

**PUBLISHED
PAPER**

pH-Metric Study on Tervalent Yttrium and Lanthanide Chelates Involving 2-Hydroxy-2-Methyl Propanoic Acid as Secondary Ligand

(MISS) S. PATNAIK and C. PANDA*

Department of Chemistry

Regional Engineering College, Rourkela-769 008, India

Studies on the formation constants for the complexes of the type ML and MAL (where M = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), Lu(III) and Y(III), A = disodium salt of ethylenediamine-tetraacetic acid and HL = 2-hydroxy-2-methyl propanoic acid) have been made at 25°C and 0.1 M ionic strength (NaClO₄) by applying Irving-Rosotti pH titration technique and its extension to ternary systems. The order of stability of the MAL complexes was found to be La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III) = Yb(III) < Lu(III).

INTRODUCTION

Potentiometric study on the binary complexes between lanthanide ions and 2-hydroxy-2-methyl propanoic acid¹⁻⁵ and chromatographic separation of lanthanide ions by 2-hydroxy-2-methyl propanoic acid as an eluting agent have been reported earlier⁶⁻⁸. Moeller and coworkers⁹ reviewed the coordination chemistry of yttrium and rare earth metal ions. The present communication describes the determination of the formation constants of yttrium and rare earth metal ions involving 2-hydroxy-2-methyl propanoic acid as secondary ligand(L) and ethylenediaminetetraacetic acid as primary ligand (A) at 25 ± 1°C and 0.1 M ionic strength (NaClO₄) by pH titration method.

EXPERIMENTAL

All chemicals used were of A.R. grade. The disodium salt of ethylenediamine tetraacetic acid was used as primary ligand. Carbonate free sodium hydroxide solution was used in pH-metric titrations. The carbonate content of sodium hydroxide was assessed by Gran's method¹⁰. pH-metric titrations were performed in nitrogen atmosphere at 25 ± 1°C, 0.1 M ionic strength (NaClO₄) using a pH-metric model, ECIL-5652 (accuracy ±0.01 pH unit).

In the first experiment, the following two solutions were prepared as per the method followed earlier¹¹⁻¹³:

1. 0.00625 M HL
2. 0.00625 M HL + 0.005 M Sm(III)

In the second experiment, the following three solutions were prepared as per Irving-Rossotti technique¹⁴

1. 0.05 M HClO₄;
2. 0.005 M HClO₄ + 0.005 M HL
3. 0.05 M HClO₄ + 0.005 M HL + 0.005 M Sm(NO₃)₃

In the third experiment, the following four solutions were prepared as per the method followed earlier¹⁵⁻¹⁷

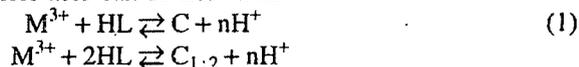
- (A) 0.05 M HClO₄
- (B) 0.05 M HClO₄ + 0.005 M HL
- (C) 0.05 M HClO₄ + 0.005 M Sm(NO₃)₃ + 0.005 M EDTA
- (D) 0.05 M HClO₄ + 0.005 M Sm(NO₃)₃ + 0.005 M EDTA + 0.005 M HL.

The initial volume in each case was kept 50 mL by the addition of suitable volume of distilled water and the ionic strength was maintained at 0.01 M by the addition of suitable amount of neutral NaClO₄ solution. These solutions were pH-metrically titrated by carbonate-free sodium hydroxide solution. Each titration was repeated to get reproducible result.

RESULTS AND DISCUSSION

In the first set of experiments, the number of protons liberated remained 1 and 2 when the metal-ligand ratio was maintained at 1:1.25 and 1:5 respectively. This indicated the formation of 1:1 and 1:2 type of complexes.

The reaction taking place between the yttrium and lanthanide ions and 2-hydroxy-2-methyl propanoic acid can be shown as



where C represents the complex and n, the number of protons liberated per gram atom of the metal ion. The charge on the complex C depends on the value of n. The value of n was calculated by the method as followed in the cadmium citrate complex¹¹, tartrate complex¹² of Y(III) and glycolate complex of lanthanide ions¹³.

The value of n did not exceed 1.0 in the pH range 2-6 in all the systems studied. Assuming the value of n to be 1 below pH 6, the values of C and then the values of equilibrium constant $-\log K_1^*$ for the reaction (1) were determined as before and the mean values were recorded in Table-1.

During the pH-titrations, insoluble compounds were obtained at pH 7.65 for La(III), 7.42 for Ce(III), 7.39 for Pr(III), 6.81 for Nd(III), 7.30 for Sm(III), 7.17 for Eu(III), 6.71 for Gd(III), 6.93 for Tb(III), 6.99 for Dy(III), 6.65 for Ho(III), 6.85 for Er(III), 6.88 for Yb(III), 7.02 for Lu(III) and 7.09 for Y(III) systems. These insoluble compounds on analysis were found to be the hydroxides of yttrium and lanthanide ions.

In the second set of experiments, the values of \bar{n}_A , \bar{n} and pL were calculated by the standard expressions¹⁴. The formation curves were obtained by plotting \bar{n}_A and \bar{n} against pH and pL respectively. The values of dissociation constant (K_1^H) of 2-hydroxy-2-methyl propanoic acid obtained from the formation curve, \bar{n}_A vs. pH, by pointwise calculation and linear plot method were found to agree

well with the K_1^H value reported earlier³. The most representative value of K_1^H was recorded in Table-1.

TABLE-1
STABILITY CONSTANTS FOR M-L AND M-A-L COMPLEXES AT $25 \pm 1^\circ\text{C}$ AND 0.1 M IONIC STRENGTH (NaClO_4) HL = 2-HYDROXY-2-METHYL PROPANOIC ACID ($\text{p}K_1^H = 3.76$)

Metal ion	$-\log K_1^*$	$\log K_1 = \log K_1^*/K_1^H$	$\log K_1$	$\log K_{M-EDTA}^{M-EDTA-L}$
	Experiment-1		Experiment-2	Experiment-3
Y(III)	2.70 ± 0.08	3.06 ± 0.08	2.71 ± 0.07	2.86 ± 0.08
La(III)	3.29 ± 0.01	2.47 ± 0.06	2.47 ± 0.07	2.67 ± 0.09
Ce(III)	3.17 ± 0.08	2.59 ± 0.08	2.64 ± 0.09	2.74 ± 0.08
Pr(III)	3.11 ± 0.07	2.65 ± 0.07	2.67 ± 0.04	2.79 ± 0.08
Nd(III)	2.97 ± 0.09	2.79 ± 0.09	2.79 ± 0.09	2.82 ± 0.08
Sm(III)	2.90 ± 0.09	2.86 ± 0.09	2.87 ± 0.08	2.88 ± 0.09
Eu(III)	2.91 ± 0.08	2.87 ± 0.08	2.92 ± 0.08	2.91 ± 0.10
Gd(III)	2.83 ± 0.08	2.93 ± 0.08	2.98 ± 0.09	2.90 ± 0.09
Tb(III)	2.81 ± 0.06	2.95 ± 0.06	3.05 ± 0.09	2.92 ± 0.10
Dy(III)	2.78 ± 0.10	2.94 ± 0.08	2.95 ± 0.06	2.94 ± 0.09
Ho(III)	2.72 ± 0.08	3.04 ± 0.08	3.05 ± 0.09	2.95 ± 0.07
Er(III)	2.57 ± 0.06	3.19 ± 0.06	3.20 ± 0.08	2.97 ± 0.09
Yb(III)	2.49 ± 0.07	3.27 ± 0.07	3.27 ± 0.09	2.97 ± 0.09
Lu(III)	2.05 ± 0.08	3.71 ± 0.08	3.71 ± 0.10	3.05 ± 0.07

The value of \bar{n} remained between 0.1 and 2.5 in the \bar{n} scale. This indicated the formation of 1:1, 1:2 and 1:3 type of complexes. The $\log K_1$ values were obtained from the formation curve \bar{n} vs. pL by half integral method of $\bar{n} = 0.5$. The $\log K_1$ values were also obtained by pointwise and linear plot method. The most representative values of $\log K_1$ were recorded in Table-1. These values of $\log K_1$ agreed well with the respective $\log K_1$ values obtained earlier^{1,2}. Only the values of $\log K_1$ were reported here with a view to comparing these values with the respective $\log K_{Ln-EDTA}^{Ln-EDTA-L}$ values of the mixed complexes. It can be shown that the equilibrium constant K_1^* is related to the stability constant K_1 in the following way

$$\log K_1^*/K_1^H = \log K_1$$

The $\log K_1$ values thus obtained in Experiment-1 agreed well with the respective $\log K_1$ values obtained in Experiment-2.

Ln-EDTA-2-Hydroxy-2-methyl propanoic acid systems

In the third set of experiments, the metal : EDTA : 2-Hydroxy-2-methyl propanoic acid ratio was maintained at 1:1:1. The pH-titration curves for the Sm-EDTA-2-hydroxy-2-methyl propanoic acid system were shown in Fig. 1. The pH-titration curves for Y(III) and other members of the lanthanide series were of similar nature.

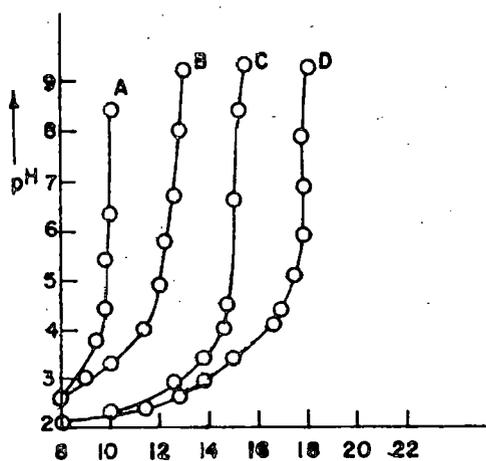


Fig.1 0.1M NaOH in ml .

Fig. 1. pH titration of 50 mL solution containing:

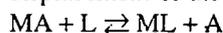
Curve A : 0.05 M HClO₄ + 0.1 M NaClO₄

Curve B: A + 0.005-M 2-hydroxy-2-methyl propanoic acid

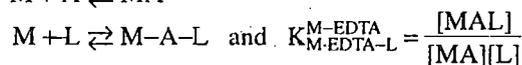
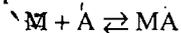
Curve C: 0.05 M HClO₄ + 0.01 M NaClO₄ + 0.005 M Sm(NO₃)₃ + 0.005 M Na₂H₂ EDTA

Curve D: C + 0.005 M 2-hydroxy-2-methyl propanoic acid

For the formation of ternary complexes, the necessary conditions like the formation of primary ligand complex, M-EDTA, at low pH and its stability at higher pH at which the combination of the secondary ligand with M-EDTA takes place were satisfied by choosing the secondary ligand (L) in such a way that the stability of the M-L complex was less than that of the primary complex, M-EDTA. Thus the possibility of ligand displacement of the following type was excluded:



The formation of the mixed complex in the present system was therefore assumed to take place in two distinctly separate steps.



(Charges were omitted for clarity)

The species present in solution were therefore MA and MAL. The possibility of formation of the MA₂ and ML₂ through reprotonation was excluded.

There may also occur hydrolysis of the primary complex, and even of M(III). In the presence of a bidentate ligand, the complex M-EDTA-L is assumed to be

formed in preference of $M-EDTA(OH)_n$. In dilute solution, it was also assumed that the polynuclear species did not exist.

The values of \bar{n}_{mix} , the average number of secondary ligands attached to the primary complexes, $M-EDTA$ and pL_{mix} , in the mixed ligand systems, were calculated by an extension of Irving-Rossotti technique¹⁵⁻¹⁷. The plots of \bar{n}_{mix}/L_{mix} vs. L_{mix} in the above $M-EDTA-L$ systems were found to be smooth curves (figure not shown). This also suggests the absence of polynuclear and protonated species¹⁷. The values of \bar{n}_{mix} did not exceed 1 in the \bar{n}_{mix} scale. Therefore, the formation constants, $\log K_{M-EDTA-L}^{M-EDTA}$ were evaluated by the method of interpolation at various \bar{n}_{mix} values. The values of formation constants thus obtained were recorded in Table-1.

The values of the stability constants, $\log K_1$ of the $Ln-L$ complexes for the light rare earths (*i.e.*, from La-Eu) were found to be less than those of the corresponding stability constants of the $Ln-A-L$ ternary complexes while the stability values of the $Ln-L$ complexes for the heavy rare earths (*i.e.*, Tb-Lu) were found to be more than those of the corresponding $Ln-A-L$ complexes. This may be due to the fact that in the light rare earth region (*i.e.*, La-Eu) the inductive effect of the methyl group in 2-hydroxy-2-methyl propanoic acid contributes significantly for the stability of the $Ln-A-L$ complexes.

The ionic radii of lanthanide ions regularly decrease with increase in atomic number. In the heavy rare earth region the lowering in the stability value of the $Ln-A-L$ complex with respect to the stability values of the $Ln-L$ complex can be ascribed to the inability of the 2-hydroxy-2-methyl propanoic acid to adapt to the smaller lanthanide ions. The position of yttrium with respect to the magnitude of the formation constant of its $Y-L$ complex in the present study is found between holmium and erbium and for the $Y-A-L$ ternary complex its position is found between neodymium and samarium. Such erratic behaviour of Y(III) has been reported elsewhere⁹.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. K.K. Tripathy, Head of the Department of Chemistry and Prof. S. Misra, Principal, Regional Engineering College, Rourkela for extending necessary research facilities.

REFERENCES

1. R.S. Kolat, Doctoral Dissertation, IOWA State University (1962).
2. G.R. Choppin and J.A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).
3. M.E. Clark and J.L. Bear, *J. Inorg. Nucl. Chem.*, **32**, 3569 (1970).
4. K. Winkler and K.B. Zuborenko, *Z. Physik. Chem.*, **238**, 348 (1968).
5. L. Braniak and D. Nobel, *Jag. Nukl. Analysenverfahren*, **3**, 417 (1983).
6. G.R. Choppin and R.J. Silva, *J. Inorg. Nucl. Chem.*, **3**, 153 (1956).
7. Pilu Zhang, Yulan Gao and Chong Peiji, *Yuanzineng Kexue Jishu*, **23**, 19 (1989).
8. Lucy Charles A. and Luong Thi Luong, *J. Chromatogr.*, **546**, 27 (1991).
9. T. Moeller, D.F. Martin, L.C. Thompson, R. Ferrus, G.R. Feistel and W.J. Randall, *Chem. Rev.*, **65**, 1 (1965).

10. G. Gran, *Analyst*, **77**, 661 (1952).
11. R.K. Patnaik and S. Pani, *J. Indian Chem. Soc.*, **34**, 673 (1957).
12. R.K. Patnaik and K.K. Tripathy, *J. Inorg. Nucl. Chem.*, **35**, 1050 (1973).
13. R.K. Patnaik and C. Panda, *J. Indian Chem. Soc.*, **57**, 23 (1980).
14. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953); 2904 (1954).
15. M.V. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 3271 (1970).
16. K.N. Munshi and T.H. Mhaske, *J. Indian Chem. Soc.*, **55**, 885 (1978).
17. M.C. Saxena and S.N. Limaye, *J. Indian Chem. Soc.*, **61**, 842 (1984).

(Received: 5 October 1995; Accepted: 18 January 1996)

AJC-1067

Studies on Complex Formation of Zinc-, Copper-, Nickel-, Cobalt- and Manganese(II) with D(+)-Saccharic Acid

(MISS) S. PATNAIK and C. PANDA*

Chemistry Department, Regional Engineering College, Rourkela-769 008

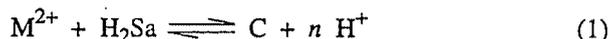
Manuscript received 16 December 1994, revised 6 July 1995, accepted 20 November 1995

The present communication describes the study of determination of stability constants of the neutral complex of some transition metal ions with D(+)-saccharic acid at low pH and the dissociation constant of its dissociation to other form of complexes at higher pH.

Results and Discussion

In the case of Ni^{II}-, Co^{II}-, Mn^{II}- and Zn^{II}-D(+)-saccharic acid systems, the liberation of proton during complex formation remained same when the metal-ligand ratio was increased from 1 : 1.25 to 1 : 5. This indicated the formation of only 1 : 1 type of complex. In the case of Cu^{II}-D(+)-saccharic acid system, both 1 : 1 and 1 : 2 types of complex formation were indicated.

The reaction between the metal ion and D(+)-saccharic acid (H₂Sa) can be represented as

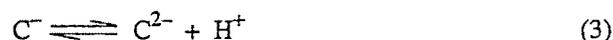


where C represents the 1 : 1 complex and *n* the number of proton liberated per g-atom of the metal ion. The values of *n* were calculated according to the method followed in earlier investigations¹. The values of *n* were found to be > 2 above pH 4.2, 5.4, 6.0, 6.0 and 5.6 for the Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Zn^{II} systems respectively. Assuming the value of *n* to be 2 below these pH values in each system, the C and then the values of equilibrium constants (-log K*) for the reaction (1) were calculated¹ (Table 1).

In the pH range 4.2-5.4 in the case of Cu^{II} system and above pH 5.4, 6.0, 6.0 and 5.6 in the case of Ni^{II}, Co^{II}, Mn^{II} and Zn^{II} systems respectively, the values of *n* were > 2 but < 3. Hence the complex (C) dissociates as

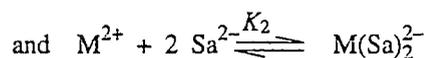
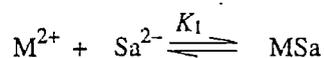


The liberation of this third proton is probably due to the coordination of one of the α-hydroxylic groups of the ligand with the metal ion. That one of the hydroxylic groups of the D(+)-saccharic acid was involved in bond formation with metal ions was established by the appearance of an ir band for the Cu^{II}- and Ni^{II}-D(+)-saccharate complexes^{2,3} at 2 600 cm⁻¹. The values of the equilibrium constant (-log K₃^{*}) for the reaction (2), were calculated as before (Table 1). Above pH 5.4 in the case of Cu^{II} system, the values of *n* were > 3 but < 4. This indicated the dissociation of the complex C- to C²⁻ and a proton as



The liberation of this proton may be due to the coordination of a hydroxylic group of the sugar acid with the Cu^{II} ion. However, the possibility of the liberation of this proton from a coordinated water molecule cannot be ruled out. The values of the equilibrium constant (-log K₃) for the reaction (3) were determined⁴ (Table 1). In the case of 1 : 2 Cu^{II}-D(+)-saccharic acid system, the values of equilibrium constant (-log K_{1,2}^{*}) for the reaction, Cu²⁺ + 2H₂Sa ⇌ C_{1:2} + nH⁺, were calculated as before⁵ (Table 1).

In experiment-2 the reactions taking place can be represented as



The values of $\bar{n}A$, \bar{n} and *pL* were obtained by standard expressions⁶. The formation curves corresponding to the proton-ligand and metal-ligand equilibrium were obtained by plotting $\bar{n}A$ and \bar{n} against pH and *pL* respectively. The

TABLE 1-PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS

Ligand : D(+)-saccharic acid, temp. = 25 ± 1°, I = 0.1 M (NaClO₄), pK₂^H = 3.13, pK₁^H = 4.2

Cation	Experiment-1				Experiment-2			
	-log K ₁ [*]	-log K ₂ [*]	-log K ₃ [*]	-log K _{1,2} [*]	log K ₁	log K ₂	log K ₁	log K ₂
Cu ^{II}	3.86	4.38	6.65	9.20	3.51	5.54	3.86	3.09
Ni ^{II}	4.02	7.33			3.35		3.70	
Co ^{II}	4.08	7.38			3.29		3.65	
Mn ^{II}	4.17	7.13			3.20		3.56	
Zn ^{II}	3.90	7.38			3.47		3.46	

$$\log K_1 = \log K_1^*/K_1^H \cdot K_2^H, \log K_2 = \log K_{1,2}^*/(K_1^H K_2^H)^2$$

NOTE

values of pK_1^H and pK_2^H of the D(+)-saccharic acid obtained by various computational methods (Table 1) agreed well with the reported values^{2,7}. The values of stability constants, $\log K_1$ and $\log K_2$ were similarly obtained by different computational methods (Table 1). The relation between the equilibrium constants (K_1^* and $K_{1:2}^*$) and stability constants (K_1 and K_2) is also shown in Table 1. The $\log K_1$ values obtained in this experiment agreed well with that obtained in experiment-1. The $\log K_2$ value for the Cu^{II} system, however, did not agree with the respective value in experiment-1. This may be ascribed to the extensive formation of polynuclear complexes in Cu^{II} -D(+)-saccharic acid system. The linear nature of the plot of \bar{n}/L vs L (figure not shown) in the Cu^{II} system also supports this view. The order of stability, $Zn < Cu > Ni > Co > Mn$, obeys Irving William's rule⁷.

Experimental

All chemical used were of A.R. grade. D(+)-Saccharic acid was derived from insoluble D(+)-calcium saccharate by ionic exchange method⁹. pH-titrations were carried out in nitrogen atmosphere with an Ecil-5652 pH meter at $25 \pm$

1° and 0.1 M ionic strength ($NaClO_4$) using CO_2 -free NaOH solution. The carbonate content of NaOH solution was assessed¹⁰. The pH-titrations were performed in duplicate to test reproducibility.

References

1. R. K. PATNAIK and S. PANI, *J. Indian Chem. Soc.*, 1957, 34, 673; K. K. TRIPATHY and R. K. PATNAIK, *J. Inorg. Nucl. Chem.*, 1973, 35, 1050; *Acta Chim. (Budapest)*, 1973, 79, 279.
2. J. G. VELASCO, J. ORTEGA and J. SANCHO, *J. Inorg. Nucl. Chem.*, 1976, 38, 889.
3. P. BENEITEZ and A. MILLAN, *Ber. Bunsenges Phys. Chem.*, 1989, 93, 217 (*Chem. Abstr.*, 1989, 110, 180290).
4. K. K. TRIPATHY and R. K. PATNAIK, *Indian J. Chem.*, 1967, 5, 511.
5. C. PANDA and R. K. PATNAIK, *J. Indian Chem. Soc.*, 1980, 57, 23.
6. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3394; 1954, 2904.
7. L. A. MAI, *J. Obsch. Chem.*, 1956, 26, 3206.
8. H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1953, 3192.
9. C. G. MACAROVICI and M. BIROU, *Rev. Roum. Chem.*, 1967, 12, 163.
10. G. GRAN, *Analyst*, 1952, 77, 661.

pH-metric Study of Bivalent Metal Chelates using D(+)-Saccharic Acid as Secondary Ligand

(MISS) S. PATNAIK and C. PANDA*

Department of Chemistry, Regional Engineering College, Rourkela-769 008

Manuscript received 16 March 1995, revised 23 August 1995, accepted 14 December 1995

Velasco *et al.*¹ reported the stability constants for the anionic complexes of D(+)-saccharic acid of the type, $(\text{CuLH}_3)^-$, $(\text{NiLH}_3)^-$, $(\text{CoLH}_3)^-$ and $\text{Mn}(\text{LH}_3)^-$, where $\text{LH}_6 = \text{D}(+)\text{-saccharic acid}$. They also reported 1 : 2 $[\text{Cu}(\text{LH}_4)_2]^{2-}$ and its polynuclear species. Beneitez and Millan² studied the composition and stability constant of 1 : 1 $\text{Ni}^{\text{II}}\text{-D}(+)\text{-saccharic acid}$ complex. Mai³ reported the dissociation constants of D(+)-saccharic acid. Macarovic⁴ made a potentiometric study of the complexes of D(+)-saccharic acid with Ti^{IV} , Zr^{IV} and Th^{IV} . Spacu *et al.*⁵ studied the conditions under which some lanthanide compounds were formed with saccharic acid. Any systematic study on the coordinating tendency of this acid has been limited despite the advantages that it may offer for coordination with metal ions due to the availability of six potential coordinating sites (four hydroxyl and two carboxylic acid groups) in its structure.

The present potentiometric study reports the formation constants of the $\text{M}^{\text{II}}\text{-EDTA-Sa}$ complexes, where disodium salt of EDTA has been used as primary ligand (A) and D(+)-saccharic acid; H_2Sa , as secondary ligand (L) at $25 \pm 1^\circ$ and at 0.1 M ionic strength (NaClO_4).

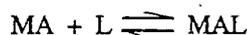
Results and Discussion

The values of \bar{n}_A , \bar{n} and pL for the M-L, binary systems were obtained by standard expressions⁶. The formation curves corresponding to the proton-ligand and metal-ligand equilibria were obtained by plotting \bar{n}_A and \bar{n} against pH and pL respectively. The $\text{p}K_1^{\text{H}}$ and $\text{p}K_2^{\text{H}}$ values of D(+)-saccharic acid were obtained by the usual Irving-Rossotti technique. The K_1^{H} and K_2^{H} values were found to be 7.413×10^{-4} and 5.754×10^{-5} respectively, which were close to the literature values 7.25×10^{-4} and 7.95×10^{-5} (Ref. 1) and 9.78×10^{-4} and 11.55×10^{-5} (Ref. 3). The metal-ligand stability constants ($\log K_1$) for the 1 : 1 M-L binary complexes were similarly evaluated by various computational methods.

The $\log K_1$ values obtained by the method of interpolation at various \bar{n} values were found to be 3.86 ± 0.07 , 3.70 ± 0.06 , 3.65 ± 0.06 , 3.56 ± 0.03 and 3.46 ± 0.03 for the Cu^{II} , Ni^{II} , Co^{II} , Mn^{II} and Zn^{II} systems respectively. In the case of $\text{Mn}^{\text{II}}\text{-Sa}$ and $\text{Mn}^{\text{II}}\text{-EDTA-Sa}$ systems in the alkaline range, the colour of the solution gradually changed from almost colourless to red. This may be due to partial oxidation of Mn^{II} by molecular oxygen⁷. Since the present pH-titra-

tions were carried out in nitrogen atmosphere, the oxidation of Mn^{II} may be due to the presence of dissolved oxygen in the solutions employed.

For the formation of ternary complexes (MAL) the necessary conditions like the formation of primary ligand complex, MA at low pH and its stability at higher pH at which the combination of the secondary ligand with MA takes place, were satisfied by choosing the secondary ligand (L) in such a way that the stability of the ML complex was much less than that of the primary complex, MA. Thus the possibility of the ligand displacement of the following type was excluded. $\text{MA} + \text{L} \rightleftharpoons \text{ML} + \text{A}$. The formation of the mixed ligand complex in the present system was therefore assumed to take place in two distinctly separate steps,



$$\text{and } K_{\text{MAL}}^{\text{MA}} = \frac{[\text{MAL}]}{[\text{MA}][\text{L}]}$$

charges are omitted. The species present in solution were therefore MA and MAL. The possibility of the formation of other species like MA_2 and ML_2 were excluded. However, there may also occur hydrolysis of MA and even of

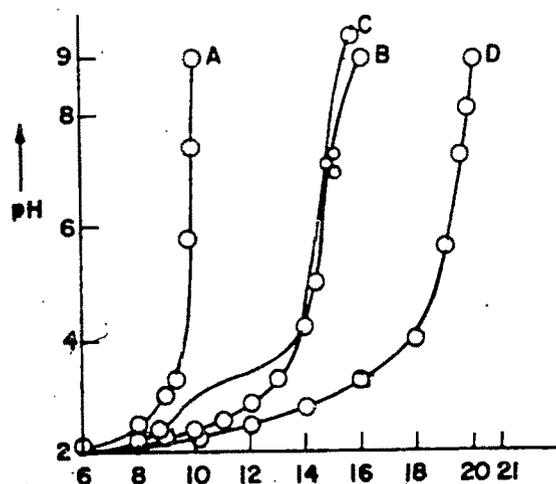
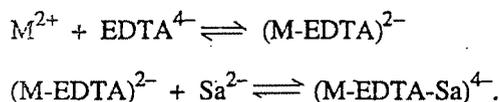


Fig. 1. pH-metric titration curves of 1 : 1 : 1 $\text{Ni}^{\text{II}}\text{-EDTA-D}(+)\text{-saccharic acid}$ system at $25 \pm 1^\circ$ and 0.1 M ionic strength (NaClO_4): (A) HClO_4 , (B) $\text{HClO}_4 + \text{H}_2\text{Sa}$, (C) $\text{HClO}_4 + \text{EDTA} + \text{NiSO}_4$ and (D) $\text{HClO}_4 + \text{EDTA} + \text{NiSO}_4 + \text{H}_2\text{Sa}$.

M(II). In the presence of a multidentate ligand like D(+)-saccharic acid, the complex MAL was assumed to be formed in preference of MA(OH)_n. In dilute solution, it was also presumed that the polynuclear species do not exist⁸.

The values of \bar{n}_{mix} , the average number of secondary ligands attached to the primary complex MA, were calculated by an extension of Irving-Rossotti technique at different pH values from the horizontal distance ($V_4 - V_3$) - ($V_2 - V_1$) in the same pH axis where V_1 , V_2 , V_3 and V_4 are the volumes of sodium hydroxide required to reach the same pH in curves A, B, C and D respectively (Fig. 1). The values of \bar{n}_{mix} and the free ligand exponent, PL_{mix} in the mixed ligand systems were calculated by the standard expressions¹⁰. The plots of $\bar{n}_{\text{mix}}/L_{\text{mix}}$ vs L_{mix} in the above M(n)-EDTA-Sa systems were found to be smooth curves (figure not shown). This also suggests the absence of polynuclear and protonated species⁹. The values of \bar{n}_{mix} did not exceed 0.5 in the \bar{n}_{mix} scale and hence the formation constants ($\log K_{\text{MAL}}^{\text{MA}}$) were calculated by the method of interpolation at various \bar{n}_{mix} values. The values of the formation constants thus obtained were found to be 3.60 ± 0.08 , 3.39 ± 0.09 , 3.33 ± 0.08 , 3.26 ± 0.10 and 3.21 ± 0.08 for the Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Zn^{II} systems respectively.

The values of stability constants of the ML complexes were found to be higher than those of the MAL complexes. The cause of this has been ascribed to the coulombic repulsion between the binary complex (M-EDTA)²⁻ and the incoming ligand, Sa²⁻ as shown by the reactions,



EDTA being a hexadentate ligand formed a very stable chelate occupying six coordination sites. Accommodation of another polydentate ligand leading to the formation of a ternary complex would therefore create an extra strain on the ternary complex and count for the lowering in the values of stability constant. The order of stability of the ternary complexes was found to be, Zn^{II} < Cu^{II} > Ni^{II} > Co^{II} > Mn^{II}. This obeys Irving-Williams natural order¹².

Experimental

All chemical used were of A.R. grade. D(+)-saccharic acid was derived from insoluble D(+)-calcium saccharate

(Sigma) by ion-exchange method¹³.

For the study of ML, binary complexes the following three solutions were prepared : (a) 0.05 M HClO₄, (b) 0.05 M HClO₄ + 0.005 M H₂Sa and (c) 0.05 M HClO₄ + 0.005 M H₂Sa + 0.005 M NiSO₄. For the study of MAL, ternary complexes, the following four solutions were prepared as per the method followed earlier^{10,11} : (A) 0.05 M HClO₄, (B) 0.05 M HClO₄ + 0.005 M H₂Sa, (C) 0.05 M HClO₄ + 0.005 M NiSO₄ + 0.005 M EDTA and (D) 0.05 M HClO₄ + 0.005 M NiSO₄ + 0.005 M EDTA + 0.005 M H₂Sa. The initial volume in each case was kept at 50 ml by the addition of suitable volume of distilled water and the ionic strength was maintained at 0.1 M by the addition of suitable amount of neutral sodium perchlorate solution. pH-metric titrations were carried out in N₂-atmosphere with a pH-meter model ECIL-5652 at 25 ± 1° using carbonate-free NaOH solution. The carbonate content of sodium hydroxide was assessed¹⁴. Each titration was repeated to get reproducible result.

Acknowledgement

The authors are thankful to Prof. K. K. Tripathy, Head of the Department, Chemistry and Prof. S. Misra, Principal, Regional Engineering College, Rourkela, for facilities.

References

1. J. G. VELASCO, J. ORTEGA and J. SANCHO, *J. Inorg. Nucl. Chem.* 1976, **38**, 389.
2. P. BENEITEZ and A. MILLAN, *Ber. Bunsenges. Phys. Chem.*, 1985, **93**, 217 (*Chem. Abstr.*, 1989, **110**, 180290).
3. L. A. MAI, *J. Obsch. Chem.*, 1956, **26**, 3206.
4. C. G. MACAROVICI, *Studi. Sicer. Chem.*, 1961, **12**, 229.
5. P. SPACU, E. ANTONESCU and S. PLOSTINARU, *Rev. Roum. Chim.*, 1966, **11**, 327.
6. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3394; 1954, 2904.
7. D. T. SAWYER, *Inorg. Chem.*, 1976, **15**, 1538.
8. P. K. BHATTACHARYA, *J. Sci. Ind. Res.*, 1981, **40**, 382.
9. S. N. LIMAYE and M. C. SAXENA, *J. Indian Chem. Soc.*, 1982, **59**, 698; 1984, **61**, 842.
10. M. V. CHDAMBARAM and P. K. BHATTACHARYA, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3271.
11. T. H. MHASKE and K. N. MUNSHI, *J. Indian Chem. Soc.*, 1978, **55**, 885.
12. H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1953, 3192.
13. C. G. MACAROVICI and M. BIROU, *Rev. Roum. Chim.*, 1967, **12**, 163.
14. G. GRAN, *Analyst*, 1952, **77**, 661.

pH-metric Study on Lanthanide(III)-EDTA-D(+)-Saccharic Acid Equilibria

(MISS) S. PATNAIK and C. PANDA*

Chemistry Department, Regional Engineering College, Rourkela-769 008

Manuscript received 23 August 1995, revised 22 January 1996, accepted 4 March 1996

Mai¹ reported the dissociation constants of D(+)-saccharic acid. Macarovici and Birou² made a potentiometric study on the complexes of D(+)-saccharic acid with Ti^{IV}, Zr^{IV} and Th^{IV}. Spacu *et al.*³ studied the conditions under which some lanthanide compounds are formed with D(+)-saccharic acid. Limaye and Saxena⁴ made a potentiometric study on the Ln(III)-EDTA-hydroxyacid ternary complexes involving malic, lactic, glycolic and gluconic acids. Moeller *et al.*⁵ reviewed the coordination chemistry of rare earth metal ions. The present communication describes determination of the formation constants of the Ln(III)-D(+)-saccharate and Ln(III)-EDTA-D(+)-saccharate complexes by pH-titration method at 25 ± 1° and 0.1 M ionic strength (NaClO₄).

Results and Discussion

In the first set of experiment (i.e. pH titrations with mixture nos. 1, 2 and 3), the metal-ligand ratio was maintained at 1:1. The values of \bar{n}_A , \bar{n} and pL were calculated by the standard expressions⁶. The proton-ligand and metal-ligand formation curves were obtained by plotting \bar{n}_A and \bar{n}

against pH and pL respectively. The values of dissociation constants (K_2^H and K_1^H) of D(+)-saccharic acid were obtained from the formation curve, \bar{n}_A vs pH and by pointwise calculation and linear plot method. These values agreed well with the K_2^H and K_1^H values reported earlier¹. The most representative values are recorded in Table 1. In the present experiment, the \bar{n} values did not exceed 1. Therefore, the values of stability constants ($\log K_1$) for the reaction $\text{Ln}^{3+} + \text{Sa}^{2-} \rightleftharpoons \text{LnSa}^+$, were obtained by the method of interpolation at various \bar{n} values and the mean values of $\log K_1$ are recorded in Table 1. During pH-titrations, insoluble compounds were obtained at the following pH for different metal ions : 3.3 (La^{III}), 3.12 (Ce^{III}), 3.11 (Pr^{III}), 3.05 (Nd^{III}), 3.01 (Sm^{III}), 2.92 (Eu^{III}), 2.90 (Gd^{III}), 2.95 (Tb^{III}), 3.03 (Dy^{III}), 3.01 (Ho^{III}), 3.22 (Er^{III}), 3.32 (Yb^{III}), 3.95 (Lu^{III}) and 3.48 (Y^{III}). These insoluble compounds on analysis were found to correspond to the general formula C₆H₈O₈Ln.6H₂O. Similar observation was also reported by Spacu *et al.*³.

Ln-EDTA-D(+)-saccharic acid system : In the second set of experiments, the metal : EDTA : D(+)-saccharic acid ratio was kept 1 : 1 : 1. The pH-titration curves for the Sm-

TABLE 1—STABILITY CONSTANTS FOR Ln-SACCHARATE AND Ln-EDTA-SACCHARATE COMPLEXES

Temp. = 25 ± 1°, ionic strength = 0.1 M (NaClO₄)

(for D(+)-Saccharic acid : $K_2^H = 7.413 \times 10^{-4}$, $K_1^H = 5.754 \times 10^{-5}$)

Cation	$\log K_{\text{Ln-Sa}}^{\text{Ln}}$	$\log K_{\text{Ln-EDTA-Sa}}^{\text{Ln-EDTA}}$
Y ^{III}	4.60	4.19
La ^{III}	4.42	3.90
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	4.05
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	4.25
Lu ^{III}	4.68	4.30

*Limits of error in the constants : ± 0.03 and ± 0.05 in log units for the binary and ternary systems respectively.

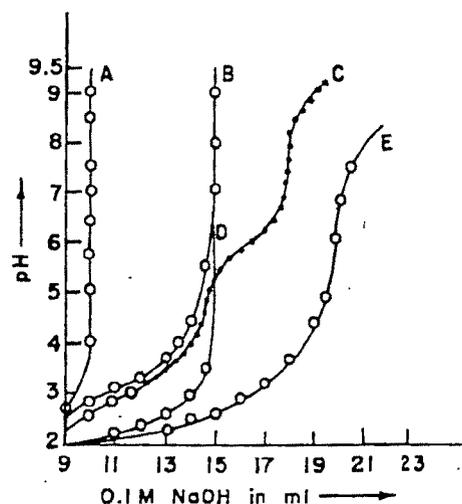


Fig. 1. pH-titration curves for the 1:1 binary, Sm^{III}-Sa and 1:1:1 ternary, Sm^{III}-EDTA-Sa systems : (A) acid, (B) H₂Sa, (C) Sm^{III}-Sa, (D) Sm^{III}-EDTA and (E) Sm^{III}-EDTA-Sa.

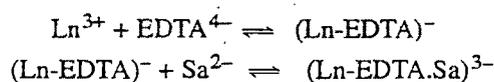
EDTA-Sa system is shown in Fig. 1. The curves for other lanthanides showed similar nature. For the formation of ternary complexes the necessary conditions, like the formation of primary ligand complex, Ln-EDTA at low pH

and its stability at higher pH at which the combination of the secondary ligand with Ln-EDTA takes place were satisfied by choosing the secondary ligand in such a way that the stability of the Ln.Sa complex is much less than that of the primary complex Ln.EDTA. Thus the possibility of ligand displacement was excluded. The species present in solution were therefore Ln.EDTA and Ln.EDTA.Sa. The strong coordinating tendency and hexadentate nature of EDTA also eliminates the possibility of disproportionation of Ln.EDTA.Sa into Ln(EDTA)₂ and Ln(Sa)₂. The non-superimposable nature of the theoretical composite curve over the mixed complex curve⁷ and the non-appearance of precipitate during pH-titration indicates the formation of mixed ligand complexes.

The values of \bar{n}_{mix} and the free ligand exponent, p_{mix}^L , were calculated by using Irving-Rossotti pH-titration technique and its extension to ternary system⁸. The plots of $\bar{n}_{\text{mix}}/L_{\text{mix}}$ vs L_{mix} were found to be smooth. This indicates the absence of protonated and polynuclear complexes⁴. The values of \bar{n}_{mix} were found to be less than 1 in each system. Therefore, the values of stability constants, $\log K_{\text{Ln.EDTA.Sa}}^{\text{Ln.EDTA}}$ were evaluated by the method of interpolation at various \bar{n}_{mix} values and the mean values are recorded in Table I.

Lanthanide ions form normally ionic compounds. Therefore the Born relation, $E = Z^2/2r(1 - 1/D)$ should hold for energy change in complexation of a gaseous ion of charge Z and radius r in a medium of dielectric constant, D . Since this energy, E is directly related to the stability constant, the $\log K_1$ values should increase linearly with Z^2/r . It was observed that this simple relationship exists in the light rare earth region (i.e. La to Eu). This equation, however, did not work while the heavy rare earths were considered, supporting the earlier observations⁵.

The values of formation constants of the ternary complexes, Ln.EDTA.Sa, were found to be less than these of the Ln.Sa, binary complexes. This lowering in the values of constants of the ternary complexes is ascribed to the extra strain created due to the extension of the coordination number of the lanthanide ions to greater than six and the coulombic repulsion between the binary complex (Ln.EDTA)⁻ and the incoming ligand Sa²⁻ as shown by the complexation reactions,



An expected trend of increase in the values of formation constant with the gradual decrease in ionic radii of the lanthanide ions with a break (minimum) at gadolinium was

observed. The position of yttrium with respect to its electrostatic model and magnitude of formation constants of its complexes were found between holmium and erbium in the lanthanide series.

Experimental

All chemicals used were of A.R. grade. The disodium salt of ethylenediaminetetraacetic acid was used as primary ligand. D(+)-Saccharic acid was derived from the insoluble D(+)-calcium saccharate by ion-exchange method². Carbonate-free NaOH solution was used in pH-metric titrations. The carbonate content of NaOH was assessed by the reported method⁹. pH-metric titrations were performed in N₂ atmosphere at 25 ± 1° and 0.1 M ionic strength (NaClO₄) using an ECIL-5652 pH meter. The following sets of solutions for the 1 : 1 binary (mixtures 1, 2 and 3) and 1 : 1 : 1 ternary (mixtures 1, 2, 4 and 5) were prepared : (1) 0.02 M HClO₄ (curve-A), (2) 0.02 M HClO₄ + 0.005 M H₂Sa (curve-B), (3) 0.02 M HClO₄ + 0.005 M H₂Sa + 0.005 M Sm(NO₃)₃ (curve-C), (4) 0.02 M HClO₄ + 0.005 M Sm(NO₃)₃ + 0.005 M EDTA (curve-D) and (5) 0.02 M HClO₄ + 0.005 M Sm(NO₃)₃ + 0.005 M EDTA + 0.005 M H₂Sa (curve-E).

The initial volume in each case was kept at 50 ml by adding distilled water and the ionic strength maintained at 0.1 M by adding NaClO₄. These solutions were pH-metrically titrated by carbonate-free 0.1 M NaOH solution.

Acknowledgement

The authors are thankful to Prof. K. K. Tripathy, Head of the Department of Chemistry and Prof. S. Misra, Principal, Regional Engineering College, Rourkela, for facilities.

References

1. L. A. MAI, *J. Obsch. Chem.*, 1956, 26, 3206.
2. C. G. MACAROVICI and M. BIROU, *Rev. Roum. Chem.*, 1967, 12, 163.
3. P. SPACU, E. ANTONESCU and S. PLOSTINARU, *Rev. Roum. Chem.*, 1966, 11, 327.
4. S. N. LIMAYE and M. C. SAXENA, *J. Indian. Chem. Soc.*, 1984, 61, 842; 1982, 59, 598.
5. T. MOELLER, D. F. MARTIN, L. C. THOMPSON, R. FERRUS, G. R. FEISTEL and W. J. RANDALL, *Chem. Rev.*, 1965, 65, 1.
6. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3394; 1954, 2904.
7. G. H. CAREY and A. E. MARTELL, *J. Am. Chem. Soc.*, 1967, 89, 2859.
8. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *J. Inorg. Nucl. Chem.*, 1970, 32, 3271.
9. G. GRAN, *Analyst*, 1952, 77, 661.