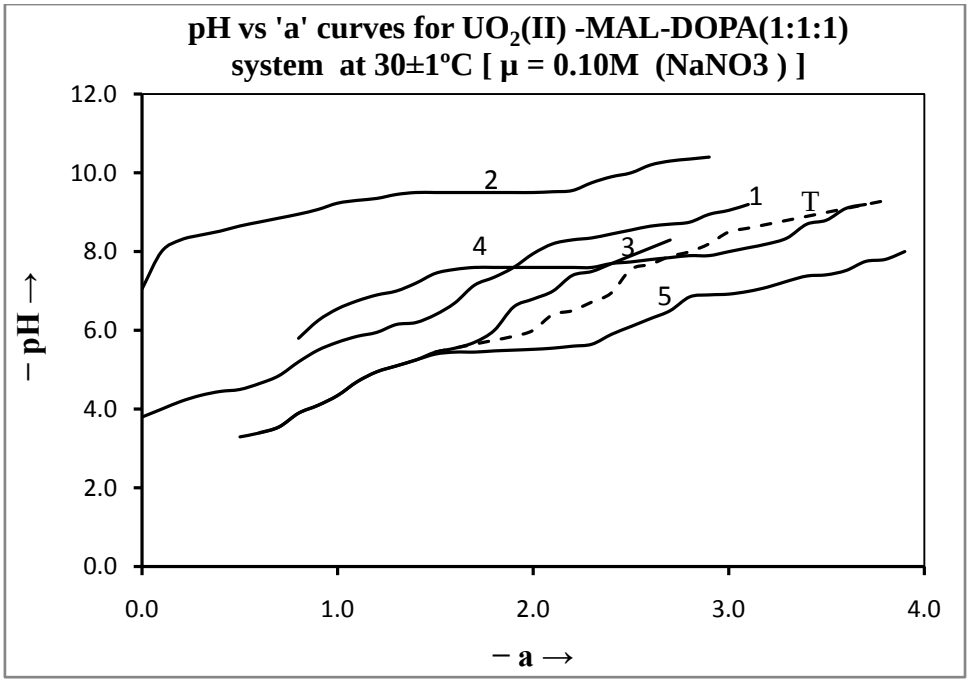

Fig. 3

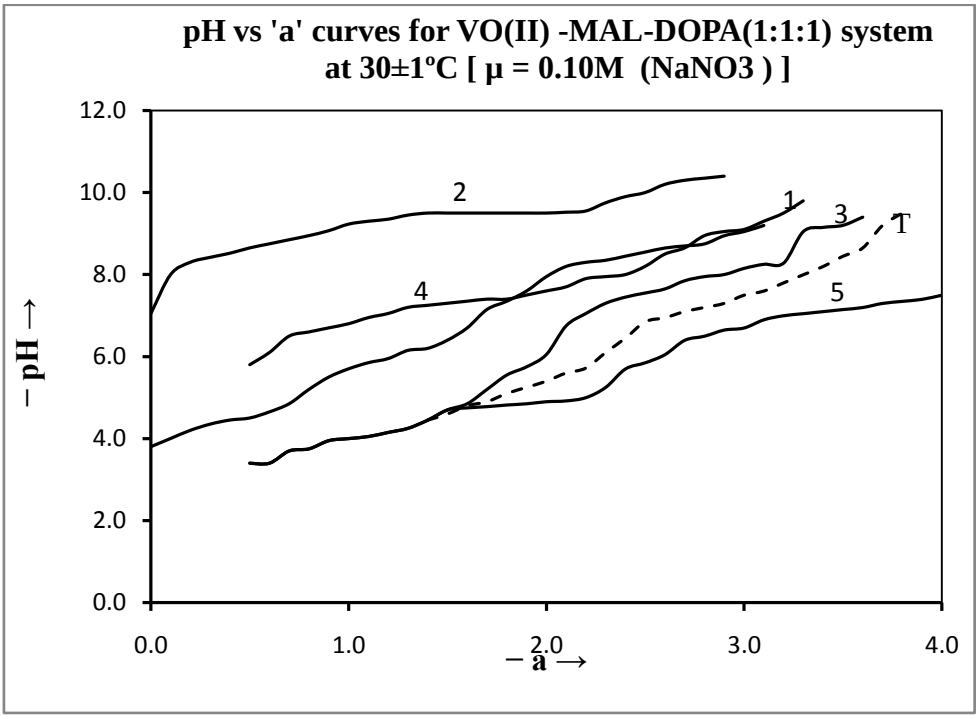

Fig. 4

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

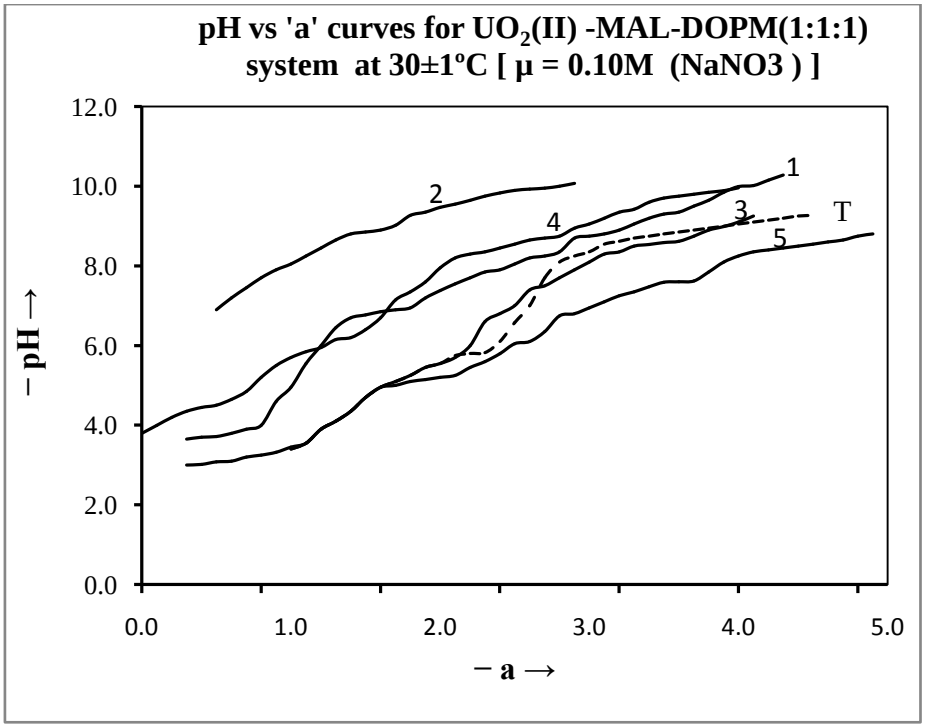

Fig. 5

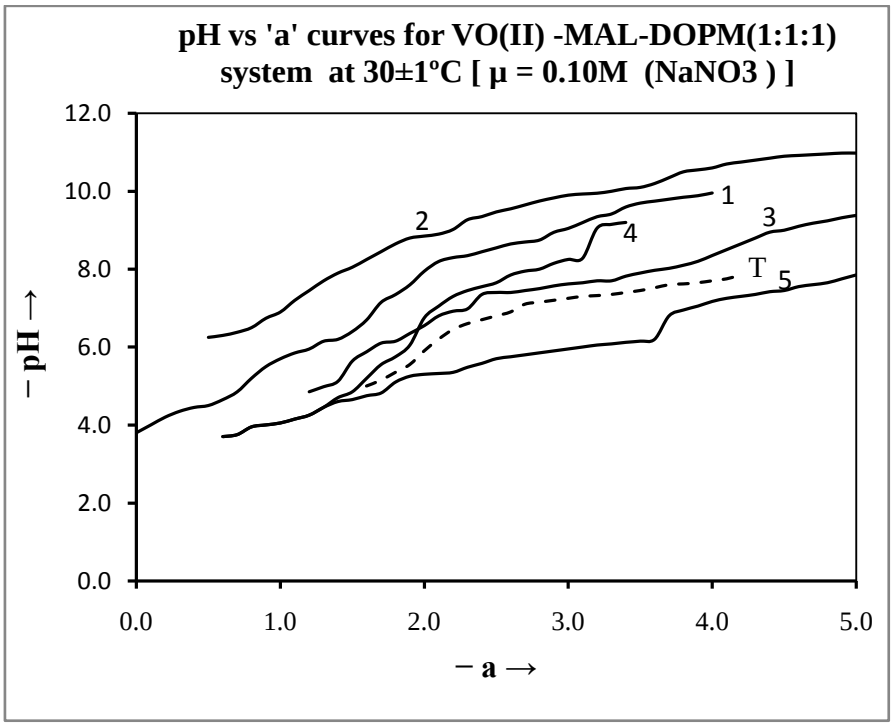

Fig. 6

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:5.1

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

Parameters	UO_2(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
$\log K^{M}_{MBH}$	6.58	6.50	6.42	6.72	6.40	6.32	6.24	6.59	6.35	6.26	6.22	6.52
$\log K^{H}_{MBH}$	-4.22	-4.18	-4.12	-4.54	-4.18	-4.11	-4.08	-4.46	-4.10	-4.06	-4.00	-4.38
$\log K^{H}_{MB}$	-5.82	-5.73	-5.65	-6.08	-5.78	-5.67	-5.56	-5.92	-5.64	-5.56	-5.42	-5.84
$\log \beta_{MBH}$	16.10	16.04	15.93	16.25	15.94	15.86	15.80	16.10	15.86	15.83	15.79	16.03
$\log \beta_{MB}$	9.59	9.52	9.43	9.78	9.51	9.42	9.36	9.70	9.45	9.36	9.24	9.64
	UO_2(II)- DOPA											
$\log K^{M}_{MH2B}$	8.53	8.48	8.40	8.74	8.48	8.42	8.32	8.68	8.40	8.38	8.26	8.61
$\log K^{H}_{MH2B}$	-6.95	-6.90	-6.85	-7.18	-6.70	-6.61	-6.52	-6.90	-6.35	-6.28	-6.20	-6.58
$\log\beta_{MH2B}$	28.21	28.18	28.10	28.52	28.12	28.06	28.00	28.46	27.99	28.96	28.84	28.38
	UO_2(II)- DOPM											
$\log K^{M}_{MH2B}$	8.98	8.90	8.82	9.33	8.74	8.56	8.42	9.10	8.48	8.32	8.26	8.98
$\log K^{H}_{MH2B}$	-4.98	-4.92	-4.88	-5.20	-4.72	-4.67	-4.60	-4.95	-4.36	-4.30	-4.24	-4.58
$\log K^{M}_{MHB}$	9.63	9.50	9.40	9.92	9.36	9.18	9.00	9.84	9.20	9.10	9.00	9.76
$\log K^{H}_{MHB}$	-5.90	-5.84	-5.80	-6.18	-5.40	-5.20	-5.10	-5.85	-5.20	-5.00	-4.80	-5.63
$\log K^{H}_{MB}$	-6.68	-6.58	-6.48	-6.89	-6.43	-6.21	-6.12	-6.76	-6.14	-6.01	-5.92	-6.46
$\log\beta_{MH2B}$	29.94	29.68	29.41	30.18	29.56	29.42	29.25	29.74	29.10	29.04	29.00	29.37
$\log\beta_{MHB}$	22.40	22.96	22.30	22.74	22.40	22.29	22.19	22.68	21.80	21.74	21.65	21.98
$\log\beta_{MB}$	18.30	18.14	18.08	18.55	17.94	17.52	17.36	18.28	17.50	17.42	17.38	17.85

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

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

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

Table: 5.2

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

Parameters	VO(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
$\log K^{M}_{MBH}$	6.67	6.62	6.62	6.89	6.62	6.58	6.51	6.83	6.56	6.50	6.43	6.78
$\log K^{H}_{MBH}$	-5.15	-5.10	-5.00	-5.38	-4.98	-4.90	-4.82	-5.10	-4.51	-4.49	-4.44	-4.80
$\log K^{H}_{MB}$	-6.97	-6.94	-6.88	-7.20	-6.90	-6.81	-6.78	-7.12	-6.70	-6.67	-6.60	-6.85
$\log \beta_{MBH}$	16.45	16.38	16.29	16.65	16.40	16.32	16.24	16.56	16.36	16.28	16.20	16.47
$\log \beta_{MB}$	10.68	10.56	10.52	10.86	10.63	10.51	10.46	10.80	10.56	10.45	10.40	10.76
	VO(II)- DOPA											
$\log K^{M}_{MH2B}$	7.70	7.59	7.52	7.94	7.62	7.54	7.48	7.89	7.55	7.48	7.36	7.81
$\log K^{H}_{MH2B}$	-6.54	-6.50	-6.44	-6.88	-6.12	-6.01	-5.92	-6.28	-5.21	-5.14	-5.03	-5.58
$\log \beta_{MH2B}$	27.39	27.32	27.28	27.58	27.31	27.24	27.20	27.50	27.26	27.20	27.13	27.41
	VO(II)-DOPM											
$\log K^{M}_{MH2B}$	10.98	10.94	10.90	11.24	10.85	10.77	10.64	11.10	10.74	10.67	10.58	10.98
$\log K^{H}_{MH2B}$	-5.52	-5.34	-5.11	-5.84	-5.23	-5.07	-5.00	-5.67	-5.06	-5.00	-4.96	-5.28
$\log K^{M}_{MHB}$	12.06	11.94	11.73	12.38	11.90	11.84	11.78	12.29	11.75	11.65	11.54	12.02
$\log K^{H}_{MHB}$	-6.68	-6.38	-6.28	-6.67	-6.40	-6.28	-6.16	-6.84	-6.12	-6.10	-6.08	-6.36
$\log K^{H}_{MB}$	-7.42	-7.38	-7.30	-7.84	-6.98	-6.94	-6.90	-7.10	-6.25	-6.21	-6.17	-6.84
$\log \beta_{MH2B}$	30.98	30.94	30.90	31.24	30.28	30.14	30.10	30.56	30.10	30.04	29.92	30.38
$\log \beta_{MHB}$	25.36	25.24	25.13	25.65	25.33	25.30	25.26	25.57	25.00	24.92	24.85	25.48
$\log \beta_{MB}$	17.78	17.68	17.55	18.85	17.54	17.47	17.34	18.60	17.32	17.12	17.00	17.72

Table: 5.3

Formation constants of (1:1:1) UO_2 (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
$logK^{M}_{MAHBH}$	27.68	27.64	27.60	27.28	27.34	27.30	27.06	27.00	26.94
$logK^{MAH}_{MAHBH}$	17.86	17.83	17.80	17.30	17.26	17.22	17.28	17.22	17.18
$logK^{MBH}_{MAHBH}$	21.30	21.26	21.22	20.30	20.25	20.20	20.16	20.10	20.05
$logK^{M}_{MABH}$	28.58	28.54	28.50	27.58	27.52	27.48	27.25	26.20	26.12
$logK^{MAH}_{MABH}$	18.64	18.62	18.50	17.69	17.63	17.60	17.46	17.42	17.38
$logK^{MBH}_{MABH}$	16.30	16.25	16.20	16.08	16.03	16.14	15.50	15.45	15.40
$logK^{MA}_{MABH}$	13.65	13.60	13.55	13.46	13.40	13.36	13.06	13.00	12.95
$logK^{MB}_{MABH}$	14.62	14.58	14.52	14.30	14.25	14.20	13.70	13.65	13.60
$logK^{MA}_{MAB}$	9.14	9.10	9..05	8.90	8.85	8.80	8.70	8.62	8.58
$logK^{MB}_{MAB}$	5.62	5.59	5.54	5.28	5.21	5.17	5.20	5.13	5.10
$logK^{H}_{MABH2}$	-4.98	-4.92	-4.82	-4.74	-4.70	-4.64	-4.55	-4.48	-4.40
$logK^{H}_{MABH}$	-6.10	- 6.06	-6.02	-5.70	-5.65	-5.60	-5.08	-5.00	-4.96
$logK^{H}_{MAB}$	-7.48	- 7.40	- 7.32	-7.28	-7.20	-7.10	- 7.00	-6.90	-6.84
$\log \beta_{MABH2}$	45.20	45.16	45.12	44.98	44.94	44.90	44.05	44.00	43.92
$\log \beta_{MABH}$	38.46	38.42	38.38	37.56	37.50	37.46	37.16	38.04	37.00
$\log \beta_{MAB}$	21.60	21.54	21.50	20.62	20.57	20.53	20.18	20.10	20.01

Table: 5.4

Formation constants of (1:1:1) VO(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	0.05	0.10M	0.15M
$\log K^{M}_{MAHBH}$	28.60	28.58	28.54	28.43	28.39	28.35	28.05	28.00	27.95
$\log K^{MAH}_{MAHBH}$	24.70	24.65	24.60	22.60	22.55	22.50	22.15	22.10	22.05
$\log K^{MBH}_{MAHBH}$	30.28	30.24	30.20	29.32	29.28	29.20	28.94	28.90	28.86
$\log K^{M}_{MABH}$	29.62	29.58	29.54	29.60	29.56	29.50	29.18	29.14	29.10
$\log K^{MAH}_{MABH}$	15.70	15.65	15.60	14.68	14.62	14.58	13.57	13.54	13.50
$\log K^{MBH}_{MABH}$	17.85	17.80	17.75	16.92	16.88	16.84	16.22	16.18	16.12
$\log K^{MA}_{MABH}$	15.00	14.95	14.90	14.80	14.76	14.72	14.69	14.66	14.64
$\log K^{MB}_{MABH}$	14.50	14.25	14.20	13.42	13.96	13.90	13.20	13.14	13.10
$\log K^{MA}_{MAB}$	10.00	9.95	9.90	9.76	9.72	9.68	9.18	9.13	9.00
$\log K^{MB}_{MAB}$	5.70	5.64	5.60	5.32	5.28	5.23	5.08	5.00	9.95
$\log K^{H}_{MABH2}$	-4.70	-4.65	-4.60	-4.00	-3.95	-3.90	-3.90	-3.84	-3.80
$\log K^{H}_{MABH}$	-5.98	- 5.94	-5.90	-5.85	-5.80	-5.76	-5.78	-5.73	-5.70
$\log K^{H}_{MAB}$	-7.04	- 7.00	- 6.96	-6.92	-6.86	-6.80	-6.60	-6.54	-6.48
$\log \beta_{MABH2}$	46.60	46.54	46.50	46.12	48.08	46.04	45.04	45.00	44.96
$\log \beta_{MABH}$	39.54	39.50	39.45	38.75	38.70	38.65	38.16	38.10	38.06
$\log \beta_{MAB}$	22.22	22.18	22.14	21.15	21.10	21.05	20.80	20.84	20.80

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

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

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

Table: 5.5

Formation constants of (1:1:1) UO_2 (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
$\log K^{M}_{MAHBH}$	26.96	26.84	26.73	26.88	26.71	26.68	26.66	26.59	26.48
$\log \beta_{MABH2}$	45.96	45.90	45.81	45.70	45.62	45.55	45.42	45.35	45.28

Table :5.6

Formation constants of (1:1:1) VO(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
$\log K^{M}_{MAHBH}$	27.32	27.21	27.12	27.26	27.12	27.01	26.96	26.88	26.82
$\log \beta_{MABH2}$	46.97	46.84	46.63	46.92	46.80	46.65	46.54	46.46	46.42

Table: 5.7

Formation constants of (1:1:1) UO_2 (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
$logK^{M}_{MAHBH2}$	20.45	20.40	20.35	20.30	20.20	20.10	20.14	20.10	20.04
$logK^{MAH}_{MAHBH2}$	5.20	5.15	5.10	5.04	4.97	4.92	4.97	4.93	4.87
$logK^{MBH2}_{MAHBH2}$	6.25	6.20	6.15	6.08	6.00	5.92	5.65	5.60	5.55
$logK^{M}_{MABH2}$	22.68	22.64	22.60	22.22	22.16	22.10	22.15	22.12	22.08
$logK^{MBH2}_{MAHBH}$	21.55	21.50	21.45	21.00	20.95	20.90	20.93	20.90	20.98
$logK^{MAH}_{MAHBH}$	8.90	8.88	8.85	6.62	6.58	6.50	6.56	6.53	6.50
$logK^{MBH}_{MAHBH}$	4.80	4.75	4.73	4.42	4.38	4.30	4.36	4.30	4.28
$logK^{MA}_{MAH2B}$	7.80	7.75	7.70	7.00	6.94	6.90	6.97	6.90	6.84
$logK^{M}_{MAHB}$	3.48	3.45	3.43	3.04	3.00	2.94	2.92	2.89	2.84
$logK^{M}_{MABH}$	22.28	22.26	22.20	22.06	22.02	21.98	21.98	21.94	21.90
$logK^{MAH}_{MAHB}$	13.82	13.78	13.74	13.15	13.10	13.08	13.06	13.01	12.97
$logK^{MBH}_{MABH}$	4.52	4.42	4.36	4.10	4.03	3.92	3.82	3.76	3.70
$logK^{MA}_{MABH}$	10.98	10.90	10.86	10.84	10.80	10.76	10.46	10.60	10.54
$logK^{MB}_{MAHB}$	5.12	5.08	5.00	4.26	4.21	4.16	4.19	4.17	4.14
$logK^{MA}_{MAB}$	14.20	14.14	14.10	14.10	14.06	14.00	14.04	14.00	13.96
$logK^{MB}_{MAB}$	5.04	4.99	4.94	5.02	4.95	4.90	4.90	4.85	4.80
$logK^{H}_{MABH3}$	-5.88	-5.82	-5.74	-5.68	-5.61	-5.54	-5.48	-5.40	-5.34
$logK^{H}_{MABH2}$	-8.98	-8.90	-8.82	-8.68	-8.60	-8.52	-8.42	-8.96	-8.90
$logK^{H}_{MABH}$	-9.92	-9.87	-9.75	-9.64	-9.78	-9.72	-9.66	-9.60	-9.53
$logK^{H}_{MAB}$	-10.99	-10.93	-10.86	-10.81	-10.72	- 10.67	-10.61	-10.55	-10.49
$\log \beta_{MABH3}$	48.00	47.94	47.88	47.84	47.80	47.72	47.12	47.08	47.00
$\log \beta_{MABH2}$	42.90	42.803	42.72	42.80	42.77	42.70	42.45	42.40	41.35
$\log \beta_{MABH}$	34.50	34.46	34.42	34.48	34.42	34.38	34.15	34.10	34.05
$\log \beta_{MAB}$	24.95	24.90	24.85	24.74	24.69	24.65	24.50	24.45	24.40

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

Table: 5.8

Formation constants of (1:1:1) VO(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
$\log K^{M}_{MAHBH2}$	20.25	20.15	20.05	20.10	20.06	20.00	19.92	19.88	19.84
$\log K^{MAH}_{MAHBH2}$	6.50	6.45	6.40	6.00	5.94	5.90	5.90	5.80	5.70
$\log K^{MBH2}_{MAHBH2}$	7.20	7.10	7.00	6.23	6.16	6.10	6.10	6.00	5.90
$\log K^{M}_{MABH2}$	23.40	23.35	23.30	23.10	23.02	22.96	22.90	22.84	22.79
$\log K^{MBH2}_{MAHBH}$	22.90	22.82	22.76	22.60	22.52	22.46	22.44	22.37	22.31
$\log K^{MAH}_{MAHBH}$	15.60	15.56	15.52	15.12	15.08	15.02	15.10	15.00	14.95
$\log K^{MBH}_{MAHBH}$	8.10	8.05	8.00	7.90	7.86	7.80	7.78	7.72	7.67
$\log K^{MA}_{MAH2B}$	12.90	12.83	12.77	12.40	12.34	12.30	12.20	12.15	12.10
$\log K^{M}_{MAHB}$	23.82	23.78	23.72	23.40	23.36	23.31	23.18	23.10	23.02
$\log K^{M}_{MABH}$	15.20	15.13	15.07	14.10	14.00	13.90	13.70	13.65	13.60
$\log K^{MAH}_{MAHB}$	6.79	6.73	6.69	6.07	6.00	5.90	5.83	5.80	5.73
$\log K^{MBH}_{MABH}$	10.50	10.40	10.30	10.20	10.12	10.10	10.06	10.00	9.96
$\log K^{MA}_{MABH}$	5.64	5.60	5.55	5.10	5.02	4.98	4.96	4.90	4.80
$\log K^{MB}_{MAHB}$	15.25	15.20	15.15	15.10	14.96	14.90	14.76	14.70	14.64
$\log K^{MA}_{MAB}$	16.20	16.15	16.00	15.90	15.80	15.70	15.15	15.10	15.05
$\log K^{MB}_{MAB}$	6.30	6.25	6.20	6.10	6.02	5.98	5.95	5.90	5.85
$\log K^{H}_{MABH3}$	-5.68	-5.60	-5.52	-5.38	-5.30	-5.22	-5.14	-5.10	-5.02
$\log K^{H}_{MABH2}$	-8.92	-8.87	-8.80	-8.00	-7.96	-7.84	-7.72	-7.65	-7.60
$\log K^{H}_{MABH}$	-9.75	-9.70	-9.65	-9.96	-9.89	-9.82	-9.80	-9.70	-9.62
$\log K^{H}_{MAB}$	-10.90	-10.87	-10.78	-10.52	-10.45	-10.40	-10.35	-10.30	-10.22
$\log \beta_{MABH3}$	48.28	48.10	48.00	47.98	47.90	47.82	47.35	47.30	47.22
$\log \beta_{MABH2}$	43.38	43.30	43.24	43.10	43.05	43.01	42.92	42.88	41.80
$\log \beta_{MABH}$	36.20	36.10	36.00	35.40	35.31	35.22	35.13	35.08	35.03
$\log \beta_{MAB}$	26.02	25.96	25.00	25.70	25.65	25.60	25.53	25.48	25.41

Table-:5.9

Thermodynamic formation constants and thermodynamic parameters

UO_2(II)-MAL-TYR

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}		
$logK^{M}_{MAB}$	21.86	122.63	20.98	121.18	20.56	119.28	76.86	153.56
$logK^{M}_{MAHBH}$	27.91	156.57	27.68	160.58	27.32	158.49	37.20	407.64
$logK^{MAH}_{MAHBH}$	18.10	101.54	17.88	103.73	17.54	101.76	35.28	226.31
$logK^{MBH}_{MAHBH}$	21.58	121.06	20.76	120.44	20.58	119.39	57.16	214.83
$logK^{H}_{MAHBH}$	-4.20	-	-3.96	-	-3.82	-	-	-
$logK^{M}_{MABH}$	28.96	162.46	27.95	162.15	27.65	160.41	75.76	292.18
$logK^{MAH}_{MABH}$	18.97	106.42	18.10	105.00	17.84	103.50	65.37	136.90
$logK^{MBH}_{MABH}$	16.75	93.96	16.46	95.49	15.84	91.89	58.26	122.73
$logK^{MA}_{MABH}$	13.94	78.20	13.85	80.35	13.34	77.39	39.79	132.49
$logK^{MB}_{MABH}$	14.82	83.14	14.68	84.70	13.98	81.10	54.43	99.18
$logK^{H}_{MABH}$	-6.54	-	-5.98	-	-5.25	-	-	-
$logK^{MA}_{MAB}$	9.10	50.05	9.01	52.27	8.92	51.75	11.07	136.32
$logK^{MB}_{MAB}$	5.96	33.43	5.65	32.77	5.50	31.90	27.21	20.29
$logK^{H}_{MAB}$	-7.85	-	-7.70	-	-7.60	-	-	-

VO(II)-MAL-TYR

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}		
$logK^{M}_{MAB}$	22.46	126.00	21.49	124.15	21.10	122.41	78.50	158.15
$logK^{M}_{MAHBH}$	28.92	162.24	28.76	166.85	28.34	164.41	37.47	426.59
$logK^{MAH}_{MAHBH}$	24.98	140.14	23.89	138.60	23.54	136.54	83.56	189.17
$logK^{MBH}_{MAHBH}$	30.54	171.33	29.78	172.77	29.34	170.21	73.30	333.54
$logK^{H}_{MAHBH}$	-4.98	-	-4.40	-	-4.10	-	-	-
$logK^{M}_{MABH}$	29.99	168.24	29.90	173.46	29.54	171.37	29.54	474.27
$logK^{MAH}_{MABH}$	16.12	90.43	15.90	92.24	14.99	86.96	74.26	57.44
$logK^{MBH}_{MABH}$	18.18	101.99	17.08	99.09	16.65	96.59	89.58	38.67
$logK^{MA}_{MABH}$	15.28	85.72	15.10	87.60	15.00	87.02	16.68	235.12
$logK^{MB}_{MABH}$	14.85	83.31	13.89	80.58	13.64	79.13	69.61	43.08
$logK^{H}_{MABH}$	-6.40	-	-6.10	-	-5.93	-	-	-
$logK^{MA}_{MAB}$	10.12	56.77	9.98	57.89	9.84	51.08	17.23	134.79
$logK^{MB}_{MAB}$	6.05	33.94	5.86	33.99	5.34	30.98	45.95	40.01
$logK^{H}_{MAB}$	-7.68	-	-7.30	-	-7.04	-	-	-

Table-:5.10

Thermodynamic formation constants and thermodynamic parameters

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}		
UO_2(II)-Mal- DOPA								
$logK^{M}_{MAHBH}$	27.28	153.04	27.10	157.22	26.98	156.52	18.05	460.39
VO(II)-Mal- DOPM								
$logK^{H}_{MAHBH}$	27.55	154.55	27.48	159.42	27.30	158.30	16.13	472.74

Table-:5.11

Thermodynamic formation constants and thermodynamic parameters

UO_2(II)-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}		
$logK^{M}_{MAB}$	25.34	142.16	25.20	146.20	24.94	144.79	25.43	396.64
$logK^{M}_{MAHBH2}$	20.83	116.85	20.54	119.16	20.36	118.12	28.17	301.95
$logK^{MAH}_{MAHBH2}$	5.45	30.57	5.30	30.74	5.14	29.82	19.14	38.86
$logK^{MBH2}_{MAHBH2}$	6.67	37.41	6.42	37.24	6.10	35.38	35.55	6.31
$logK^{H}_{MAHBH2}$	-5.98	-	-5.86	-	-5.62	-	-	-
$logK^{M}_{MAHBH}$	22.96	78.20	22.76	132.04	22.54	130.76	25.98	350.77
$logK^{M}_{MAHBH}$	21.89	122.80	21.38	124.03	21.20	122.99	40.20	280.12
$logK^{MBH2}_{MAHBH}$	9.20	51.61	8.98	52.09	8.72	50.58	29.81	74.29
$logK^{MAH}_{MAHBH}$	5.10	28.61	4.92	28.54	4.80	27.84	18.05	35.61
$logK^{MA}_{MAHBH}$	7.95	44.60	7.35	42.64	7.14	41.42	39.66	14.36
$logK^{H}_{MAHBH}$	-9.10	-	-8.98	-	-8.70	-	-	-
$logK^{M}_{MAHB}$	3.64	20.42	3.40	19.72	3.30	19.14	19.96	0.76
$logK^{M}_{MABH}$	22.84	128.13	22.34	129.60	22.18	128.67	38.29	304.82
$logK^{MAH}_{MABH}$	14.08	78.99	13.54	78.55	13.27	76.98	48.00	104.16
$logK^{MBH}_{MABH}$	5.99	33.60	5.86	33.99	5.72	33.18	16.68	57.63
$logK^{MA}_{MABH}$	11.20	62.83	10.99	63.75	10.79	62.59	25.16	128.28
$logK^{MB}_{MABH}$	4.80	26.92	4.62	26.80	4.42	25.64	25.52	11.48
$logK^{H}_{MABH}$	-10.12	-	-9.94	-	-9.89	-	-	-
$logK^{MA}_{MAB}$	14.68	82.35	14.43	83.71	14.20	82.38	29.40	180.36
$logK^{MB}_{MAB}$	5.38	30.18	5.25	30.45	5.06	29.35	20.10	34.46
$logK^{H}_{MAB}$	-11.08	-	-11.00	-	-10.91	-	-	-

VO(II)-MAL-DOPM

Parameter	20°C		30°C		40°C		$-\Delta H^o$ kJmol^{-1}	ΔS^o Jk^{-1}mol^{-1}
	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}	$\log K_{\mu\to0}$	$-\Delta G^o$ kJmol^{-1}		
$\log K^{M}_{MAB}$	25.81	144.79	25.58	148.45	25.14	145.45	42.07	349.05
$\log K^{M}_{MAHBH2}$	20.98	117.70	20.32	117.88	20.21	117.25	43.62	250.06
$\log K^{MAH}_{MAHBH2}$	6.82	38.26	6.35	36.84	6.18	35.85	37.33	1.53
$\log K^{MBH2}_{MAHBH2}$	6.95	38.99	6.58	38.17	6.30	37.01	33.91	16.27
$\log K^{H}_{MAHBH2}$	-5.90	-	-5.55	-	-5.40	-	-	-
$\log K^{M}_{MAHBH}$	23.78	133.40	23.54	136.56	23.24	134.82	33.64	340.23
$\log K^{M}_{MAHBH}$	23.10	129.69	22.94	133.08	22.78	132.16	19.69	374.90
$\log K^{MBH2}_{MAHBH}$	15.90	89.20	15.48	89.90	15.40	89.34	28.44	205.64
$\log K^{MAH}_{MAHBH}$	8.45	47.40	8.25	47.86	8.12	47.10	19.83	93.62
$\log K^{MA}_{MAHBH}$	24.18	135.65	23.80	138.07	23.46	136.10	44.03	31.09
$\log K^{H}_{MAHBH}$	-9.15	-	-8.60	-	-8.25	-	-	-
$\log K^{M}_{MAHB}$	13.20	74.05	12.68	73.56	12.56	72.86	36.65	125.60
$\log K^{M}_{MABH}$	15.50	86.95	15.26	88.53	15.10	87.60	92.45	314.06
$\log K^{MAH}_{MABH}$	6.92	38.82	6.54	37.94	6.28	36.43	37.88	2.29
$\log K^{MBH}_{MABH}$	10.93	61.31	10.58	61.38	10.48	60.80	25.98	119.28
$\log K^{MA}_{MABH}$	5.60	31.41	5.42	31.44	5.16	29.39	27.62	13.02
$\log K^{MB}_{MABH}$	15.58	87.40	15.36	89.11	15.24	88.41	20.24	228.61
$\log K^{H}_{MABH}$	-9.92	-	-9.86	-	-9.68	-	-	-
$\log K^{MA}_{MAB}$	16.38	91.89	16.10	93.40	16.04	93.05	19.42	246.23
$\log K^{MB}_{MAB}$	6.64	37.25	6.54	37.94	6.24	36.20	25.98	39.06
$\log K^{H}_{MAB}$	-11.12	-	-10.85	-	-10.61	-	-	-

Representative Speciation Curves

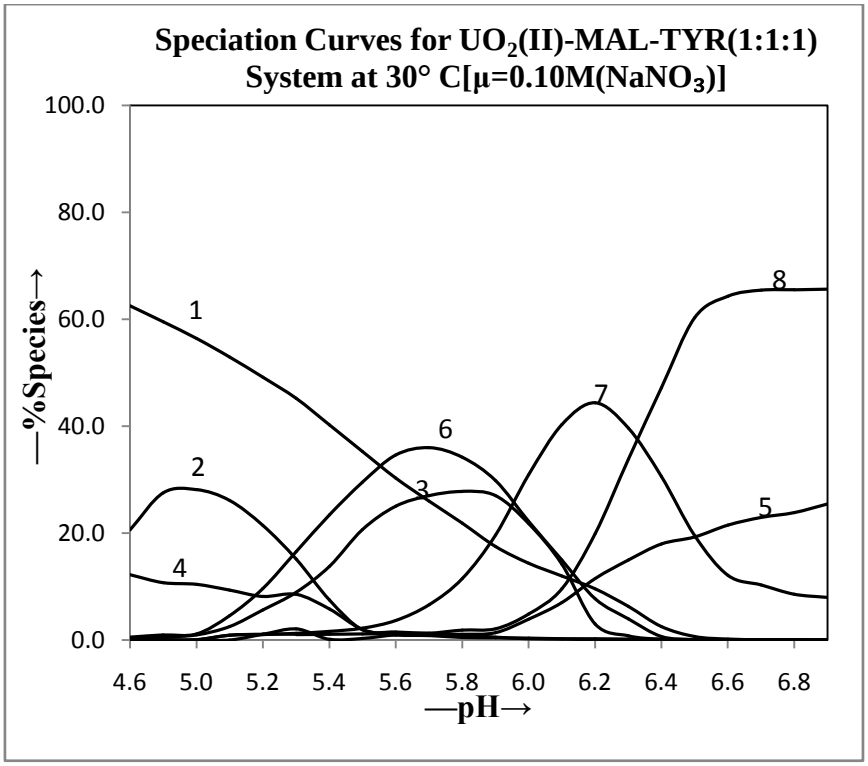

Fig. 7

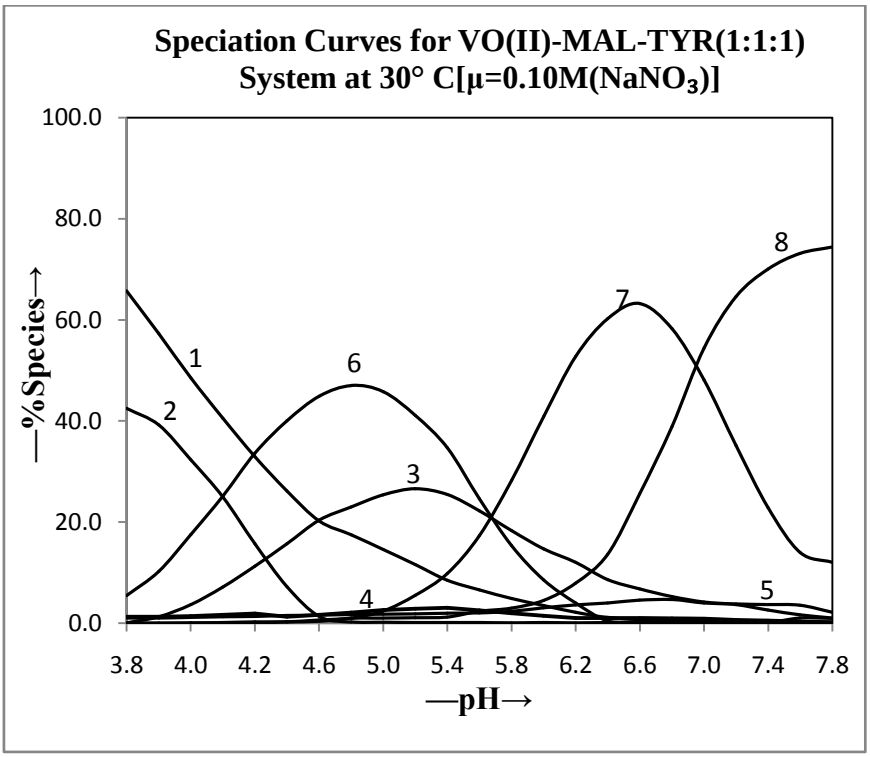

Fig. 8

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

Table: 5.12

Experimental values and concentration of different species for UO_2(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	4.6	1.18	62.50	20.58	0.20	12.21	0.00	0.54	0.01	0.00
2	4.7	1.28	59.49	27.54	0.55	10.74	0.00	0.95	0.03	0.01
3	5.0	1.42	56.41	28.12	0.98	10.42	0.00	1.15	0.05	0.05
4	5.1	1.48	52.94	26.13	2.54	9.34	0.01	4.58	0.90	0.90
5	5.2	1.52	49.14	21.45	5.65	8.15	1.05	9.65	1.00	1.10
6	5.3	1.64	45.21	15.15	8.95	8.54	2.09	16.54	1.27	1.05
7	5.4	1.68	40.26	7.49	13.80	5.81	0.15	23.40	1.59	1.09
8	5.5	1.72	35.24	1.89	20.65	1.99	0.28	29.50	2.20	1.15
9	5.6	1.79	30.28	1.48	25.00	0.98	0.95	34.62	3.64	1.20
10	5.7	1.87	25.98	1.25	26.98	0.84	1.01	36.00	6.59	1.28
11	5.8	1.95	21.84	0.98	27.79	0.49	1.08	34.19	11.48	1.85
12	5.9	2.00	17.49	0.54	26.99	0.40	1.38	29.84	19.65	2.10
13	6.0	2.08	14.37	0.25	21.78	0.34	3.90	22.19	30.89	4.85
14	6.1	2.17	12.00	0.18	14.18	0.26	6.98	14.95	40.27	9.56
15	6.2	2.25	9.58	0.09	3.00	0.24	11.50	7.71	44.38	19.87
16	6.3	2.36	6.26	0.07	0.78	0.21	14.95	3.98	39.62	33.84
17	6.4	2.45	2.51	0.03	0.12	0.18	17.98	0.65	30.57	47.15
18	6.5	2.62	0.65	0.02	0.02	0.09	19.25	0.08	19.54	60.28
19	6.6	2.74	0.21	0.01	0.00	0.00	21.50	0.02	12.12	64.31
20	6.7	2.89	0.09	0.00	0.00	0.00	22.94	0.00	10.32	65.41
21	6.8	3.15	0.08	0.00	0.00	0.00	23.84	0.00	8.57	65.50
22	6.9	3.36	0.02	0.00	0.00	0.00	25.45	0.00	7.95	65.60

Table: 5.13

Experimental values and concentration of different species for VO(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	3.8	0.68	65.73	42.47	0.04	1.23	1.00	5.45	0.00	0.00
2	3.9	0.86	57.20	39.15	1.25	1.25	1.02	10.21	0.00	0.00
3	4.0	0.96	48.48	32.28	3.65	1.38	1.10	17.51	0.01	0.00
4	4.1	1.10	40.51	24.95	7.12	1.62	1.25	25.12	0.02	0.10
5	4.2	1.30	32.91	15.68	11.28	1.89	1.32	33.58	0.06	0.20
6	4.4	1.49	26.12	7.20	15.69	1.25	1.48	40.00	0.26	0.25
7	4.6	1.64	20.17	1.29	20.35	1.64	1.54	44.89	0.58	0.38
8	4.8	1.73	17.45	0.21	22.98	2.08	1.68	46.98	1.02	0.95
9	5.0	1.78	14.54	0.14	25.37	2.57	1.77	45.78	2.37	0.99
10	5.2	1.83	11.54	0.10	26.59	2.84	1.84	41.10	5.48	1.03
11	5.4	1.91	8.45	0.09	25.41	2.99	1.95	34.65	9.78	1.18
12	5.6	1.96	6.54	0.08	22.18	2.54	2.00	24.59	17.25	2.32
13	5.8	2.04	4.85	0.02	18.25	1.96	2.34	15.31	28.21	2.95
14	6.0	2.09	3.45	0.10	14.69	1.45	3.01	8.54	40.84	4.48
15	6.2	2.16	2.10	0.02	11.98	1.01	3.60	3.95	52.75	7.89
16	6.4	2.25	1.10	0.09	8.58	0.96	3.98	0.42	60.21	13.58
17	6.6	2.32	1.03	0.08	6.74	0.85	4.51	0.32	63.20	25.54
18	6.8	2.44	1.00	0.02	5.24	0.74	4.65	0.30	58.21	38.89
19	7.0	2.56	0.90	0.01	4.18	0.51	3.97	0.21	48.12	54.39
20	7.2	2.71	0.70	0.00	3.67	0.42	3.75	0.18	35.14	64.54
21	7.4	2.92	0.54	0.00	2.58	0.32	3.68	0.10	22.85	70.00
22	7.6	3.17	0.38	0.00	1.64	0.14	3.54	0.98	14.00	73.10
23	7.8	3.50	0.20	0.00	0.98	0.1	2.11	0.90	12.03	74.38

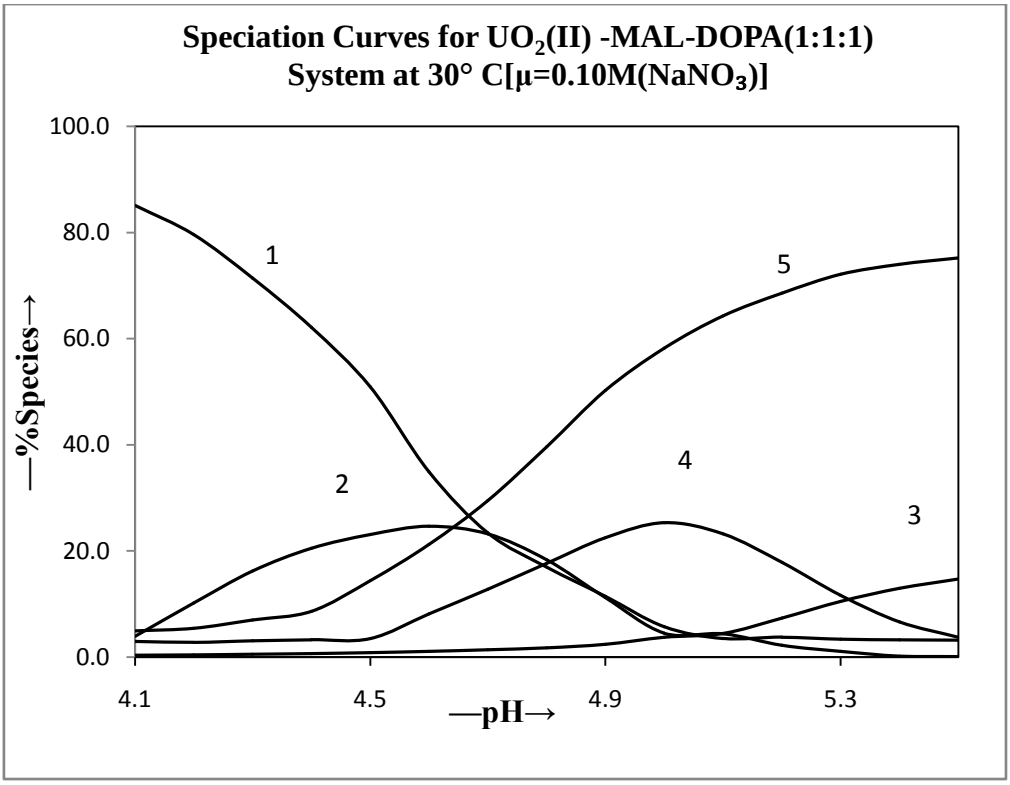

Fig. 9

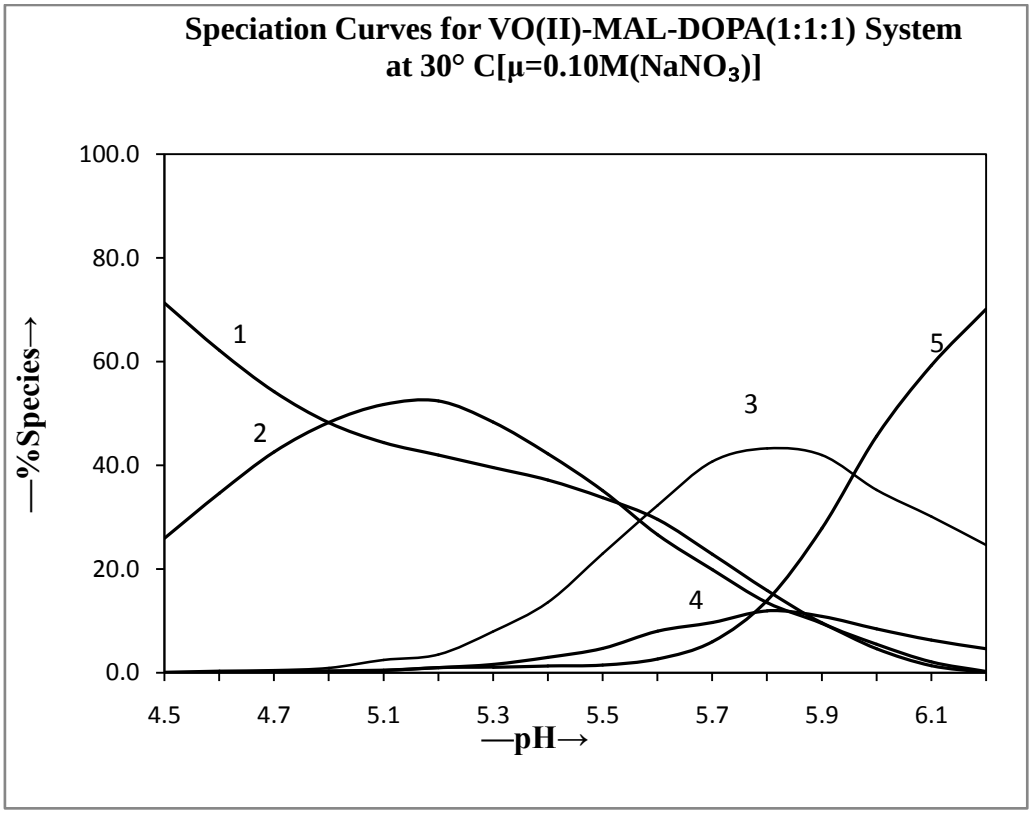

Fig. 10

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

Table: 5.14

Experimental values and concentration of different species for UO_2(II)-MAL-DOPA (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[$MABH_2$]
1	4.1	1.46	85.11	3.95	0.35	2.99	4.93
2	4.2	1.54	79.61	10.20	0.44	2.79	5.42
3	4.3	1.62	71.42	16.25	0.56	3.09	6.99
4	4.4	1.70	62.10	20.54	0.70	3.29	8.66
5	4.5	1.75	50.88	23.12	0.88	3.49	14.42
6	4.6	1.80	34.92	24.68	1.11	8.12	21.24
7	4.7	1.83	23.38	23.21	1.39	12.82	29.51
8	4.8	1.86	16.98	18.32	1.75	17.65	39.64
9	4.9	1.89	11.49	11.20	2.45	22.49	50.21
10	5.0	1.90	5.72	4.51	3.77	25.34	58.21
11	5.1	1.91	3.51	4.41	4.49	23.23	64.31
12	5.2	1.92	3.76	2.21	7.39	17.85	68.58
13	5.3	1.93	3.37	1.12	10.52	11.67	72.10
14	5.4	1.96	3.26	0.21	12.95	6.67	74.01
15	5.5	1.98	3.18	0.10	14.74	3.76	75.21

Table: 5.15

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

S.NO.	pH	TITRE	[M]	[MAH]	[MA]	[MBH_2]	[$MABH_2$]
1	4.5	1.08	71.28	25.94	0.12	0.02	0.00
2	4.6	1.18	62.15	34.64	0.35	0.05	0.00
3	4.7	1.28	54.18	42.58	0.48	0.18	0.10
4	5.0	1.42	48.21	48.25	0.91	0.32	0.25
5	5.1	1.48	44.35	51.69	2.45	0.48	0.39
6	5.2	1.52	41.95	52.39	3.48	0.95	0.95
7	5.3	1.64	39.54	48.33	7.95	1.59	1.05
8	5.4	1.68	37.16	42.21	13.58	2.95	1.29
9	5.5	1.72	33.74	35.12	22.95	4.68	1.44
10	5.6	1.87	29.54	26.59	32.25	7.99	2.65
11	5.7	2.00	22.85	19.85	40.74	9.68	5.98
12	5.8	2.16	15.84	13.49	43.25	11.92	13.95
13	5.9	2.31	9.58	9.48	41.96	10.87	27.84
14	6.0	2.52	5.48	4.58	35.25	8.42	45.62
15	6.1	2.65	2.05	1.36	30.12	6.25	59.25
16	6.2	2.74	0.24	0.01	24.64	4.62	70.12

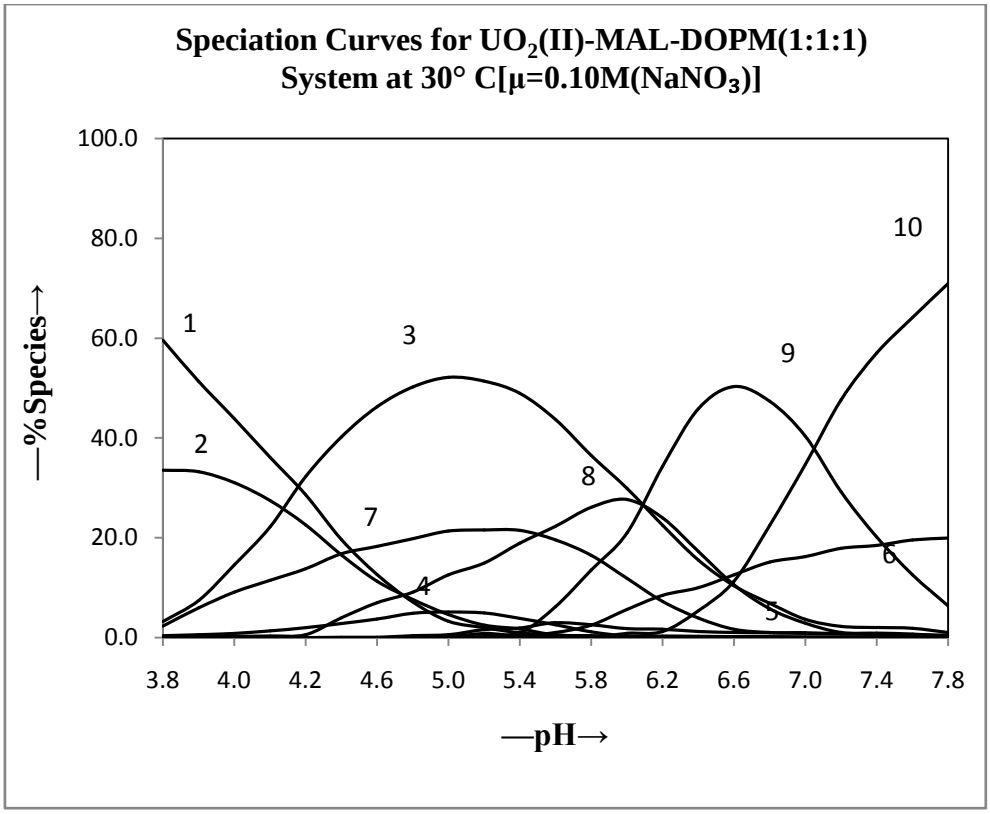

Fig. 11

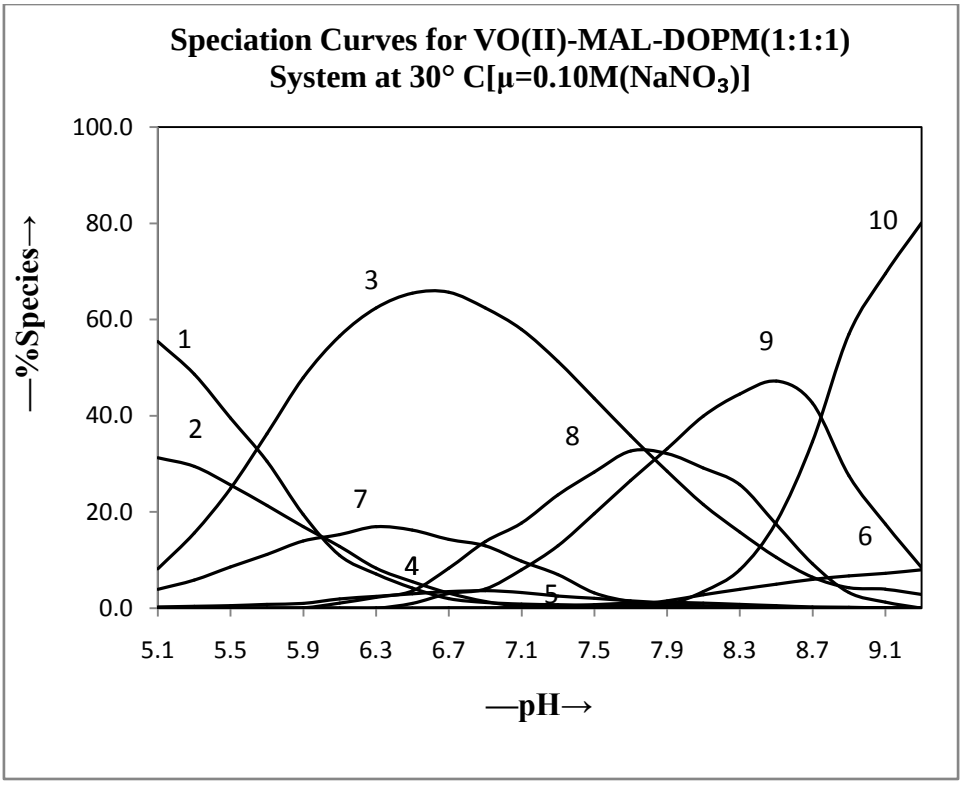

Fig. 12

Where, 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: 5.16

Experimental values and concentration of different species for UO_2(II)-MAL-DOPM (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	pH	TITRE	[M]	[MAH]	[MA]	[MBH2]	[MBH]	[MB]	[$MABH_3$]	[$MABH_2$]	[MABH]	[MAB]
1	3.8	0.68	59.55	33.51	3.21	0.35	0.00	0.00	2.32	0.12	0.00	0.00
2	3.9	0.86	51.32	33.22	7.45	0.55	0.00	0.00	5.95	0.15	0.00	0.00
3	4.0	0.96	43.85	31.01	14.56	0.84	0.00	0.00	9.12	0.24	0.00	0.00
4	4.1	1.10	36.12	27.41	22.15	1.35	0.00	0.00	11.48	0.32	0.00	0.00
5	4.2	1.30	28.62	22.54	32.25	1.95	0.00	0.00	13.80	0.58	0.00	0.00
6	4.4	1.49	19.64	16.51	40.21	2.84	0.05	0.00	16.80	3.94	0.00	0.00
7	4.6	1.64	12.65	11.25	46.25	3.69	0.08	0.00	18.25	6.95	0.00	0.00
8	4.8	1.73	7.08	7.62	50.21	4.85	0.36	0.00	19.82	9.09	0.00	0.00
9	5	1.78	3.28	4.62	52.12	5.10	0.58	0.12	21.32	12.58	0.15	0.00
10	5.2	1.83	1.99	2.47	51.36	4.90	1.58	0.17	21.56	14.95	0.84	0.00
11	5.4	1.91	0.92	1.69	48.95	3.84	1.94	0.38	21.48	18.92	0.95	0.00
12	5.6	1.96	0.48	0.51	43.65	2.54	2.98	0.99	19.57	22.32	6.24	0.00
13	5.8	2.04	0.24	0.36	36.48	1.15	2.58	2.48	16.50	26.07	13.54	0.01
14	6.0	2.09	0.12	0.15	29.85	0.33	1.78	5.62	11.84	27.65	20.95	0.85
15	6.2	2.16	0.10	0.02	22.48	0.30	1.65	8.48	7.21	23.98	34.32	1.20
16	6.4	2.25	0.05	0.02	15.48	0.27	1.23	9.98	3.89	17.25	45.84	5.35
17	6.6	2.32	0.02	0.10	10.36	0.20	1.00	12.58	1.65	10.58	50.29	11.25
18	6.8	2.44	0.01	0.09	6.85	0.18	0.95	15.12	1.00	5.74	47.30	22.52
19	7.0	2.56	0.00	0.05	3.65	0.11	0.84	16.23	0.98	2.85	40.32	34.68
20	7.2	2.71	0.00	0.02	2.25	0.09	0.75	17.85	0.75	1.02	29.15	47.65
21	7.4	2.92	0.00	0.01	2.00	0.04	0.64	18.45	0.62	0.88	20.14	56.98
22	7.6	3.17	0.00	0.00	1.85	0.02	0.51	19.52	0.50	0.71	12.58	64.14
23	7.8	3.50	0.00	0.00	1.00	0.00	0.47	19.95	0.32	0.25	6.32	70.95

Table: 5.17

Experimental values and concentration of different species for UO_2(II)-MAL-DOPM (1:1:1) system at 30±1°C [μ=0.10M($NaNO_3$)]

S.NO.	pH	TITR	[M]	[MAH]	[MA]	[MBH2]	[MBH]	[MB]	[$MABH_3$]	[$MABH_2$]	MABH]	[MAB]
1	5.1	1.53	55.40	31.25	8.15	0.25	0.00	0.00	3.95	0.00	0.00	0.00
2	5.3	1.58	48.62	29.48	15.64	0.38	0.00	0.00	5.87	0.00	0.00	0.00
3	5.5	1.65	39.52	25.64	24.89	0.54	0.00	0.00	8.59	0.00	0.00	0.00
4	5.7	1.72	30.54	21.35	36.24	0.78	0.00	0.00	11.20	0.02	0.00	0.00
5	5.9	1.82	19.47	16.95	47.89	1.02	0.00	0.00	13.95	0.09	0.00	0.00
6	6.1	1.87	10.98	12.84	56.54	1.95	0.00	0.00	15.28	1.05	0.00	0.00
7	6.3	1.92	7.08	8.28	62.38	2.45	0.01	0.00	16.95	2.28	0.01	0.00
8	6.5	1.98	4.18	5.50	65.48	2.98	0.02	0.00	16.25	3.58	1.02	0.00
9	6.7	2.01	1.99	3.15	65.68	3.45	0.03	0.00	14.28	8.28	3.06	0.00
10	6.9	2.09	1.20	1.36	62.38	3.65	0.09	0.00	12.95	13.84	4.00	0.00
11	7.1	2.21	0.84	0.37	57.95	3.28	0.20	0.02	9.75	17.68	8.00	0.00
12	7.3	2.35	0.75	0.24	51.32	2.54	0.42	0.07	6.99	23.52	12.95	0.01
13	7.5	2.57	0.62	0.11	43.65	2.04	0.74	0.24	3.19	28.25	19.62	0.20
14	7.7	2.68	0.54	0.08	35.84	1.54	1.07	0.69	1.37	32.65	26.51	0.50
15	7.9	2.84	0.41	0.04	28.48	1.05	1.22	1.54	0.84	32.14	33.10	0.75
16	8.1	3.08	0.32	0.02	21.56	0.46	1.08	2.78	0.48	29.16	39.95	3.45
17	8.3	3.18	0.20	0.01	15.84	0.17	0.78	3.95	0.35	25.65	44.54	7.95
18	8.5	2.39	0.14	0.00	10.58	0.05	0.50	5.00	0.15	17.45	47.21	17.89
19	8.7	3.74	0.10	0.00	6.48	0.02	0.29	5.98	0.11	9.25	42.62	34.58
20	8.9	4.10	0.10	0.00	4.25	0.00	0.16	6.68	0.08	3.25	27.54	56.95
21	9.1	4.98	0.08	0.00	3.95	0.00	0.09	7.24	0.04	1.24	17.48	69.54
22	9.3	5.32	0.02	0.00	2.87	0.00	0.05	7.98	0.02	0.00	8.45	80.10

Table: 5.18

Value of Δlog K for ternary complexes.

Parameters	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
	UO_2(II)-MAL-TYR					
$\log\beta_{MABH2}$	45.62	17.25	45.10	17.00	44.38	16.41
$\log\beta_{MABH}$	38.84	15.83	37.78	15.04	37.46	14.87
$\log\beta_{MAB}$	21.86	5.32	20.98	4.64	20.56	4.36
	VO(II)-MAL-TYR					
$\log\beta_{MABH2}$	46.90	17.25	45.54	17.03	43.00	13.68
$\log\beta_{MABH}$	39.86	16.23	39.12	15.81	38.60	15.68
$\log\beta_{MAB}$	22.46	4.62	21.40	3.85	21.10	3.89
	UO_2(II)-MAL-DOPA					
$\log\beta_{MABH2}$	40.30	-0.34	40.28	-0.21	40.18	-0.14
	VO(II)-MAL-DOPA					
$\log\beta_{MABH2}$	42.28	1.70	42.14	1.69	42.08	1.82
	UO_2(II)-MAL-DOPM					
$\log\beta_{MABH3}$	48.25	4.92	47.98	5.29	47.04	5.20
$\log\beta_{MABH2}$	43.20	8.34	43.08	8.40	42.86	8.03
$\log\beta_{MABH}$	34.84	5.34	34.78	5.45	34.54	6.11
$\log\beta_{MAB}$	25.34	-0.49	25.20	-0.04	24.62	-0.24
	VO(II)-MAL-DOPM					
$\log\beta_{MABH3}$	48.54	4.20	48.20	4.69	47.69	4.45
$\log\beta_{MABH2}$	43.64	4.99	43.25	4.73	43.10	4.77
$\log\beta_{MABH}$	36.48	3.85	35.86	3.54	35.43	3.50
$\log\beta_{MAB}$	26.21	0.38	25.98	0.63	25.74	1.57

5.4 Results and discussion:

The observation of pH vs. 'a' curves (Figs. 1-6) reveals the following facts. The ligand A (malonic acid) titration curve 1 shows two inflections at a≈1 and a≈2 thereby indicating that the protons are released in two distinct steps. Curve 2 representing the titration curve of secondary ligand B (tyr, dopa and dopm) reveals the liberation of proton at pH≈8.0 which indicates 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 depicting the metal-ligand A - ligand B (1:1:1) titration of UO_2(II)/VO(II) –MAL- TYR/DOPA/DOPM ternary systems, 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 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 as a result of its coordination with 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 binary and ternary metal-ligand complex species and computation of the data are done by standard methods [13-20] as described in preceding chapters. The multiple equilibria existing in case of the UO_2(II)/VO(II)-mal-catecholamines are same as in case of Cd(II)/Gd(III)-mal-catecholamines. These equilibria are given in equations 1 to 43 of chapter-4.

Speciation curves are obtained for various systems by using SCOGS computer program.[21-24] Speciation curves for UO_2(II)/VO(II)-MAL-TYR are shown in figs. 7-8. The patterns observed are almost similar. 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 in to existence. But 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 $2 \leq a \leq 3$. Thereafter the MAB species is formed by the coordination of ligand B to MA complex. At a≈2 formation of MAB species commences 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 chapter-4).

Figures 9 and 10 correspond to the UO_2(II)/VO(II)-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. Formation of $MABH_2$ by coordination of H_2B species to MA complex is understood via the equilibrium given in equation 27 (chapter-4)

As pointed out earlier 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 UO_2 (II)/VO(II)-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 this indicates that all the proton in ternary complex species are attached to dopm site. After pH≈6.5 concentration of free metal M, MAH and MA species decreases whereas formation of $MABH_3$ increases continuously and attains maximum value at pH≈7.5. 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 chapter-4). 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 chapter-4). The percent of MAB species is about 80% thereby confirming it to be the most prominent species in the higher pH range.

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 tyrosine/dopa/dopm acts as secondary ligands. The equilibrium constants and speciation profile obtained in UO_2(II)/VO(II)-malonic acid-tyr/dopa/dopm systems follow the same trend as observed with Cd(II)/Gd(III). It is therefore concluded that the coordination mode of tyr/dopa/dopm with UO_2(II) and VO(II) are same as described with Cd(II) and Gd(III)(Ref.chapter-4). Hence it can be concluded that complexation behavior is governed more by the nature of ligand as compared to metals.

In most of the systems the values of ΔlogK are found to be positive which indicate that the ternary complexes are more stable than the binary complexes. However, the negative values of ΔlogK in some of UO_2(II) systems indicate the less stability of ternary complexes. This is probably

due to the steric hindrance in the coordination of secondary ligands in UO_2(II) primary ligand complex. This can be attributed to the presence of two axial oxygen atoms in case of dioxouranium (VI).[24-25] Value of ΔlogK are given in table 5.18.

The values of ΔG°, ΔH° and ΔS° are presented in table 5.9-5.11. Negative value of ΔG° and ΔH° confirms the spontaneous nature of complexation reaction this further indicates the reaction are exothermic and metal complexes are fairly strong. Positive ΔS° values are also in support of formation of strong metal-ligand species.

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