

3.1 Introduction:

The chemistry of oxocations has been very interesting because the metal-oxygen multiple bond in them could be used as an internal molecular probe to understand more about the nature of metal-ligand bonds as M-L bonds perturb the more sensitive double bonds. The importance of UO₂(II) and VO(II) in biological systems is imparted mainly by the rich oxygen chemistry.

Dioxouranium(VI), is one of the most studied oxocations for which a large number of complexes with flexible coordination geometries are possible.^[1-3] Due to the spectral properties (absorption and luminescence) and excited-state electron-transfer properties of the UO₂(II) ion, dioxouranium(VI) complexes have possible applications in solar energy conversion systems.^[4] On the other hand UO₂(II) cation is radioactive in nature and hence hazardous. It is present in the aquatic ecosystem and its environmental hazard is due more to its high chemical toxicity towards a wide number of living organisms than to its radioactivity.^[5-7] Recently, it was stated that the uranyl complexes show antimicrobial activity.^[8-10]

The knowledge of uranium (and its waste products) behavior in environment is of great concern for many scientists in several research fields. The importance of this cation, from different points of view, is extensively discussed.^[11-14] The chemistry of dioxouranium(VI) is dominated by the formation of several mono- and polynuclear hydrolytic species.^[15] Due to its high reactivity, it shows a strong tendency to interact with several organic and inorganic ligands, forming a wide number of complex species with quite high stability.^[16-20] This is particularly relevant in the study of dioxouranium(VI) speciation in natural and/or waste waters, where other metals and the above cited organic and inorganic ligands could be simultaneously present in

different concentrations too.^[21-25] Speciations of uranium (VI) complexes of malonic acid have been studied in micellar media.^[26] Stability constants of the complexes of different stoichiometry formed by uranium (VI) with dicarboxylic acid and various types of ligands have been studied potentiometrically.^[27-30]

Vanadium is an element with a very rich chemistry that forms an enormous variety of compounds. The study of this element became an intensive field of research in the last decade after being identified in biological systems and related with potential therapeutic properties.^[31-51]

VO(II) being associated as important catalysts exerting defense and protection functions and being also a cofactor of nitrogenase in the fixation of dinitrogen. As a micronutrient in living organisms, vanadium is important to prevent growth retardation and skeletal deformations in animals, and possibly participates in regulation of enzymatic processes. Further some complexes of vanadyl have shown insulin-mimetic actions.^[52-54] A class of very promising complexes consists of neutral vanadyl complexes with bidentate anionic ligands L⁻ with composition VOL₂. Bis(maltolato)oxovanadium(IV) became the benchmark compound for the new molecules with anti-diabetic action^[55-60] and its derivative bis(ethylmaltolato) oxovanadium(IV) got to the clinical trials.^[61]

The transformation of a vanadium compound in the organism and the distribution between the bioligands of the blood is an important aspect of the drug metabolism and mechanism of action. These processes are related to the thermodynamic stability of the vanadium complexes and to the interaction with the proteins human serum apo-transferrin (HTF), human serum albumin (HAS), and immunoglobulins (IG) and low molecular mass ligands (lactic acid and citric acid) of the blood serum.^[62]

Realization of the significance of uranyl and vanadyl complexes prompted us to investigate several mixed ligand systems involving these cations.

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

1. UO₂(II) – Malonic acid – Nitrilotriacetic acid
2. UO₂(II) – Malonic acid – Iminodiacetic acid
3. VO(II) – Malonic acid – Nitrilotriacetic acid
4. VO(II) – Malonic acid – Iminodiacetic acid

In addition to these ternary systems, the following binary systems were also re-examined under identical conditions.

1. UO₂ (II)-Malonic acid
2. UO₂ (II)-Nitrilotriacetic acid
3. UO₂ (II)-Iminodiacetic acid
4. VO (II)-Malonic acid
5. VO (II)-Nitrilotriacetic acid
6. VO (II)-Iminodiacetic acid

3.2. Experimental and computational methods:

Experimental details and methods for computation of equilibrium constants are same as described in the last chapter. 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. 1-4. The prototatonation constants of the ligands are tabulated in table 2.1 (chapter-2) and the metal-ligand binary and ternary equilibrium constants are given in tables 3.1-3.6. The percent distributions of various species are given in tables 3.9-3.12 and the speciation curves are presented in figs. 5-8. 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 (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) by the methods as described in the previous chapters. These values are given in tables 3.7 - 3.8.

3.3. Curves and tables:

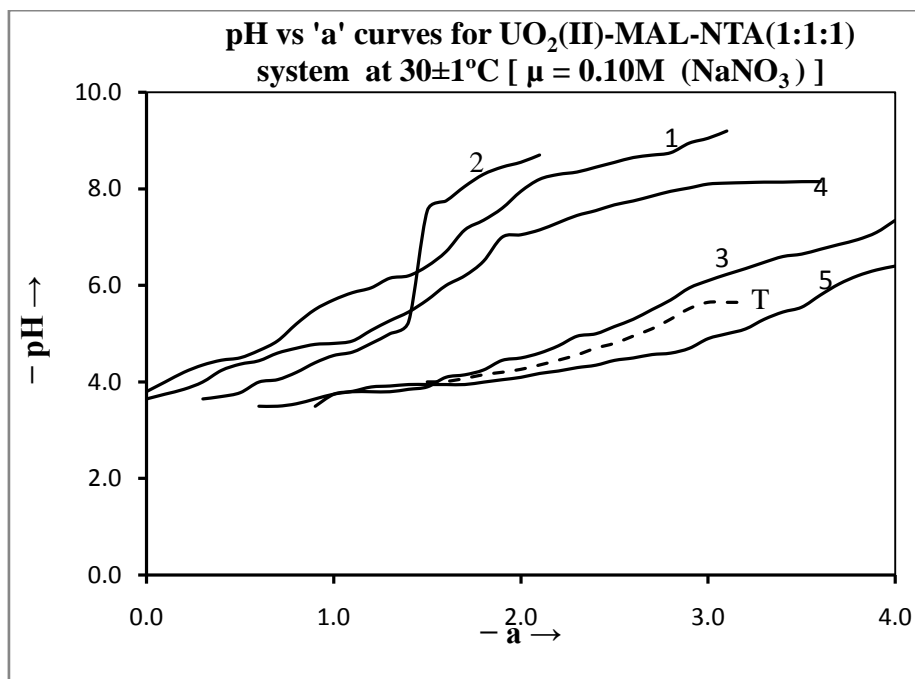


Fig. 1

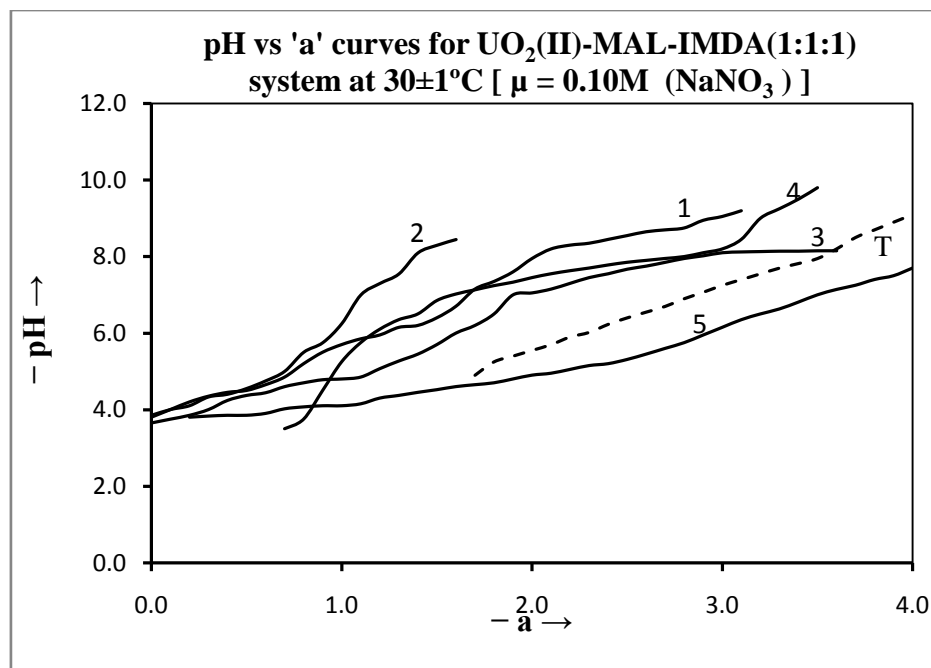


Fig. 2

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

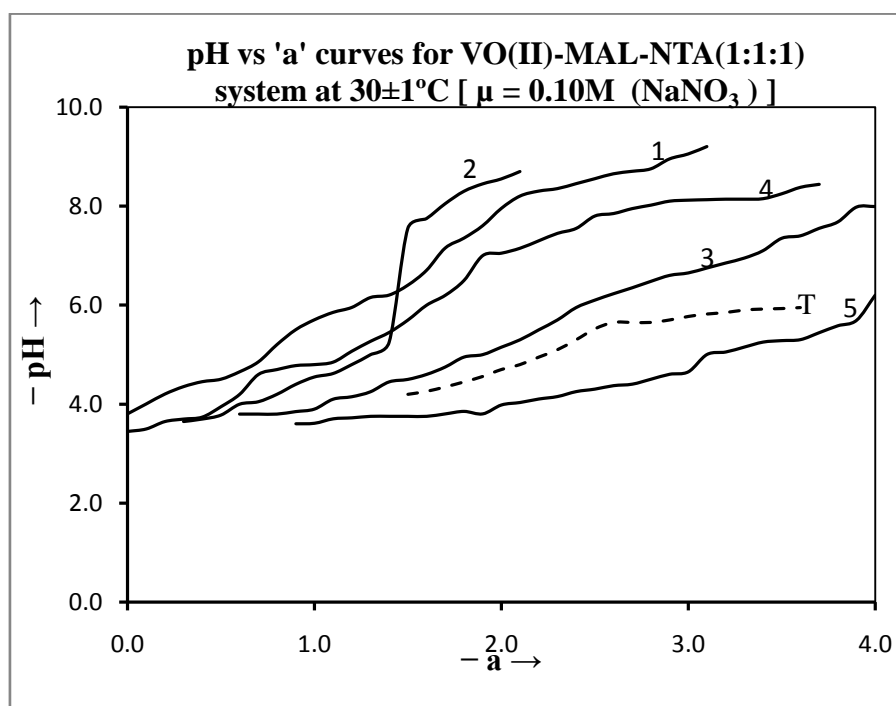


Fig. 3

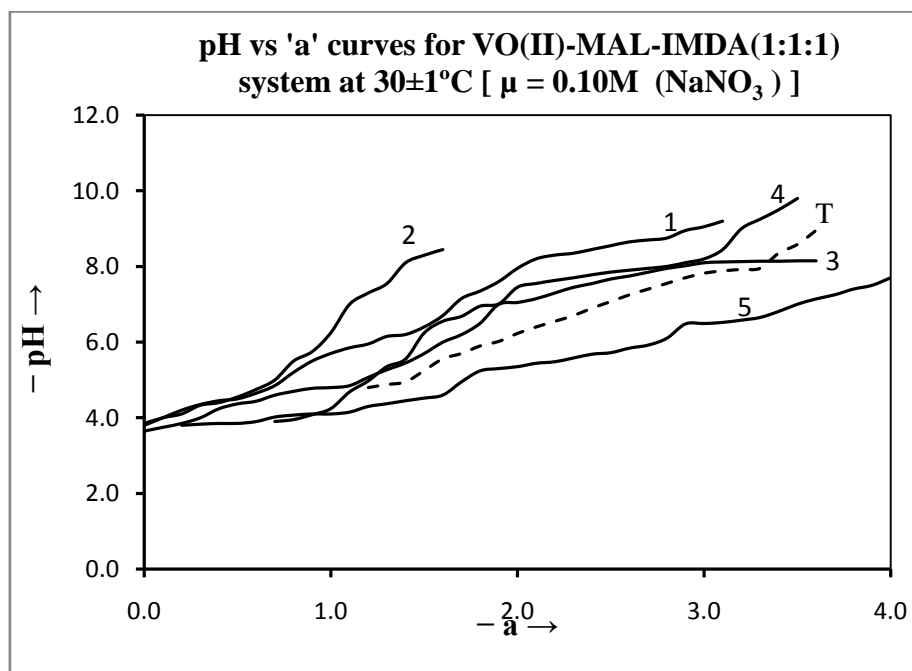


Fig. 4

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: 3.1
Formation constants of (1: 1) binary systems at different
temperatures and ionic strengths

Parameters	$UO_2(II)$ - Malonic Acid(MAL)											
	$20\pm 1^\circ C$				$30\pm 1^\circ C$				$40\pm 1^\circ C$			
	0.05M	0.10M	0.15M	$\mu \rightarrow 0$	0.05M	0.10M	0.15M	$\mu \rightarrow 0$	0.05M	0.10M	0.15M	$\mu \rightarrow 0$
$\log K_{MAH}^M$	5.05	5.02	5.00	5.25	4.96	4.90	4.84	5.10	4.82	4.79	4.70	5.03
$\log K_{MAH}^H$	-4.22	-4.16	-4.11	-4.40	-4.04	-4.00	-3.92	-4.28	-3.84	-3.79	-3.70	-4.00
$\log K_{MA}^H$	-5.30	-5.24	-5.20	-5.46	-5.22	-5.18	-5.12	-5.40	-5.20	-5.12	-5.04	-5.32
$\log \beta_{MAH}$	11.94	11.89	11.80	12.12	11.79	11.74	11.70	12.00	11.64	11.60	11.54	11.94
$\log \beta_{MA}$	6.54	6.49	6.41	6.76	6.42	6.39	6.30	6.64	6.38	6.30	6.21	6.56
	$UO_2(II)$ - Nitrilotriacetic Acid(NTA)											
$\log K_{MBH}^M$	3.50	3.43	3.36	3.82	3.30	3.23	3.16	3.62	3.18	3.10	3.02	3.45
$\log K_{MBH}^H$	-4.82	-4.76	-4.68	-4.99	-4.69	-4.62	-4.54	-5.02	-4.57	-4.50	-4.42	-4.89
$\log K_{MB}^H$	-5.98	-5.91	-5.84	-6.10	-5.79	-5.72	-5.61	-6.00	-5.54	-5.48	-5.40	-5.68
$\log \beta_{MBH}$	12.84	12.80	12.74	13.18	12.72	12.65	12.60	13.12	12.54	12.48	12.40	12.88
$\log \beta_{MB}$	8.81	8.75	8.68	9.10	8.61	8.56	8.48	8.96	8.46	8.42	8.38	8.76
	$UO_2(II)$ - Iminodiacetic Acid(IMDA)											
$\log K_{MBH}^M$	2.96	2.88	2.81	3.28	2.40	2.32	2.28	2.82	2.28	2.20	2.14	2.51
$\log K_{MBH}^H$	-5.03	-4.97	-4.90	-5.34	-4.74	-4.69	-4.60	-4.98	-4.50	-4.42	-4.36	-4.73
$\log K_{MB}^H$	-6.48	-6.40	-6.32	-6.80	-6.24	-6.19	-6.08	-6.45	-6.00	-5.91	-5.82	-6.10
$\log \beta_{MBH}$	8.52	8.45	8.39	8.84	8.20	8.12	8.08	8.68	8.08	8.00	7.95	8.40
$\log \beta_{MB}$	5.34	5.27	5.20	5.78	5.18	5.10	5.02	5.59	5.10	5.02	5.96	5.48

$$\log \beta_{MAH} = \log K_{MAH}^M + \log \beta_1^{HA}$$

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

$$\log \beta_{MA} = \log K_{MA}^M$$

$$\log \beta_{MB} = \log K_{MB}^M$$

Table: 3.2

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

Parameters	VO(II)- Malonic Acid(MAL)											
	20±1°C				30±1°C				40±1°C			
	0.05M	0.10M	0.15M	$\mu \rightarrow 0$	0.05M	0.10M	0.15M	$\mu \rightarrow 0$	0.05M	0.10M	0.15M	$\mu \rightarrow 0$
$\log K_{MAH}^M$	5.50	5.41	5.36	5.58	5.42	5.37	5.29	5.55	5.36	5.29	5.20	5.48
$\log K_{MAH}^H$	-4.36	-4.30	-4.24	-4.82	-4.18	-4.11	-4.04	-4.45	-3.94	-3.90	-3.82	-4.25
$\log K_{MA}^H$	-5.80	-5.75	-5.70	-5.96	-5.70	-5.62	-5.58	-5.87	-5.60	-5.54	-5.50	-5.65
$\log \beta_{MAH}$	12.82	12.78	12.68	13.00	12.74	12.71	12.64	12.95	12.70	12.64	12.58	12.85
$\log \beta_{MA}$	6.86	6.81	6.76	6.98	6.73	6.67	6.61	6.82	6.31	6.28	6.20	6.45
	VO(II)- Nitritotriacetic Acid(NTA)											
$\log K_{MBH}^M$	3.62	3.54	3.48	3.88	3.46	3.40	3.31	3.55	3.32	3.24	3.18	3.50
$\log K_{MBH}^H$	-4.95	-4.90	-4.86	-5.15	-4.80	-4.72	-4.69	-5.08	-4.60	-4.52	-4.47	-4.90
$\log K_{MB}^H$	-6.90	-6.84	-6.79	-7.07	-6.82	-6.75	-6.69	-6.95	-6.56	-6.50	-6.43	-6.75
$\log \beta_{MBH}$	13.50	13.45	13.40	13.65	13.38	13.32	13.26	13.42	13.14	13.10	13.03	13.24
$\log \beta_{MB}$	6.66	6.60	6.53	6.80	6.40	6.32	6.28	6.58	6.08	6.00	5.91	6.18
	VO(II)- Iminodiacetic Acid(IMDA)											
$\log K_{MBH}^M$	2.42	2.35	2.30	2.60	2.27	2.21	2.16	2.50	2.24	2.15	2.07	2.38
$\log K_{MBH}^H$	-4.06	-3.98	-3.91	-4.26	-3.93	-3.87	-3.76	-4.08	-3.66	-3.60	-3.51	-3.80
$\log K_{MB}^H$	-5.64	-5.58	-5.50	-5.84	-5.42	-5.36	-5.30	-5.68	-5.24	-5.18	-5.10	-5.50
$\log \beta_{MBH}$	8.42	8.36	8.30	8.60	8.30	8.32	8.26	8.55	8.10	8.00	7.94	8.25
$\log \beta_{MB}$	5.35	5.29	5.2	5.50	5.04	4.95	4.88	5.25	4.71	4.62	4.56	4.83

Table: 3.3

Formation constants of (1:1:1) $UO_2(II)$ -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
$\log K_{MABH_2}^M$	21.30	21.24	21.20	20.24	20.19	20.11	19.32	19.24	19.20
$\log K_{MABH_2}^{MAH}$	13.16	13.10	13.04	12.96	12.92	12.86	12.84	12.80	12.73
$\log K_{MABH_2}^{MBH}$	11.70	11.65	11.58	11.58	11.52	11.48	11.46	11.41	11.36
$\log K_{MABH}^M$	17.84	17.78	17.71	17.53	17.48	17.41	17.07	17.00	16.93
$\log K_{MABH}^{MAH}$	15.06	14.99	14.92	14.92	14.87	14.84	14.42	14.38	14.32
$\log K_{MABH}^{MBH}$	12.80	12.74	12.70	12.65	12.60	12.52	12.32	12.26	12.21
$\log K_{MABH}^{MA}$	12.42	12.38	12.32	12.29	12.21	12.18	12.12	12.00	11.96
$\log K_{MABH}^{MB}$	12.10	12.06	12.00	12.03	11.96	11.92	11.58	11.54	11.50
$\log K_{MAB}^{MA}$	14.82	14.76	14.71	14.54	14.49	14.42	14.36	14.30	14.25
$\log K_{MAB}^{MB}$	14.04	13.98	13.93	13.90	13.84	13.78	13.81	13.76	13.71
$\log K_{MABH_2}^H$	-3.79	-3.73	-3.67	-3.61	-3.53	-3.43	-3.48	-3.40	-3.32
$\log K_{MABH}^H$	-4.69	-4.65	-4.58	-4.30	-4.24	-4.19	-4.06	-4.00	-3.93
$\log K_{MABH}^H$	-5.94	-5.90	-5.82	-5.64	-5.60	-5.51	-5.47	-5.41	-5.36
$\log \beta_{MABH_2}$	35.18	35.10	35.02	34.92	34.89	34.83	34.70	34.62	34.50
$\log \beta_{MABH}$	29.94	29.89	29.82	29.70	29.64	29.58	29.19	29.14	28.08
$\log \beta_{MAB}$	19.84	19.78	19.72	19.61	19.58	19.50	19.22	19.18	22.12

$$\log \beta_{MABH_2} = \log K_{MABH_2}^M + \log \beta_1^{HA} + \log \beta_1^{HB}$$

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

$$\log \beta_{MAB} = \log K_{MAB}^M$$

Table: 3.4

**Formation constants of (1:1:1) $UO_2(II)$ -MAL-IMDA 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
$\log K_{MABH_2}^M$	17.21	17.14	17.08	16.87	16.80	16.71	16.32	16.25	16.20
$\log K_{MABH_2}^{MAH}$	11.30	11.26	11.20	10.43	10.37	10.32	10.34	10.30	10.28
$\log K_{MABH_2}^{MBH}$	12.49	12.42	12.36	11.75	11.68	11.62	11.65	11.60	11.55
$\log K_{MABH}^M$	18.99	18.92	18.87	18.69	18.61	18.56	18.44	18.38	18.11
$\log K_{MABH}^{MAH}$	12.70	12.64	12.59	12.22	12.13	12.08	12.08	12.02	11.98
$\log K_{MABH}^{MBH}$	15.94	15.88	15.82	15.80	15.74	15.68	15.73	15.66	15.60
$\log K_{MABH}^{MA}$	12.10	12.02	11.96	11.73	11.67	11.60	11.62	11.54	11.47
$\log K_{MABH}^{MB}$	11.83	11.78	11.70	11.12	11.07	11.01	11.04	11.00	10.96
$\log K_{MAB}^{MA}$	12.92	12.86	12.81	12.37	12.31	12.24	12.30	12.23	12.16
$\log K_{MAB}^{MB}$	12.20	12.12	12.07	12.02	11.95	11.90	11.89	11.80	11.74
$\log K_{MABH_2}^H$	-4.04	-3.98	-3.92	-3.80	-3.75	-3.70	-3.86	-3.81	-3.76
$\log K_{MABH}^H$	-4.70	-4.64	-4.59	-4.22	-4.15	-4.08	-4.11	-4.04	-4.00
$\log K_{MABH}^H$	-5.67	-5.60	-5.55	-5.48	-5.40	-5.34	-5.30	-5.22	-5.14
$\log \beta_{MABH_2}$	32.00	31.92	31.86	31.91	31.86	31.80	31.81	31.72	31.68
$\log \beta_{MABH}$	26.52	26.42	26.34	26.24	26.18	26.10	26.10	26.03	25.97
$\log \beta_{MAB}$	17.90	17.83	17.77	17.20	17.27	17.20	17.10	17.12	17.09

Table: 3.5

Formation constants of (1:1:1) $VO(II)$ -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
$\log K_{MABH_2}^M$	22.08	21.97	21.92	21.36	21.30	21.22	20.18	20.10	20.02
$\log K_{MABH_2}^{MAH}$	16.92	16.85	16.80	16.80	16.73	16.67	15.92	15.85	15.79
$\log K_{MABH_2}^{MBH}$	16.01	15.95	15.90	15.94	15.89	15.58	15.10	15.05	14.92
$\log K_{MABH}^M$	25.90	25.84	25.79	25.46	25.39	25.31	24.50	24.45	24.40
$\log K_{MABH}^{MAH}$	18.24	18.18	18.09	17.96	17.91	17.87	17.09	17.01	16.96
$\log K_{MABH}^{MBH}$	16.99	16.94	16.90	16.84	16.80	16.74	15.54	15.48	15.40
$\log K_{MABH}^{MA}$	13.21	13.14	13.08	12.02	12.97	12.89	12.18	12.14	12.10
$\log K_{MABH}^{MB}$	11.60	11.52	11.48	10.60	10.52	10.46	9.92	9.85	9.80
$\log K_{MAB}^{MA}$	15.31	15.26	15.20	14.41	14.36	14.28	13.72	13.64	13.59
$\log K_{MAB}^{MB}$	12.22	12.18	12.12	12.02	11.96	11.90	11.10	11.05	11.00
$\log K_{MABH_2}^H$	-4.16	-4.12	-4.08	-4.04	-3.96	-3.90	-3.50	-3.42	-3.38
$\log K_{MABH}^H$	-5.41	-5.35	-5.30	-4.70	-4.62	-4.58	-4.20	-4.12	-4.08
$\log K_{MABH}^H$	-6.84	-6.74	-6.54	-6.26	-6.10	-6.87	-6.81	-6.68	-6.50
$\log \beta_{MABH_2}$	39.30	39.24	39.20	38.35	38.27	38.22	38.16	38.10	38.04
$\log \beta_{MABH}$	35.30	35.26	35.20	34.30	34.24	34.20	33.21	33.14	33.10
$\log \beta_{MAB}$	27.51	27.42	27.38	26.40	26.35	26.30	25.30	25.26	25.20

Table: 3.6

Formation constants of (1:1:1) $VO(II)$ -MAL-IMDA 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
$\log K_{MABH_2}^M$	20.53	20.42	20.30	20.03	19.97	19.92	19.95	19.88	18.80
$\log K_{MABH_2}^{MAH}$	12.05	11.95	11.84	11.87	11.81	11.77	11.05	10.94	10.76
$\log K_{MABH_2}^{MBH}$	10.65	10.50	10.39	9.71	9.65	9.60	9.40	9.32	9.20
$\log K_{MABH}^M$	22.72	22.59	22.46	22.40	22.34	22.30	21.38	21.24	21.18
$\log K_{MABH}^{MAH}$	15.34	15.12	15.91	15.08	15.02	14.99	14.94	14.84	14.72
$\log K_{MABH}^{MBH}$	12.82	12.62	12.50	12.62	12.58	12.52	12.00	11.88	11.74
$\log K_{MABH}^{MA}$	11.45	11.18	11.02	11.12	11.08	11.02	10.80	10.65	10.42
$\log K_{MABH}^{MB}$	10.33	10.20	10.05	9.24	9.17	9.12	8.50	9.32	8.14
$\log K_{MAB}^{MA}$	8.98	8.90	8.80	7.10	7.01	6.98	6.55	6.45	6.30
$\log K_{MAB}^{MB}$	12.58	12.50	12.39	12.96	12.91	12.87	12.78	12.69	12.55
$\log K_{MABH_2}^H$	-4.12	-3.94	-3.83	-3.70	-3.61	-3.68	-3.47	-3.44	-3.56
$\log K_{MABH}^H$	-4.46	-4.32	-4.26	-4.45	-4.30	-4.16	-4.20	-4.08	-3.98
$\log K_{MABH}^H$	-5.98	-5.68	-5.60	-5.46	-5.35	-5.24	-5.10	-5.00	-4.89
$\log \beta_{MABH_2}$	34.80	34.64	34.53	34.30	34.24	34.20	34.18	34.10	34.00
$\log \beta_{MABH}$	31.10	30.96	30.82	30.88	30.84	30.80	30.54	30.42	30.28
$\log \beta_{MAB}$	22.62	22.48	22.32	22.38	22.33	22.30	22.65	22.42	22.32

Table: 3.7

Thermodynamic formation constants and thermodynamic parameters.

 $UO_2(II)$ -MAL-NTA

Parameter	20°C		30°C		40°C		$-\Delta H^\circ$ kJmol ⁻¹	ΔS° Jk ⁻¹ mol ⁻¹
	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹		
$\log K_{MAB}^M$	20.12	112.87	19.90	115.45	19.48	113.01	40.75	246.61
$\log K_{MABH_2}^M$	21.55	120.89	20.48	118.81	19.88	115.33	99.56	69.88
$\log K_{MABH_2}^{MAH}$	13.32	74.72	13.22	76.69	13.10	76.00	13.67	208.32
$\log K_{MABH_2}^{MBH}$	11.98	67.20	11.92	69.15	11.85	68.74	8.06	201.81
$\log K_{MABH_2}^H$	-4.06	-	-3.92	-	-3.68	-	-	-
$\log K_{MAHB}^M$	23.10	129.59	22.86	132.62	22.70	136.64	24.07	359.58
$\log K_{MABH}^M$	23.80	133.52	23.72	137.61	23.62	141.55	11.21	417.40
$\log K_{MABH}^{MAH}$	15.28	85.72	15.22	88.30	14.65	84.99	42.26	150.11
$\log K_{MABH}^{MBH}$	13.05	73.21	12.90	74.84	12.54	72.75	32.82	138.43
$\log K_{MABH}^{MA}$	12.95	72.65	12.60	73.10	12.34	71.59	36.92	121.20
$\log K_{MABH}^{MB}$	12.38	69.45	12.24	71.01	11.75	68.16	41.16	91.65
$\log K_{MABH}^H$	-4.96	-	-4.62	-	-4.32	-	-	-
$\log K_{MAB}^{MA}$	15.10	84.71	14.88	86.32	14.59	84.64	31.86	180.36
$\log K_{MAB}^{MB}$	14.25	79.94	14.10	81.80	13.98	81.10	16.41	216.55
$\log K_{MAB}^H$	-6.28	-	-5.95	-	-5.50	-	-	-

 $UO_2(II)$ -MAL-IMDA

Parameter	20°C		30°C		40°C		$-\Delta H^\circ$ kJmol ⁻¹	ΔS° Jk ⁻¹ mol ⁻¹
	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	log $K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹		
$\log K_{MAB}^M$	18.20	102.10	17.76	103.03	17.60	105.47	35.01	227.46
$\log K_{MABH_2}^M$	17.52	98.28	17.23	99.96	16.62	99.60	57.57	139.77
$\log K_{MABH_2}^{MAH}$	11.65	65.35	10.79	62.59	10.61	63.58	59.35	17.04
$\log K_{MABH_2}^{MBH}$	12.75	71.52	12.10	70.19	11.92	71.43	47.86	78.31
$\log K_{MABH_2}^H$	-4.32	-	-4.11	-	-4.00	-	-	-
$\log K_{MAHB}^M$	19.25	107.99	18.99	110.17	18.85	112.96	23.79	286.63
$\log K_{MABH}^M$	20.68	116.01	20.60	119.51	20.50	122.85	11.21	357.66
$\log K_{MABH}^{MAH}$	12.95	72.65	12.61	73.15	12.39	74.25	33.64	132.30
$\log K_{MABH}^{MBH}$	16.18	90.77	16.10	93.86	16.02	96.00	9.84	276.10
$\log K_{MABH}^{MA}$	12.39	69.50	12.19	70.72	11.90	71.31	30.77	132.30
$\log K_{MABH}^{MB}$	12.09	67.82	11.48	66.60	11.38	68.20	40.20	91.71
$\log K_{MABH}^H$	-4.98	-	-4.62	-	-4.48	-	-	-
$\log K_{MAB}^{MA}$	13.30	74.61	12.62	73.21	12.52	75.03	44.03	101.47
$\log K_{MAB}^{MB}$	12.51	70.18	12.36	71.70	12.18	72.99	20.51	169.45
$\log K_{MAB}^H$	-5.85	-	-5.63	-	-5.50	-	-	-

Table: 3.8

Thermodynamic formation constants and thermodynamic parameters.

VO(II)-MAL-NTA

Parameter	20°C		30°C		40°C		$-\Delta H^\circ$ kJmol ⁻¹	ΔS° Jk ⁻¹ mol ⁻¹
	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹		
$\log K_{MAB}^M$	27.68	149.67	26.55	154.03	25.42	152.39	139.09	53.99
$\log K_{MABH_2}^M$	22.15	124.26	21.58	125.19	20.34	121.83	115.09	30.06
$\log K_{MABH_2}^{MAH}$	17.10	95.93	16.95	98.53	16.10	96.48	66.33	103.39
$\log K_{MABH_2}^{MBH}$	16.14	90.54	16.12	93.52	15.30	91.69	57.16	116.79
$\log K_{MABH_2}^H$	-4.45	-	-4.40	-	-3.75	-	-	-
$\log K_{MAHB}^M$	27.92	155.51	27.60	160.12	27.51	164.86	12.71	487.10
$\log K_{MABH}^M$	26.04	146.08	25.60	148.52	24.75	148.32	82.19	219.04
$\log K_{MABH}^{MAH}$	18.38	103.11	18.07	104.83	17.18	102.96	77.81	88.07
$\log K_{MABH}^{MBH}$	17.05	95.65	16.90	98.04	15.75	64.39	77.13	60.79
$\log K_{MABH}^{MA}$	13.40	75.17	13.10	76.00	12.50	73.71	71.11	15.31
$\log K_{MABH}^{MB}$	11.80	66.19	10.85	62.94	10.05	60.23	106.67	-139.77
$\log K_{MABH}^H$	-5.85	-	-4.95	-	-4.58	-	-	-
$\log K_{MAB}^{MA}$	15.51	87.01	14.60	84.70	13.87	83.12	99.70	-44.99
$\log K_{MAB}^{MB}$	12.30	69.00	12.18	70.66	11.25	69.42	70.16	-1.14
$\log K_{MAB}^H$	-7.10	-	-6.98	-	-6.59	-	-	-

VO(II)-MAL-IMDA

Parameter	20°C		30°C		40°C		$-\Delta H^\circ$ kJmol ⁻¹	ΔS° Jk ⁻¹ mol ⁻¹
	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹	$\log K_{\mu \rightarrow 0}$	$-\Delta G^\circ$ kJmol ⁻¹		
$\log K_{MAB}^M$	22.92	128.58	22.45	130.24	21.85	126.76	66.74	211.00
$\log K_{MABH_2}^M$	20.77	116.52	20.15	116.90	20.05	116.32	40.75	255.99
$\log K_{MABH_2}^{MAH}$	12.37	69.39	11.95	69.32	11.35	65.84	64.00	18.57
$\log K_{MABH_2}^{MBH}$	11.00	61.71	9.88	57.31	9.65	55.98	57.16	-56.67
$\log K_{MABH_2}^H$	-4.60	-	-3.97	-	-3.84	-	-	-
$\log K_{MAHB}^M$	24.98	140.14	24.50	142.13	24.44	141.79	76.99	372.60
$\log K_{MABH}^M$	25.45	142.77	25.35	147.07	25.25	146.49	30.36	44.5.17
$\log K_{MABH}^{MAH}$	15.84	88.86	15.20	88.18	14.13	81.97	12.30	-65.10
$\log K_{MABH}^{MBH}$	13.13	73.66	12.72	73.79	12.20	70.77	108.18	53.42
$\log K_{MABH}^{MA}$	11.90	66.67	11.23	65.15	11.03	58.18	57.98	53.61
$\log K_{MABH}^{MB}$	10.80	60.58	9.63	55.86	9.20	53.17	50.32	-116.03
$\log K_{MABH}^H$	-4.98	-	-4.80	-	-4.65	-	-	-
$\log K_{MAB}^{MA}$	9.15	51.33	8.98	50.09	8.80	51.05	21.60	101.28
$\log K_{MAB}^{MB}$	12.78	71.69	12.15	70.48	12.06	69.96	40.61	103.39
$\log K_{MAB}^H$	-6.10	-	-5.90	-	-5.75	-	-	-

Representative Speciation Curves

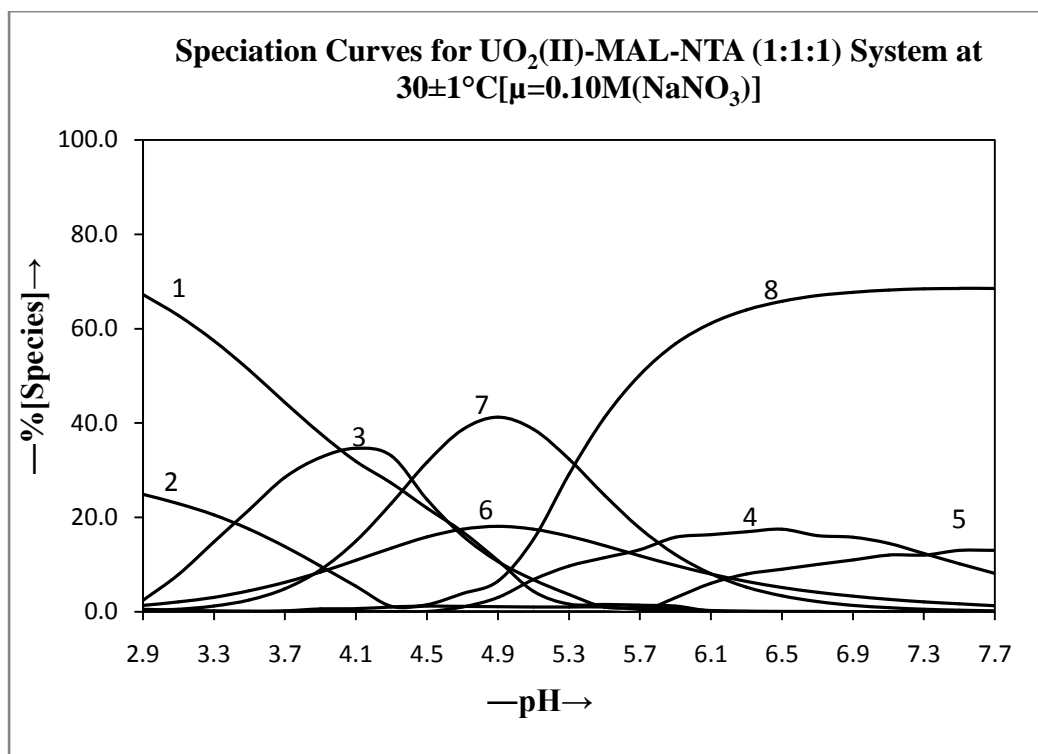


Fig. 6

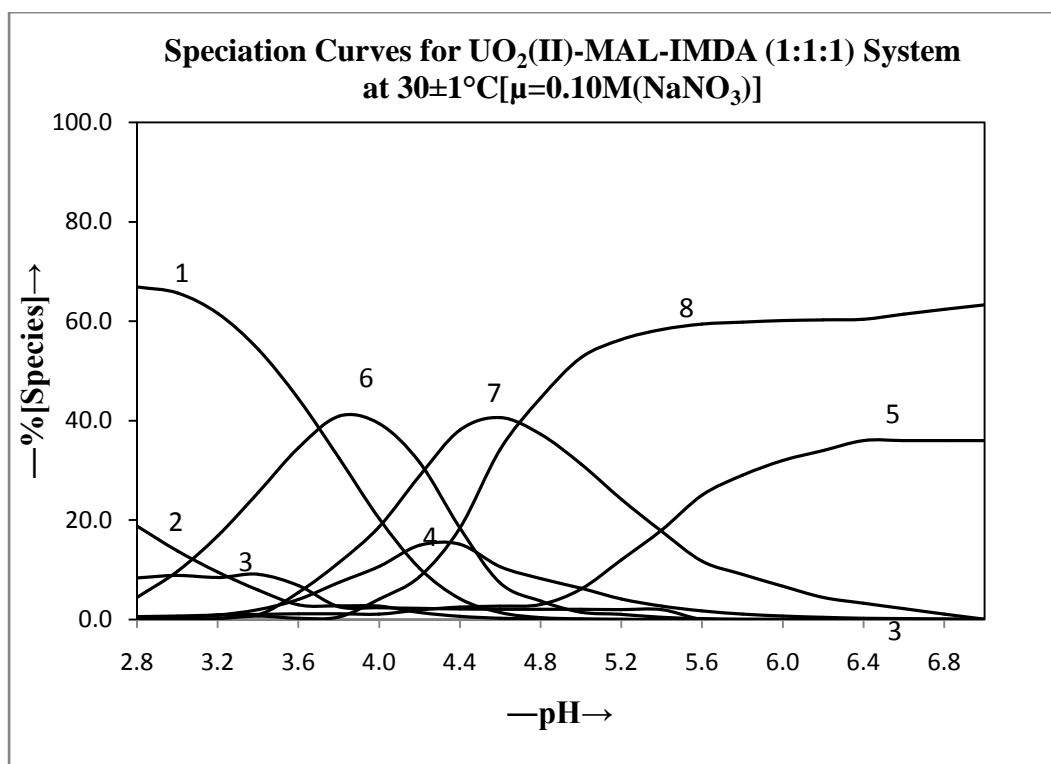


Fig. 7

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

Table: 3.9

Experimental values and concentration of different species for
 $UO_2(II)$ -MAL-NTA (1:1:1) system at $30\pm 1^\circ C$ [$\mu=0.10M(NaNO_3)$]

S.NO.	P ^H	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[MABH ₂]	[MABH]	[MAB]
1	2.9	0.60	67.23	24.92	2.42	0.00	0.54	1.36	0.24	0.00
2	3.1	0.95	62.80	22.95	7.84	0.00	0.33	2.06	0.54	0.01
3	3.3	1.02	57.49	20.53	14.77	0.00	0.19	3.06	1.19	0.02
4	3.5	1.10	51.19	17.46	21.66	0.00	0.11	4.43	2.48	0.07
5	3.7	1.15	44.39	13.80	28.48	0.00	0.06	6.21	4.87	0.21
6	3.9	1.18	37.76	9.71	32.71	0.00	0.03	8.40	8.90	0.62
7	4.1	1.22	31.91	5.42	34.65	0.00	0.02	10.91	14.99	0.64
8	4.3	1.28	27.27	1.17	33.06	0.05	0.01	13.51	23.00	1.00
9	4.5	1.32	21.99	1.23	23.78	0.03	0.00	15.86	31.69	1.45
10	4.7	1.36	16.93	1.14	16.12	1.01	0.00	17.51	38.62	3.86
11	4.9	1.39	10.82	1.09	10.63	3.01	0.00	18.09	41.22	6.52
12	5.1	1.43	4.34	1.00	6.78	6.84	0.00	17.52	38.64	15.37
13	5.3	1.46	1.61	0.99	3.67	9.66	0.00	16.02	32.33	29.18
14	5.5	1.50	1.54	0.99	0.98	11.43	0.00	14.01	24.72	41.09
15	5.7	1.58	1.38	0.53	0.86	13.14	0.00	11.85	17.69	50.23
16	5.9	1.66	1.20	0.28	0.64	15.77	3.00	9.81	12.11	56.76
17	6.1	1.76	0.10	0.14	0.27	16.37	6.00	7.99	8.04	61.15
18	6.3	1.86	0.00	0.07	0.11	16.94	8.00	6.45	5.24	64.00
19	6.5	1.95	0.00	0.04	0.04	17.52	9.00	5.17	3.37	65.80
20	6.7	1.98	0.00	0.02	0.02	16.12	10.00	4.13	2.15	67.00
21	6.9	2.02	0.00	0.01	0.01	15.78	11.00	3.29	1.37	67.73
22	7.1	2.04	0.00	0.00	0.00	14.51	12.00	2.62	0.87	68.20
23	7.3	2.08	0.00	0.00	0.00	12.31	12.00	2.08	0.55	68.45
24	7.5	2.14	0.00	0.00	0.00	10.18	13.00	1.65	0.35	68.55
25	7.7	2.22	0.00	0.00	0.00	8.10	13.00	1.30	0.22	68.53

Table: 3.10

**Experimental values and concentration of different species for
 $UO_2(II)$ -MAL-IMDA (1:1:1) system at $30 \pm 1^\circ C$ [$\mu=0.10M(NaNO_3)$]**

S.NO.	P ^H	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[MABH ₂]	[MABH]	[MAB]
1	2.8	0.09	66.87	18.76	8.33	0.58	0.15	4.45	0.15	0.01
2	3.0	0.35	65.67	13.78	8.85	0.72	0.38	9.70	0.38	0.05
3	3.2	0.59	61.53	9.52	8.44	0.87	0.89	16.83	0.89	0.19
4	3.4	0.79	54.31	5.91	9.09	1.01	1.97	25.54	0.97	0.68
5	3.6	0.89	44.37	2.93	6.81	1.12	4.05	34.55	5.45	0.22
6	3.8	1.02	32.49	2.74	2.57	1.16	7.44	40.89	11.44	0.48
7	4.0	1.44	20.27	2.68	2.38	1.09	10.66	39.37	18.66	4.10
8	4.2	1.69	10.31	1.40	2.23	1.90	14.90	31.58	28.90	8.60
9	4.4	1.84	4.16	0.63	2.13	2.49	15.12	18.42	38.12	18.43
10	4.6	1.94	1.38	0.25	2.07	2.70	10.60	7.32	40.60	34.26
11	4.8	1.96	0.40	0.09	2.04	3.03	8.25	3.70	37.25	44.52
12	5.0	2.28	0.11	0.03	2.02	6.12	6.28	1.44	31.28	52.63
13	5.2	2.32	0.03	0.01	2.01	12.06	4.13	1.01	24.13	56.30
14	5.4	2.38	0.01	0.00	2.01	18.03	2.66	0.41	17.66	58.32
15	5.6	2.45	0.00	0.00	0.00	25.01	1.70	0.17	11.70	59.43
16	5.8	2.65	0.00	0.00	0.00	29.01	1.08	0.07	9.08	59.81
17	6.0	2.74	0.00	0.00	0.00	32.00	0.68	0.03	6.68	60.09
18	6.2	2.79	0.00	0.00	0.00	34.00	0.43	0.01	4.43	60.27
19	6.4	2.82	0.00	0.00	0.00	36.00	0.27	0.00	3.27	60.38
20	6.6	2.88	0.00	0.00	0.00	36.00	0.17	0.00	2.17	61.38
21	6.8	2.93	0.00	0.00	0.00	36.00	0.11	0.00	1.11	62.35
22	7.0	2.99	0.00	0.00	0.00	36.00	0.07	0.00	0.07	63.29

Representative Speciation Curves

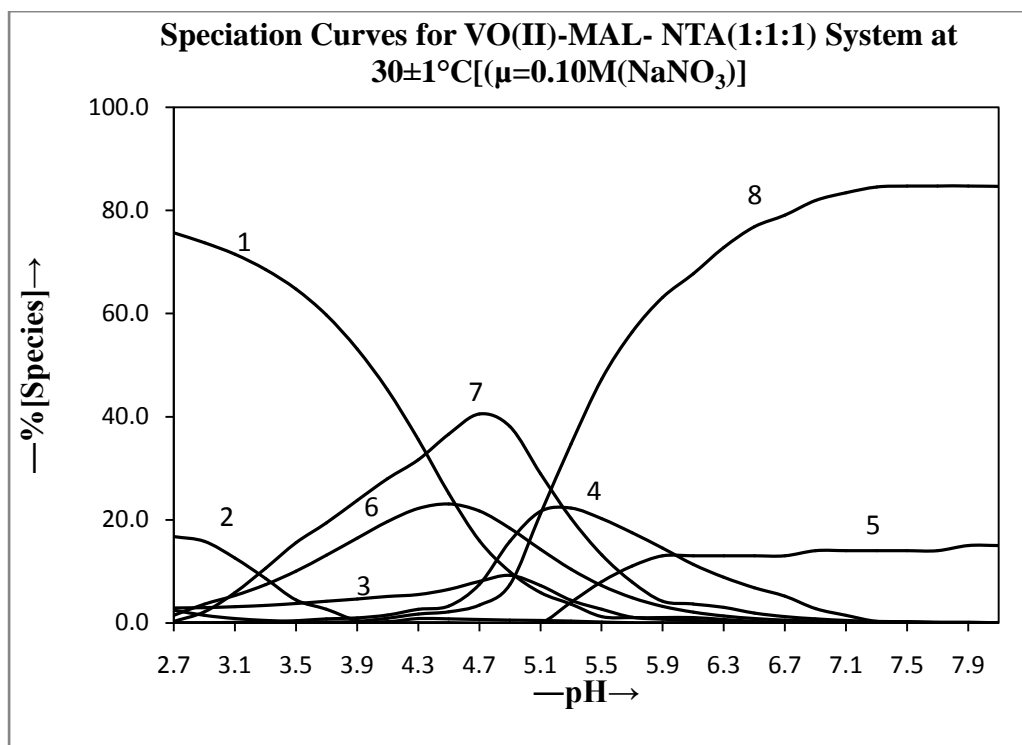


Fig. 8

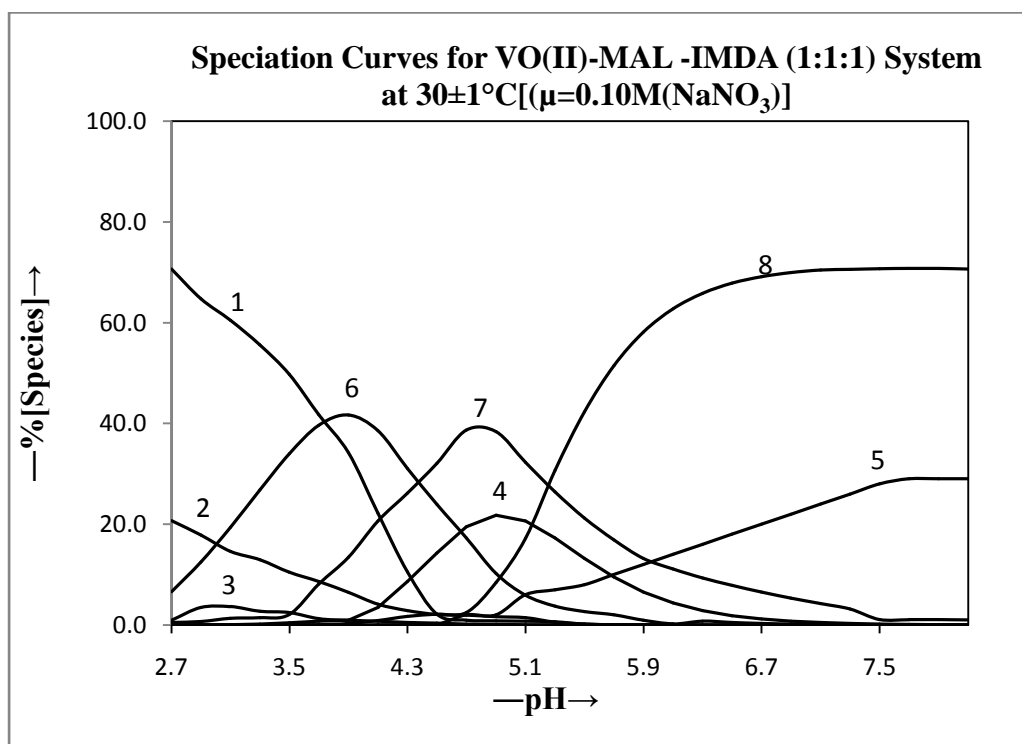


Fig. 9

Where, Curve 1: [M]; 2 [MAH]; 3 [MA]; 4 [MBH]; 5 [MB]; 6 [MABH₂]; 7 [MABH]; 8 [MAB]

Table: 3.11

**Experimental values and concentration of different species for
VO(II)-MAL-NTA (1:1:1) system at $30\pm 1^\circ C$ [$\mu=0.10M(NaNO_3)$]**

S.NO.	P ^H	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[MABH ₂]	[MABH]	[MAB]
1	2.7	0.30	75.67	16.72	2.87	0.01	2.46	1.46	0.31	0.00
2	2.9	0.72	73.72	15.80	2.98	0.03	1.45	3.65	2.18	0.00
3	3.1	0.95	71.48	12.58	3.16	0.07	0.84	5.29	5.84	0.00
4	3.3	1.12	68.55	8.62	3.41	0.18	0.47	7.43	10.62	0.01
5	3.5	1.22	64.73	4.44	3.74	0.42	0.25	10.06	15.53	0.02
6	3.7	1.33	59.70	2.62	4.17	0.76	0.13	13.13	19.39	0.08
7	3.9	1.54	53.14	0.45	4.65	0.96	0.07	16.43	23.77	0.27
8	4.1	1.62	45.15	0.25	5.13	1.50	0.03	19.66	28.00	0.90
9	4.3	1.68	35.56	0.85	5.49	2.61	0.01	22.18	31.65	1.72
10	4.5	1.78	25.12	0.75	6.51	3.25	0.01	23.07	36.64	2.14
11	4.7	1.83	15.96	0.65	8.06	7.48	0.00	21.68	40.53	3.48
12	4.9	1.92	9.88	0.55	9.22	15.81	0.00	18.35	38.08	7.45
13	5.1	2.01	5.84	0.44	7.24	21.65	0.00	14.25	28.91	21.21
14	5.3	2.04	3.61	0.32	4.35	22.29	4.00	10.39	20.26	34.67
15	5.5	2.09	1.19	0.16	2.63	20.22	8.00	7.23	13.19	47.28
16	5.7	2.12	1.00	0.06	1.10	17.50	11.00	4.87	7.91	56.43
17	5.9	2.16	1.00	0.04	0.72	14.52	13.00	3.21	4.19	63.11
18	6.1	2.22	1.00	0.02	0.47	11.35	13.00	2.08	3.66	67.73
19	6.3	2.26	0.65	0.00	0.30	8.84	13.00	1.34	3.00	72.83
20	6.5	2.32	0.30	0.00	0.19	6.83	13.00	0.85	1.91	76.82
21	6.7	2.36	0.00	0.00	0.12	5.17	13.00	0.54	1.21	79.11
22	6.9	2.39	0.00	0.00	0.08	2.75	14.00	0.34	0.77	81.92
23	7.1	2.41	0.00	0.00	0.05	1.47	14.00	0.22	0.49	83.44
24	7.3	2.54	0.00	0.00	0.03	0.30	14.00	0.14	0.31	84.56
25	7.5	2.58	0.00	0.00	0.02	0.19	14.00	0.09	0.19	84.71
26	7.7	2.63	0.00	0.00	0.01	0.12	14.00	0.05	0.12	84.76
27	7.9	2.68	0.00	0.00	0.01	0.08	15.00	0.03	0.08	84.76
28	8.1	2.77	0.00	0.00	0.00	0.05	15.00	0.02	0.05	84.65

Table: 3.12

**Experimental values and concentration of different species for
VO(II)-MAL-IMDA (1:1:1) system at $30\pm 1^\circ C$ [$\mu=0.10M(NaNO_3)$]**

S.NO.	p ^H	TITRE	[M]	[MAH]	[MBH]	[MA]	[MB]	[MABH ₂]	[MABH]	[MAB]
1	2.7	0.3	70.67	20.72	0.96	0.01	0.00	6.62	0.46	0.00
2	2.9	0.72	64.72	17.83	3.50	0.03	0.00	12.53	0.65	0.00
3	3.1	0.95	60.48	14.58	3.65	0.07	0.00	19.39	1.29	0.00
4	3.3	1.12	55.55	12.92	2.74	0.18	0.00	26.77	1.43	0.01
5	3.5	1.22	49.73	10.44	2.49	0.42	0.00	34.00	2.06	0.02
6	3.7	1.33	41.70	8.62	1.23	0.76	0.01	39.65	8.13	0.08
7	3.9	1.54	34.14	6.45	0.97	0.96	0.01	41.64	13.43	0.27
8	4.1	1.62	22.15	4.12	0.73	3.51	0.02	38.53	20.66	0.90
9	4.3	1.68	10.56	2.85	0.52	8.61	0.05	31.08	26.18	1.72
10	4.5	1.78	2.12	2.05	0.34	14.25	0.10	23.91	32.07	2.14
11	4.7	1.83	0.96	1.95	0.20	19.48	2.00	17.26	38.68	2.48
12	4.9	1.92	0.82	1.65	0.11	21.81	2.00	10.19	38.35	8.45
13	5.1	2.01	0.72	1.44	0.05	20.65	6.00	5.91	32.25	17.21
14	5.3	2.04	0.61	0.53	0.02	17.29	7.00	3.72	26.39	30.67
15	5.5	2.09	0.19	0.16	0.01	13.22	8.00	2.66	21.23	42.28
16	5.7	2.12	0.05	0.06	0.00	9.50	10.00	2.00	16.87	51.43
17	5.9	2.16	0.01	0.04	0.00	6.52	12.00	0.91	13.21	58.11
18	6.1	2.22	0.00	0.02	0.00	4.35	14.00	0.21	11.08	62.73
19	6.3	2.26	0.00	0.00	0.00	2.84	16.00	0.77	9.34	65.83
20	6.5	2.32	0.00	0.01	0.00	1.83	18.00	0.49	7.85	67.82
21	6.7	2.36	0.00	0.00	0.00	1.17	20.00	0.31	6.54	69.11
22	6.9	2.39	0.00	0.01	0.00	0.75	22.00	0.19	5.34	69.92
23	7.1	2.41	0.00	0.00	0.00	0.47	24.00	0.12	4.22	70.44
24	7.3	2.54	0.00	0.00	0.00	0.30	26.00	0.08	3.14	70.56
25	7.5	2.58	0.00	0.00	0.00	0.19	28.00	0.05	1.09	70.71
26	7.7	2.63	0.00	0.00	0.00	0.12	29.00	0.04	1.05	70.76
27	7.9	2.68	0.00	0.01	0.00	0.08	29.00	0.03	1.03	70.76
28	8.1	2.77	0.00	0.00	0.00	0.05	29.00	0.02	1.02	70.65

Table: 3.13

Value of $\Delta \log K$ for ternary complexes.

Parameters	20°C		30°C		40°C	
	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$
$UO_2(II)$-MAL-NTA						
$\log \beta_{MABH_2}$	35.32	10.02	34.83	9.71	34.92	10.10
$\log \beta_{MABH}$	30.18	10.24	29.38	9.61	29.34	9.90
$\log \beta_{MAB}$	19.72	3.75	19.50	3.89	19.28	3.96
$UO_2(II)$-MAL-IMDA						
$\log \beta_{MABH_2}$	32.28	11.32	32.21	11.53	32.13	11.79
$\log \beta_{MABH}$	26.76	11.16	26.62	11.30	26.42	11.46
$\log \beta_{MAB}$	18.20	5.66	17.76	5.53	17.60	5.56
$VO(II)$-MAL-NTA						
$\log \beta_{MABH_2}$	39.50	12.95	38.52	12.15	38.30	12.21
$\log \beta_{MABH}$	35.45	14.92	34.36	14.19	33.35	13.66
$\log \beta_{MAB}$	27.68	13.90	26.55	13.22	25.42	12.79
$VO(II)$-MAL-IMDA						
$\log \beta_{MABH_2}$	35.00	13.40	34.75	13.25	34.38	13.18
$\log \beta_{MABH}$	31.35	15.77	30.95	15.65	30.88	16.18
$\log \beta_{MAB}$	22.92	10.44	22.45	10.45	21.85	10.57

3.4. Results and discussion:

The titration curves for UO₂(II)/VO(II) – ligand ‘A’ – ligand ‘B’ systems (where ligand ‘A’ = malonic acid and ligand ‘B’ = nitrilotriacetic acid/iminodiacetic acid) are given in figs 1-4

Curves 1 to 5 represent the ligand A, ligand B, metal-ligand A, metal-ligand B and metal-ligand A-ligand B titration curves respectively. Curve ‘T’ represents theoretical composite curve in all the figs.

As evident from figs. 1-4 the deviation of metal–ligand curves (curves 3 and 4) from ligand curves suggests the formation of binary complexes. Formation of ternary complexes is evident from mixed ligand titration curve 5 which is placed on right hand side of binary metal-ligand titration curves 3 and 4 in the pH range ≈ 4.0 to 8.0, thereby suggesting that the additional alkali is required to neutralize the protons liberated by two ligand simultaneously. The non-superimposable nature of theoretical composite curve from the initial pH shows that the metal ion interacts with both the ligand simultaneously which further supports the formation of mixed ligand complexes. A weak inflection at ‘a’ = 2.0 in curve 5 indicates the formation of biprotonated (MABH₂) ternary complex upto pH ≈ 4.0 . Above this pH deprotonation of MABH₂ lead to the formation MABH (pH ≈ 6.0) which is further deprotonated to form MAB complex (pH ≈ 8.0). Formation of MAB is alternatively considered according to equilibria given in equation 18 of chapter - 2. 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 ^[63-69] which have already been discussed in the previous chapter. From tables 4.7 and 4.8 it is evident that $\log K_{MAB}^{MA}$ and $\log K_{MAB}^{MB}$ are almost same which again indicates that the

ligand A and B coordinate simultaneously leading to the formation of MAB complex.

Speciation curves are obtained for various systems which are presented in figs. 5-8. Speciation curves of all the systems under investigation in this chapter are seen to follow the same trend. Ternary complexes $MABH_2$, $MABH$ and MAB are formed. Formation of $MABH_2$ and $MABH$ species are evident, but is confined up to $pH \approx 5.5$ and its percentage remain less than 30%. Nonprotonated ternary complexes MAB comes into existence up to $pH \approx 5.5$ and its concentration increases appreciably. It is observed that the percentage of MAB species is maximum $\approx < 75\%$ extending up to $pH \approx 7.0$ 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 vanadyl complexes is found to be more than that of uranyl complexes. This can be attributed to the presence of two axial oxygen atoms on uranium in case of uranyl which poses a double steric restriction for approach of the ligand to the metal ion in comparison to single axial oxygen on vanadium in vanadyl.^[70-71]

The positive values of $\Delta \log K$ show that all mixed ligand complexes formed are more stable than their corresponding binary complexes. This is in agreement with earlier reports.^[72-74] Values are given in table 3.13.

The metal-ligand stability constant $\log K$ decrease with an increase in temperature and ionic strengths. The negative value of enthalpy change (ΔH°) for the complexation suggests that all the reactions are exothermic and favorable at lower temperature. The negative value of ΔG° indicates that both dissociation of the ligand and formation of metal-ligand complex are spontaneous process. The positive ΔS° values for most of the

metal complexes indicate that the formations of these complexes are entropically favoured, while negative change in entropy (ΔS°) values for some metal complexes suggest a highly solvated metal complexes.

3.5. References:

1. K.W. Bagnall, G. Wilkinson, R.D. Gillard, J.A. Mc. Cleverty
Comprehensive Coordination Chemistry, Pergamon Press, Oxford
Eds., 3, 1129, (1987).
2. S. A. Abdel-Latif, Synth. React. Inorg. Met.- Org. Nano-Met.
Chem. 31, 1355 (2001).
3. A.D. Keramidas, M.P. Rikkou, C. Drouza, C.P. Raptopoulou, A.
Terzis, I. Pashalidas, J. Radiochim. Acta, 90, 549 (2002).
4. O. Signorni, and E.R. Dockal, Polyhedron, 15(2), 245(1996).
5. M.P. Jensen, K.L. Nash, L.R. Morss, E.H. Appleman, M.A.
Schmidt, J.S. Gaffney, N.A. Marley, S.B. Clark, (Eds.), Am.
Chem. Soc. Symposium Series, Washington, 651, 272(1996).
6. P.W. Swarzenski, B.A. McKee, J.M. Skei, J.F. Todd, Mar. Chem.
67, 181(1999).
7. C. Cantaluppi, S. Degetto, Ann. Chim. 90, 665(2000).
8. M.E. Moustafa, Spectroscopy Lett. 38, 23 (2005).
9. M.M. Mashaly, T.M. Ismail, S.B. El-Marghy, H.A. Habib, J.
Coord. Chem. 57, 1099 (2004).
10. G.A. Thakur, S.V. Athlekar, S.R. Dharwadkar, M.M. Shaikh, Acta
Pol. Pharm. Drug Res. 64, 9(2007).

11. C. De Stefano, A. Gianguzza, T. Leggio, S. Sammartano, *J. Chem. Eng. Data*, 47(3), 533 (2002).
12. A. Gianguzza, D. Milea, F.J. Millero, S. Sammartano, *Mar. Chem.* 85, 103 (2004).
13. F. Crea, D. Milea, S. Sammartano, *Talanta*, 65 229 (2005).
14. F. Crea, D. Milea, S. Sammartano, *Ann. Chim.*, 95, 767 (2005).
15. R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, N.H. Rand, F.J. Mompean, M. Illemassene, C. Domenech-Orti, K. Ben Said (Eds.), France, (2003).
16. F. Crea, A. De Robertis, S. Sammartano, *Ann. Chim.*, 93, 1027 (2003).
17. C. De Stefano, A. Gianguzza, A. Pettignano, S. Sammartano, *Biophys. Chem.* 117, 147(2005).
18. A. Gianguzza, A. Pettignano, S. Sammartano, *J. Chem. Eng. Data* 50, 1576 (2005).
19. S. Berto, F. Crea, P.G. Daniele, C. De Stefano, E. Prenesti, S. Sammartano, *Ann. Chim.*, (2006).
20. F. Crea, C. De Stefano, A. Pettignano, S. Sammartano, *Thermochim. Acta*, 414, 185 (2004).
21. J. Buffle, *Complexation Reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood, Chichester, (1988).

22. W. Stumm, J.J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, 3rd Eds., John Wiley & Sons Inc, New York, (1996).
23. D.M. Templeton, F. Ariese, R. Cornelis, L.G. Danielsson, H. Muntau, H.P. Van Leeuwen, R. Lobinski, Pure Appl. Chem. 72 (8), 1453 (2000).
24. B.I. Escher, L. Sigg, in: H.P. Van Leeuwen, W.K. Oster, Physicochem. Kinetics and Transport Biointerfaces, John Wiley & Sons, New York, 205 (2004).
25. De Stefano, A. Gianguzza , D. Milea, A. Pettignano , S. Sammartano, J. Alloys and Compounds, 424, 93 (2006)
26. B. B. V. Sailaja, T. Kebede, G. N. Rao, M. S. P. Rao, Indian J. Chem., 40A, 852(2001).
27. K. S. Rajan, A. E. Martell, J. Inorg. Nucl. Chem., 26, 789(1964).
28. S. S. Patil, and M. M. Shaikh, Acta Polo. Pharmaceutica Drug Res., 69(4), 679 (2012).
29. A. Didarul Chowdhury, N. Mohammad Uddin and Md. Akter H. Sarker Chiang Mai, J. Sci. 35(3), 483(2008)
30. F. Crea, A. De Robertis, C. De Stefano, S. Sammartano, J. Solution Chem. 36, 479(2007).
31. K. H. Thompson, C. Orvig, Coord. Chem. Rev., 219, 1033(2001).

32. Y. Shechter, I. Goldwasser, M. Mironchik, M. Fridkin, D. Gefel, *Coord. Chem. Rev.*, 237, 3(2003).
33. H. Sakurai, Y. Yoshikawa, H. Yasui, *Chem. Soc. Rev.* 37, 2383(2008).
34. T. Kiss, T. Jakusch, D. Hollender, A. Dörnyei, Vanadium: The Versatile Metal; K. Kustin, J. Costa Pessoa, D.C. Crans, (Eds) *Am. Chem. Soc.*, Washington DC, 974, 323(2007).
35. T. Kiss, T. Jakusch, D. Hollender, A. Dörnyei, E. A. Enyedy, J. Costa Pessoa, H. Sakurai, A. Sanz-Medel, *Coord. Chem. Rev.*, 252, 1153(2008).
36. T. Jakusch, J. Costa Pessoa, T. Kiss, *Coord. Chem. Rev.*, 255, 2218(2011).
37. T. Kiss, T. Jakusch, B. Gyurcsik, A. Lakatos, É. A. Enyedy, É. Sija, *Coord. Chem. Rev.*, 256, 125(2012).
38. T. Jakusch, D. Hollender, E. A. Enyedy, C. S. Gonzalez, M. Montes-Bayon, A. Sanz-Medel, J. Costa Pessoa, I. Tomaz, T. Kiss, *Dalton Trans.*, 2428(2009).
39. I. Correia, T. Jakusch, E. Cobbinna, S. Mehtab, I. Tomaz, N. V. Nagy, A. Rockenbauer, J. Costa Pessoa, T. Kiss, *Dalton Trans.*, 41, 6477(2012).

40. S. Mehtab, G. Gonçalves, S. Roy, A. I. Tomaz, T. Santos-Silva, M. F. A. Santos, M. J. Romão, T. Jakusch, T. Kiss, J. Costa Pessoa, *Inorg. Biochem.*, 121, 187(2013).
41. G. Gonçalves, A. I. Tomaz, I. Correia, L. F. Veiros, M. M. C. A. Castro, F. Avecilla, L. Palacio, M. Maestro, T. Kiss, T. Jakusch, M. H. V. Garcia, J. Costa Pessoa, *Dalton Trans.*, 42, 11841(2013).
42. D. Sanna, G. Micera, E. Garribba, *Inorg. Chem.*, 49, 174(2010).
43. D. Sanna, G. Micera, E. Garribba, *Inorg. Chem.*, 50, 3717(2011).
44. D. Sanna, G. Micera, E. Garribba, *Inorg. Chem.*, 52, 11975(2013).
45. D. Sanna, K. Varnagy, S. Timari, G. Micera and E. Garribba, *Inorg. Chem.*, 50, 10328(2011).
46. D. Sanna, M. Serra, G. Micera, and E. Garribba, *Inorg. Chem.*, 53, 1449(2014).
47. S. Kundu, S. Maity, T. Weyhermüller, and P. Ghosh, *Inorg. Chem.*, 52, 7417(2013).
48. T. Koleša-Dobravc, E. Lodyga-Chruscinska, M. Symonowicz, D. Sanna, A. Meden, F. Perdih, and E. Garribba *Inorg. Chem.*, 53, 7960(2014).
49. J. Briucal, V. Lubes, M. L. Araujo, F. Brito, *J. Chil. Chem. Soc.*, 49, 285(2004).

50. D. C. Crans, J. J. Smee, E. Gaidamauskas, L. Yang, *Chem. Rev.*, 104, 849(2004).
51. A. Butler, J. V. Walker, *Chem. Rev.*, 93, 1937(1993).
52. M. Rangel, A. Leite, and M. J. Amorim, *Inorg. Chem.*, 45, 8086(2006).
53. D. Rehder, *Angew. Chem. Int. Ed. Engl.*, 30, 148(1991)
54. D. Rehder, *Biometals*, 5, 3(1992).
55. A.M. Cortizo, S.B. Etcheverry, *Mol. Cell. Biochem.* 145, 97 (1995),
56. A. L. Ramalho Mercê, I. H. Zamuner Spir, M. J. Oruña Salmón, R. A. Giannoni, and A. S. Mangrich, *J. Braz. Chem. Soc.*, 10(6), 463 (1999).
57. K. H. Thompson, C. Orvig, *J. Inorg. Biochem.*, 100, 1925 (2006).
58. K.H. Thompson, J. H. Mc Neill, C. Orvig, *Chem. Rev.*, 99, 2561(1999).
59. K. H. Thompson, D. Liboiron Barry, R.H. Graeme,; C. Orvig, *Medicinal Inorganic Chemistry*; J. L. Sessler, , S. R. Doctrow, T. J. McMurry, , S. J. Lippard, , (Eds.) *Am. Chem. Soc*, Washington, DC, 903, 384(2005).
60. K. H. Thompson, C. Orvig, *Metal Ions in Biological Systems*, H. Sigel, A. Sigel, (Eds.), *Marcel Dekker*, New York, 41, 221(2004).

61. K. H. Thompson, J. Lichter, C. LeBel, M. C. Scaife, J. H. McNeill, C. Orvig, *J. Inorg. Biochem.*, 103, 554(2009).
62. D. Sanna, G. Micera, E. Garribba, *Inorg. Chem.*, 48, 5747(2009).
63. D. Legett, *Computational Methods of Calculation of Stability Constants*, Plenum Press, New York, (1985).
64. S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, 74, 5052 (1952).
65. S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, 77, 1477 (1955).
66. R. Nayan and A. K. Dey, *Indian J. Chem.*, 14A, 892 (1976).
67. I. G. Sayce, *Talanta*, 15, 1397(1968).
68. I. G. Sayce, *Talanta*, 18, 653 (1971).
69. I. G. Sayce and V. S. Sharma, *Talanta*, 19, 831 (1972).
70. S. Bashir, S. Raashid Maqsood, G. Mustafa Peerzada, B. Khan, and M. Ahmad Rizvi, *J. Inorg. Chem.* 1, (2014).
71. Y. Z. Yousif and F. J. M. Al-Imarah, *Trans. Met. Chem.*, 14(2), 123(1989).
72. D. T. Promila and R. Lonibala, *J. Chem. Eng. Data.*, 55, 1166, (2010).
73. S. V. Singh Thakur, M. Farooqui and S. D. Naikwade, *J. Chem. Bio and Phy. Sci.*, 4(1), 1(2014).
74. H. Sigel, *Cordination Chemistry*, Pergamon Press, Oxford, UK (1980).