

CHAPTER - 4
SUMMARY

CHAPTER - IV

SUMMARY

The literature survey indicates that the studies on the formation constants of the M-EDTA.Pa systems are surprisingly missing. Similarly, The studies on the M-Sa systems have been limited and the studies on the M.EDTA.Sa systems have not been attempted at all in the past three decades. It is therefore felt worth while to study the M.Sa, M.Pa, M.EDTA.Sa and M.EDTA.Pa systems by potentiometric method at 25°C and 0.1M ionic strength (NaClO₄). For the determination of the formation constants of M.Sa and M.Pa binary complexes two separate methods namely the Irving-Rossotti method and Patnaik and Coworker method have been employed and the values obtained by two methods are found to agree well with each other (Table- A& B, Page 223 & 224).

For the determination of the formation constants of the M.EDTA.Sa and M.EDTA.Pa ternary complexes, a modified Irving-Rossotti method as adopted by Bhattacharya and coworkers has been employed. In a few cases, Thompson and Lorass method has also been employed to verify the reliability of the results obtained by Bhattacharya and Coworkers. The values of formation constants of the ternary complexes obtained by the two methods are found to agree well with each other. (Table - C and D, Page - 225 & 226).

The proton ligand stability constants (pK_1^H) and metal ligand stability constants $\log K_{ML}^M$ ($\log K_1$) for the binary complexes and $\log K_{MAL}^{MA}$ ($\log K$) for the ternary complexes have been evaluated by various computational methods.

The pK_2^H and pK_1^H value of saccharic acid are found to be 3.13 and 4.24 at 25°C and 0.1M ionic strength (NaClO₄). The pK_1^H value of 2-hydroxy-2-methyl propanoic

acid under the same temperature and ionic strength is found to be 3.76. The proton-ligand stability constants obtained in the present investigation are found to agree well with the literature values.

M-L binary complexes :

The values of the stability constants of the M-L binary complexes have been compared with those of the M-A-L ternary complexes by taking various factors such as inductive effect, steric effect & coulombic interaction etc. ^{taken} into account.

M-A-L ternary complexes :

In the case of ternary complexes, the secondary ligands (L) are chosen judiciously in such a way that the stability of the ML complexes are much less than those of the primary complexes, MA. By doing this, the possibility of the ligand displacement of the following type has been excluded.



The formation constants of the M.EDTA. Sa and M.EDTA. Pa system have been evaluated keeping M : L : A ratio 1 : 1 : 1 and the values have been summarised in the Table - C and Table-D respectively.

The stability values have been correlated with some physical characteristics (such as ionic radii, atomic number and z^2 / r) of the metal ions.

The findings of the present investigation

1. When the stability values of M.Sa and M.EDTA.Sa systems are compared it is observed that the coulombic interaction between the two negatively charged ligand species during the complex formation destabilises the ternary complex (Table-

F). A peculiarity, however, is observed in the comparison of the stability values between the M.Pa and M.EDTA.Pa systems. The (+I) inductive effect of the methyl group, of Pa favours the formation of the ternary complex in the light rare earth region while its steric effect destabilises the ternary complex in the heavy rare earth (Table-E)

2. The stability values of Ln-Sa binary complexes when plotted against atomic number shows an increasing trend from La(III) to Lu(III) systems with a break at Gd(III). Fig 77b. The Gadolinium break takes place due to the occurrence of a cross-over point at around gadolinium where the coordination number changes from 8 to 9.

Stability values of M(II). Sa binary complexes where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) when plotted against atomic number increase upto Cu(II) system and then drop considerably at Zn(II) (Zn(II) not being a transition metal ion). Fig 81a.

3. The stability values of Ln-Pa binary complexes when plotted against atomic number shows an increasing trend from La(III) to Lu(III) system (Fig. 78b). Gadolinium break is not so prominent.

The stability values of M(II). Pa binary complexes (where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) when plotted against atomic number increase upto Cu(II) and then drop considerably at Zn(II) Fig. 82a.

4. The formation constants, $\log K_1$ for the Ln(III) . Sa, M(II).Sa, Ln(III).Pa and M(II) . Pa systems are also obtained by Patnaik and coworkers method. The values of $\log K_1$ obtained by these two methods agree well with each other within experimental error.

5. The stability values of Ln-EDTA-Sa ternary complexes when plotted against atomic number shows an increasing trend from La(III) to Lu(III) with a break at Gd(III) (fig. no. 79b).

Stability values of M(II) - EDTA - Sa ternary complexes when plotted against atomic increase upto Cu(II) and drop considerably at Zn(II) (fig. no. 81b)

6. The stability values of Ln-EDTA-Pa ternary complexes when plotted against atomic number shows a regular increase from La(III) to Lu(III) with a break at Gd(III) (fig. no. 80b).

The stability values of M(II)-EDTA-Pa ternary complexes when plotted against atomic number shows maximum at Cu(II) and drops at Zn(II) (fig no. 82b).

7. The plots of formation constants of the ternary complexes against z^2/r in the case of Ln.EDTA-Sa (fig. no. 79a) and Ln.EDTA.Pa (fig. no. 80a) systems are found to exhibit linearity in the light rare earth region. This linearity is not observed in the heavy rare earth region.

The linearity of the plot in the light rare earth region is due to the ionic nature of the metal ligand bond while the non-linearity of the plot in the heavy rare earth region is due to the partial covalent nature of the metal-ligand bond. A break at gadolinium is also observed.

8. The position of yttrium with respect to the formation constants, remains sometimes in the light rare earth region and at other times in the heavy rare earth region.
9. The order of the stability constants, $\log K_{M(II)AL}^{M(II)L}$ of the transition metal complexes are found to be

Zn(II) < Cu(II) > Ni(II) > Co(II) > Mn(II).

This agrees well with Irving-William's order.

TABLE - A

Stability constants of M-Saccharate complexes (Charges are omitted)
at 25°C and 0.1 M ionic strength (NaClO₄)

Sl. No.	Atomic Number	Metal ions	Irving-Rossotti log K ₁	Patnaik & Co-workers log K ₁
Fig. 1a / 1b	39	Y(III)	4.60	4.51
Fig. 2a / 2b	57	La(III)	4.42	4.14
Fig. 3a / 3b	58	Ce(III)	4.45	4.21
Fig. 4a / 4b	59	Pr(III)	4.49	4.26
Fig. 5a / 5b	60	Nd(III)	4.53	4.29
Fig. 6a / 6b	62	Sm(III)	4.56	4.32
Fig. 7a / 7b	63	Eu(III)	4.60	4.36
Fig. 8a / 8b	64	Gd(III)	4.51	4.35
Fig. 9a / 9b	65	Tb(III)	4.54	4.42
Fig. 10a / 10b	66	Dy(III)	4.57	4.45
Fig. 11a / 11b	67	Ho(III)	4.60	4.48
Fig. 12a / 12b	68	Er(III)	4.64	4.51
Fig. 13a / 13b	70	Yb(III)	4.67	4.54
Fig. 14a / 14b	71	Lu(III)	4.68	4.56
Fig. 15a / 15b	25	Mn(II)	3.55	3.20
Fig. 16a / 16b	27	Co(II)	3.64	3.29
Fig. 17a / 17b	28	Ni(II)	3.70	3.36
Fig. 18a / 18b	29	Cu(II)	3.86	3.51
Fig. 19a / 19b	30	Zn(II)	3.46	3.48

TABLE - B

Stability constants of M-2-Hydroxy-2-methyl propanoic acid (Charges are omitted)
at 25°C and 0.1 M ionic strength (NaClO₄)

Sl. No.	Atomic Number	Metal ions	Irving-Rossotti			Patnaik & Co-workers log K ₁	★ log K ₁
			A	B	C		
Fig. 20a/20b	39	Y(III)	2.71	2.62	2.62	2.71	2.86
Fig. 21a/21b	57	La(III)	2.50	2.44	2.44	2.48	----
Fig. 22a/22b	58	Ce(III)	2.63	2.54	2.54	2.59	2.43
Fig. 23a/23b	59	Pr(III)	2.71	2.65	2.63	2.66	----
Fig. 24a/24b	60	Nd(III)	2.79	2.68	2.78	2.80	2.62
Fig. 25a/25b	62	Sm(III)	2.87	2.73	2.79	2.87	2.75
Fig. 26a/26b	63	Eu(III)	2.92	2.75	2.83	2.89	2.70
Fig. 27a/27b	64	Gd(III)	2.98	2.84	2.80	2.94	2.82
Fig. 28a/28b	65	Tb(III)	3.05	2.92	2.80	2.96	2.83
Fig. 29a/29b	66	Dy(III)	2.95	2.82	2.80	2.94	----
Fig. 30a/30b	67	Ho(III)	3.05	2.99	2.96	3.04	3.06
Fig. 31a/31b	68	Er(III)	3.20	3.14	2.96	3.19	3.07
Fig. 32a/32b	70	Yb(III)	3.27	3.16	3.02	3.27	3.15
Fig. 33a/33b	71	Lu(III)	3.71	3.70	3.66	3.72	---
Fig. 34a/34b	25	Mn(II)	2.34	2.32	2.35	2.14	---
Fig. 35a/35b	27	Co(II)	2.43	2.50	2.49	2.18	---
Fig. 36a/36b	28	Ni(II)	2.46	2.50	2.45	2.28	---
Fig. 37a/37b	29	Cu(II)	2.90	2.90	2.90	2.89	---
Fig. 38a/38b	30	Zn(II)	2.25	2.25	2.25	1.13	---

A = Pointwise calculation method

B = Half integral method

C = Linear plot method

★ The Values of log K₁, obtained by G.R. Choppin and J.A. Chopporian at 25°C and 2M ionic strength (NaClO₄) (A personal communication to A.E. Martell)

TABLE - C

Stability constants of M-EDTA-Saccharic acid chelates (Charges are omitted) at 25°C and 0.1M ionic strength (NaClO₄)

Sl. No.	Atomic Number	Metal ions	log K	log K*
Fig. 39a	39	Y(III)	4.19	4.25
Fig. 40a	57	La(III)	3.91	3.95
Fig. 41a	58	Ce(III)	3.97	-----
Fig. 42a	59	Pr(III)	4.01	-----
Fig. 43a	60	Nd(III)	4.05	-----
Fig. 44a	62	Sm(III)	4.08	4.15
Fig. 45a	63	Eu(III)	4.12	-----
Fig. 46a	64	Gd(III)	4.01	-----
Fig. 47a	65	Tb(III)	4.08	4.21
Fig. 48a	66	Dy(III)	4.13	-----
Fig. 49a	67	Ho(III)	4.17	4.28
Fig. 50a	68	Er(III)	4.21	-----
Fig. 51a	70	Yb(III)	4.25	4.32
Fig. 52a	71	Lu(II)	4.25	-----
Fig. 53a	25	Mn(II)	3.26	-----
Fig. 54a	27	Co(II)	3.30	-----
Fig. 55a	28	Ni(II)	3.39	-----
Fig. 56a	29	Cu(II)	3.60	3.72
Fig. 57a	30	Zn(II)	3.21	-----

log K* : Values evaluated by Thompson and Lorass's method.

TABLE - D

Stability constants of M-EDTA-2-Hydroxy-2-methyl propanoic acid chelates
(Charges are omitted) at 25°C and 0.1 M ionic strength (NaClO₄)

Sl. No.	Atomic Number	Metal ions	log K	log K*
Fig. 58a	39	Y(III)	2.85	2.88
Fig. 59a	57	La(III)	2.64	2.73
Fig. 60a	58	Ce(III)	2.74	-----
Fig. 61a	59	Pr(III)	2.79	-----
Fig. 62a	60	Nd(III)	2.82	-----
Fig. 63a	62	Sm(III)	2.88	2.92
Fig. 64a	63	Eu(III)	2.91	-----
Fig. 65a	64	Gd(III)	2.90	-----
Fig. 66a	65	Tb(III)	2.92	2.96
Fig. 67a	66	Dy(III)	2.94	-----
Fig. 68a	67	Ho(III)	2.95	2.94
Fig. 69a	68	Er(III)	2.97	-----
Fig. 70a	70	Yb(III)	2.97	3.12
Fig. 71a	71	Lu(III)	3.09	-----
Fig. 72a	25	Mn(II)	2.88	-----
Fig. 73a	27	Co(II)	2.90	-----
Fig. 74a	28	Ni(II)	2.93	-----
Fig. 75a	29	Cu(II)	3.16	3.23
Fig. 76a	30	Zn(II)	2.86	-----

log K* : Values evaluated by Thompson and Lorass's method.

TABLE - E

A comparison between the stability values of Ln-Pa and Ln-A-Pa complexes at 25°C and 0.1M ionic strength (NaClO₄)
(Pa = 2-hydroxy-2-methyl⁻ propanoic acid)

Metal Ion	* $\frac{\text{Ln - Pa}}{\log K_1}$	$\frac{\text{Ln - A - Pa}}{\log K}$
Y (III)	2.71	2.85
La (III)	2.50	2.64
Ce (III)	2.63	2.74
Pr (III)	2.71	2.79
Nd (III)	2.79	2.82
Sm (III)	2.87	2.88
Eu (III)	2.92	2.91
Gd (III)	2.98	2.90
Tb (III)	3.05	2.92
Dy (III)	2.95	2.94
Ho (III)	3.05	2.95
Er (III)	3.20	2.97
Yb (III)	3.27	2.97
Lu (III)	3.71	3.09
Mn (II)	2.34	2.88
Co (II)	2.43	2.90
Ni (II)	2.46	2.93
Cu (II)	2.90	3.16
Zn (II)	2.25	2.86

This table indicates $\log K_1 < \log K$ (La-Sm). The (+I) inductive effect of methyl group favours formation of ternary complexes while $\log K_1 > \log K$ (Eu-Lu), the steric effect of methyl group destabilises the ternary complexes.

* $\log K_1$ values obtained by point-wise calculation method are tabulated here for comparison.

TABLE - F

A comparison between the stability values of the M-Sa and M.EDTA.Sa systems at 25°C and 0.1M ionic strength (NaClO₄)

Metal Ion	* $\frac{M \cdot Sa}{\log K_1}$	$\frac{M.EDTA.Sa}{\log K}$
Y (III)	4.60	4.19
La (III)	4.42	3.91
Ce (III)	4.45	3.97
Pr (III)	4.49	4.01
Nd (III)	4.53	4.05
Sm (III)	4.56	4.08
Eu (III)	4.60	4.12
Gd (III)	4.51	4.01
Tb (III)	4.54	4.08
Dy (III)	4.57	4.13
Ho (III)	4.60	4.17
Er (III)	4.64	4.21
Yb (III)	4.67	4.24
Lu (III)	4.68	4.25
Mn (II)	3.55	3.26
Co (II)	3.64	3.30
Ni (II)	3.70	3.39
Cu (II)	3.86	3.60
Zn (II)	3.46	3.21

* Values obtained by Irving-Rossotti method are presented here.

The order of stability constants of M.Sa systems in terms of lanthanide ions is found to be $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+}$. Similarly the relative order of stability constants of M-Pa systems in terms of lanthanide ions is found to be $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+}$.

The relative order of stability constants of M.EDTA.Sa systems in terms of lanthanide ions is found to be $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+}$. Similarly the relative order of stability constants of M.EDTA.Pa systems in terms of lanthanide ions is found to be $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} = \text{Yb}^{3+} < \text{Lu}^{3+}$.

A few abbreviations for some common reagents have been mentioned below.

Name of the compound	Molecular structure	Abbreviation
D(+)-Saccharic acid	$ \begin{array}{c} \text{COOH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{OH} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{COOH} \end{array} $	H_2Sa
2-Hydroxy-2-methyl propanoic acid	$ \begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C} - \text{C} - \text{COOH} \\ \\ \text{CH}_3 \end{array} $	HPa

Name of the compound	Molecular structure	Abbreviation
Disodium salt of ethylene diamine N, N, N', N' - tetraacetic acid	$ \begin{array}{c} \text{NaOOC} - \text{CH}_2 \qquad \qquad \text{CH}_2 - \text{COOH} \\ \qquad \qquad \qquad \diagdown \qquad \qquad \diagup \\ \qquad \qquad \qquad \text{N} - \text{CH}_2 - \text{CH}_2 - \text{N} \\ \qquad \qquad \qquad \diagup \qquad \qquad \diagdown \\ \text{HOOC} - \text{CH}_2 \qquad \qquad \text{CH}_2 - \text{COONa} \end{array} $	Na ₂ H ₂ EDTA
Ionic strength	NaClO ₄	μ
Lanthanide ions		Ln(III)
Primary ligand	H ₄ EDTA	A
Secondary ligand	H ₂ Sa and HPa	L
Average number of secondary ligands attached to the primary complex MA		\bar{n}_{mix}
Free ligand exponent of secondary ligand		P ^L mix
Metals (both transition and rare earth metals)		M
Formation constants of binary complexes	log K _{ML} ^M	log K ₁
Formation constants of ternary complexes	log K _{MAL} ^{MA}	log K

The following papers have been published in different journals.

Title of paper	Journal, Vol., Year, Page
1. P ^H - Metric Study on Tervalent Yttrium & Lanthanide chelates involving 2-Hydroxy-2-methyl propanoic acid as secondary ligand.	Asian J. of Chemistry, Vol. 8, 1996, 425.
2. Studies on complexes between Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) and D(+) - Saccharic acid	J. Indian Chem. Soc., Vol - 74, 1997, 216
3. P ^H - Metric Study of Bivalent Metal Chelates using D(+)-Saccharic acid as secondary ligand	J. Indian Chem. Soc., Vol - 74, 1997, 330.
4. P ^H - Metric Study on Ln(II).EDTA.D(+) - Saccharic acid Equilibria.	J. Indian. Chem. Soc., Vol-74, 1997, 494.