

Studies on stability constants of binary and ternary chelates of lanthanide (III) ions

T.S. Saini*^a and R.G. Sharma^b

^aDepartment of chemistry, Govt. P.G. College, Jind-126102, Haryana India.

^bDepartment of chemistry, N.A.S. College, Meerut, 250001U.P, India.

E-mail. drtejsingh.65@gmail.com

Abstract

The stability constants of binary and ternary chelates of Iminodiacetic acid (IMDA) and 3,5-Dinitrosalicylic acid (3,5-DNSA) with lanthanide (III) (Ln=La (III), Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Er (III) and Yb (III)) have been evaluated pH-metrically, using Ramamoorthy and Santapa method in aqueous solutions at temp 30.0 ± 0.5 °C in an ionic strength $\mu=0.10$ M KNO_3 . The binary formation constants of metal chelates of lanthanides with these ligands have been determined individually and ternary formation constants have also been reported in which Iminodiacetic acid (IMDA) acts as primary ligand whereas, 3,5- dinitrosalicylic acid (3,5-DNSA) as a secondary ligand. Stability Constants are discussed in terms of basicity of ligand, statistical and stereochemical phenomenon. Thermodynamics parameter like change in free energy (ΔG) have also been evaluated and discussed.

Keywords: Stability constant, Lanthanides, Thermodynamics, Basicity, Ligand

I. Introduction

The inner coordination shell of lanthanides normally contains 8 to 9 waters of hydration, some of which are displaced during complexation which leads to the development of a ternary complex¹⁻⁴. In comparison to the development of binary complexes, the complexation of lanthanides with carboxylate ligands to generate ternary complexes has received more attention⁵⁻⁷. Moreover, Iminodiacetic acid (IMDA) and 3,5-Dinitrosalicylic acid (3,5-DNSA) are very interesting ligands since, they contain multiple potential binding sites for chelation. The lanthanoid cations have hard acidic nature which facilitates their interaction with hard bases having oxygen as donor atom such as salicylates and acetates^{4, 8, 9}. Mohamed taha *et al.* have designed some Eu(III) complexes with gallic acid and amino acids like alanine, leucine, isoleucine, and tryptophan which were further studied by glass electrode potentiometry and their overall stability constants were calculated to be 17.29, 11.33, 17.23, and 21.52, respectively¹⁰. The stability constant of the immobilized metal ion chelate complexes can be influenced by different factors such as, composition of buffer, nature of ligands, pH, solvents, temperature, ionic strength and effect of metal ions as well^{11, 12}. Formation thermodynamics of binary and ternary lanthanide(III) complexes with 1-10 phenanthroline (phen) and chloride ion have also been reported by titration Calorimetry, Spectrophotometry by researchers¹³ in N,N- dimethylformamide. The stability constant of metal chelates of Cephalexin, an antibiotic drug with bivalent transition metals have been evaluated pH - metrically¹⁴. Stability constants of complexes of copper, nickel etc. with Succinylsulfathiazole have also been determined potentiometrically by investigators¹⁵. Mixed ligand complexes of lanthanides with poly(aminocarboxylic) acids have been studied using Absorption Spectroscopy by reseachers¹⁶. International Conferences¹⁷ on Coordination Chemistry have developed a vast field in which large number of chelates and their stability constants have been reported. Absorption spectral study of mixed ligand complexes of some lanthanides with polyamine polycarboxylic acids have been reported by investigators¹⁸. Binary and ternary complexes of lanthanides with poly (amino carboxylic) acid in presence of acetylacetone have also been reported recently by researchers¹⁹⁻²⁴. The present communication reports the results of the study of Ln-IMDA-3,5-DNSA equilibria in solutions using Irving-Rossotti method²⁵ for determination of protonation constant of ligands and then Ramamoorthy and Santapa¹ method helps to determine the formation constants of binary and ternary chelates.

Experimental Section

The lanthanides were supplied by Indian Rare Earths Ltd. (99.99 % purity) and other chemicals also standard purity (BDH Analar, E. Merck G.R., Fluka). The composition of Lanthanide nitrates reported as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and solutions were prepared by dissolving in double distilled water and standardized gravimetrically by precipitating the metal oxalates and subsequently ignition and weighing as metal oxides. Solutions of lanthanides nitrates, Iminodiacetic acid and 3,5-dinitrosalicylic acids of required strength (0.005 M) were prepared by direct weighing. Nitric acid (0.004M) was prepared from stock solution was standardized against standard sodium hydroxide solution. Similarly, potassium nitrate of (2M) strength was prepared and from which desired ionic strength of medium maintained. During present work, the pH titrations were carried out at 30.0 ± 0.5 °C with the help of digital pH meter 335 systronics using a combined electrode and calibrated by using buffer tablets of pH 4.0 and 9.0. The experiments were performed in specially designed double walled beaker of capacity 250 ml made of borosil glass. All titration were performed in duplicate in order to established the reproducibility of the measurements, keeping the total volume 50.0 ml in each titration. The following sets of solution were prepared and titrated against standard alkali (0.4M) in order to determine the protonation constant of ligands by Irving and Rossotti method at different ionic strengths.

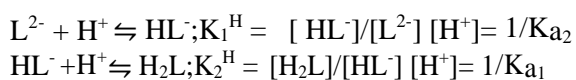
- (i) 0.004M HNO_3
- (ii) 0.004M HNO_3 + 0.003M ligand IMDA/ 3,5-DNSA
- (iii) 0.004M HNO_3 + 0.003M ligand IMDA/ 3,5-DNSA + 0.0005M metal ion solution.

Potassium nitrate solution added as required to maintained ionic strengths ($\mu=0.05, 0.10, 0.15,$ and 0.20M). The formation constants $\log K_{\text{MA}}$, $\log K_{\text{MB}}$ and $\log K_{\text{MAB}}$ for ternary complexes have been determined by Ramamorthy and Santapa method using following titrations at ionic strength 0.10M KNO_3

- (i) 0.004M HNO_3
- (ii) 0.004M HNO_3 + 0.0005M IMDA /3,5-DNSA
- (iii) 0.004M HNO_3 + 0.0005M IMDA /3,5-DNSA + 0.0005 M metal ion
- (iv) 0.004M HNO_3 + 0.0005M IMDA + 0.0005M 3,5-DNSA + 0.0005 M metal ion for ternary systems. Different values were refined by computational techniques such as interpolation at half n values, the point-wise method, curve fitting method and correction term method.

II. Results and Discussion

During present research work, Bjerrum-Calvin^{26, 27} pH-metric titration technique as modified by Irving and Rossotti²⁵ have been used in the determination of protonation constant(s) of ligands under the conditions similar to those for the determination of metal stability constant(s). The main advantage of the pH-titration technique is that the measurements are quick and the instruments are less expensive. In order to determine the metal-ligand stability constants, a prior knowledge of the dissociation constants of the ligand is essential. The protonation constants $\log K_1^{\text{H}}$ and $\log K_2^{\text{H}}$ of iminodiacetic acid and 3,5-dinitrosalicylic acids, each having two replaceable hydrogen atoms represented by H_2L . Follow the following equilibria.



In the logarithmic forms:

$$\log K_1^{\text{H}} = -\log K_{\text{a}2} \text{ or } \text{p}K_{\text{a}2} \text{ and } \log K_2^{\text{H}} = -\log K_{\text{a}1} \text{ or } \text{p}K_{\text{a}1}$$

The proton-ligand stability constants of these ligands are determined by same set of experiments using the acid curve and ligand titration curves, then the proton-ligand formation curves are obtained by

plotting the values of n_A versus pH. From these formation curves proton-ligand stability constants ($\log k_1^H$ and $\log k_2^H$) of Iminodiacetic acid and 3,5-Dinitrosalicylic acid determined at different ionic strengths ($\mu = 0.05, 0.10, 0.15$ and 0.20 M KNO_3) at temp 30.0 ± 0.5 °C by Irving and Rossoti method using different computational techniques and reported in table 1.

Table 1. Proton ligand Stability Constants of Iminodiacetic acid and 3,5-Dinitrosalicylic acid at various ionic strengths (30.0 ± 0.5 °C)

Method used	$\mu= 0.05$		$\mu= 0.10$		$\mu= 0.15$		$\mu=0.20$			
	$\log k_1^H$	$\log k_2^H$	$\log k_1^H$	$\log k_2^H$	$\log k_1^H$	$\log k_2^H$	$\log k_1^H$	$\log k_2^H$		
1) Interpolation	9.45	2.60	9.36	2.54	9.30	2.48	9.25	2.45		
At half n_A values	7.32	2.20	7.25	2.10	7.18	2.05	7.10	1.95		
2) Point-wise	9.45	2.62	9.37	2.57	9.31	2.50	9.25	2.43		
Calculation	7.34	2.34	7.29	2.24	7.21	2.13	7.14	2.09		
3) Correction term	9.45	2.62	9.37	2.57	9.31	2.50	9.25	2.43		
Method	7.36	2.34	7.29	2.24	7.19	2.14	7.14	2.04		
4) Curve fitting	9.44	2.58	9.35	2.52	9.28	2.47	9.24	2.41		
Method	7.26	2.20	7.18	2.08	7.22	2.00	7.18	1.98		
Mean values										
Iminodiacetic acid			9.45	2.60	9.36	2.55	9.30	2.49	9.25	2.42
			± 0.01	± 0.02	± 0.01	± 0.03	± 0.02	± 0.02	± 0.01	± 0.01
3,5-Dinitrosalicylic acid			7.32	2.27	7.25	2.16	7.20	2.08	7.14	2.00
			± 0.06	± 0.07	± 0.07	± 0.10	± 0.02	± 0.06	± 0.04	± 10.05

These results resemble with the values reported in earlier literature. The effects of different ionic strengths of the medium observed on protonation constants and results indicate that values decrease with increase in ionic strength of the medium, which indicates the vital role of medium in chelation reaction. Stability constants of binary (1: 1) systems of trivalent lanthanides determined with Iminodiacetic acid and 3,5-Dinitrosalicylic acid at ionic strength ($\mu = 0.10$ M KNO_3) and temp. 30.0 ± 0.5 °C individually by Ramamoorthy and Santapa method. The formation constants $\log K_{MA}$ and $\log K_{MB}$ were determined by using expression.

$$K_{MA} = \frac{T_{M^-} [A^0].X}{[A^0]^2.X}$$

$$K_{MB} = \frac{T_M - [B^0].X}{[B^0]^2.X}$$

Where total free ligand concentrations

$$A^0 = 2T_L + P - T_{OH} - [H^+] / ([H^+] / K_2) + (2[H^+]^2 / K_1 K_2)$$

$$X = 1 + [H^+] / K_2 + [H^+]^2 / K_1 K_2$$

Where

$$T_M = [\text{metal ion}]_{\text{total}}$$

$$A^\circ = [\text{free ligand}]_{\text{total}}$$

$$T_{OH} = [\text{NaOH}]$$

$$T_L = [\text{ligand}]_{\text{total}}$$

$$[H^+] = [\text{free hydrogen ion}]$$

$$P = [\text{HNO}_3] \text{ initial also } T_M = T_L$$

K_1 and K_2 are first and second dissociation constants of the ligands.

Stability constants of ternary (1:1:1) chelates of trivalent lanthanides with Iminodiacetic acid which acts as a primary ligand and 3,5-dinitrosalicylic acid as secondary ligand, determined by using an expression and values of K_{MAB} were determined.

$$K_{MAB} = T_M - [1/2 [A^\circ].X] / (1/2)^3 [A^\circ]^3 X$$

Where, A^0 is total primary and secondary free ligands concentration. The values of stability constants $\log K_{MA}$ and $\log K_{MB}$ for binary and $\log K_{MAB}$ for ternary complexes have been determined with the help of various computer programs in C language. The change in the free energies of formation were determined by using the following expression

$$\Delta G^0 = - 2.303 RT \log K_{MA} \setminus K_{MB} \setminus \log K_{MAB}$$

For binary and ternary complexes results reported in table 2.

Table 2. Formation constants and change in Free Energies of binary and ternary complexes of trivalent lanthanides with Iminodiacetic acid and 3, 5-Dinitrosalicylic acid.

System	Stoichiometry	pH range	log K	$-\Delta G^0(\text{Kcal/mole})$
La(III)-IMDA	1:1	1.90-2.26	10.39±0.10	14.4110±0.1387
Ce(III)-IMDA	1 : 1	1.80-2.28	10.41±0.13	14.4387±0.1803
Pr(III)-IMDA	1:1	1.85-2.65	10.37±0.14	14.3832±0.1942
Nd(III)-IMDA	1:1	1.75-2.17	10.45±0.18	14.4942±0.2497
Sm(III)-IMDA	1:1	1.68-1.98	10.51±0.12	14.5774±0.1664
Gd(III)-IMDA	1: 1	1.71-2.09	10.48±0.13	14.5358±0.1803
Dy(III)-IMDA	1:1	1.69-2.11	10.49±0.15	14.5497±0.2081
Er(III)-IMDA	1 : 1	1.63-1.93	10.54±0.13	14.6190±0.1803
Yb(III)-IMD.\	1 : 1	1.58-1.96	10.56±0.14	14.6467±0.1942
La(III)-3,5-DNSA	1:I	2.60-2.95	08.48±0.29	11.7618±0.4022
Ce(III)-3,5-DNSA	1:1	2.50-2.65	08.16±0.13	11.3179±0.1803
Pr(III)-3,5-DNSA	1 : 1	2.55-2.70	08.30±0.1 8	11.5121±0.2497
Nd(III)-3,5-DNSA	1:1	2.47-2.62	08.11±0.11	11.2486±0.1526
Sm(III)-3,5-DNSA	1:1	2.41-2.96	08.26±0.40	11.5467±0.5548
Gd(III)-3,5-DNSA	1:1	2.55-2.99	08.34±0.59	11.5676±0.8183

Dy(III)-3,5-DNSA	1 : 1	2.43-2.98	08.26±0.57	11.5467±0.7906
Er(III)-3,5-DNSA	1 : 1	2.37-2. 72	08.09±0. 32	11.2209±0.4438
Yb(III)-3,5-DNSA	I: 1	2.33-2.68	08.03±0.25	11.1376±0.3467
La(III)-IMDA-3,5-DNSA	1:1:1	5.30-6.00	10.61±0.36	14.71 61±0.4995
Ce(III)-IMDA-3,5-DNSA	1:1:1	5.68-6.25	10.81±0.19	14.9935±0.2635
Pr(III)-IMDA-3,5-DNSA	1:1:1	5.71-6.26	10.77±0.19	14.9380±0.2635
Nd(III)-IMDA-3,5-DNSA	1:1:1	5.65-6.16	10.79± 0.1 2	14.9657±0.1664
Sm(III)-IMDA-3,5-DNSA	1:1:1	5.53-6.10	10.99±0.17	15.2431±0.2358
Gd(III)-IMDA-3,5-DNSA	1:1:1	5.77-6.24	10.97±0.28	15.2 1 54±38840
Dy(III)-IMDA-3,5-DNSA	1:1:1	5.55-6.14	10.90±0.19	15.1599±0.2635
Er(III)-IMDA-3,5-DNSA	1:1:1	5.50-6.22	11.04±0.20	15.3125±0.2774
Yb(III)-IMDA-3,5-DNSA	1:1:1	5.45-6,21	11.09±0.32	15.3818±0.4438

The potentiometric curves of nine trivalent lanthanides involved found to be very similar in nature for binary and ternary systems. When curves obtained by plotting graph, pH versus volume of alkali added indicated inflection at $m = 5.0$ for acid curve and at $m = 6.0$ for ligand curves confirmed the formation of 1:1 binary complexes. m being the number of moles of base added per mole of the metal ion.

The ternary system of Ln (III)-IMDA-3,5-DNSA showed inflections in curves at $m = 7.0$ indicating the formation of 1:1:1 ternary complexes. The formation of heteroligand-metal complexes in these systems is further evidenced by (i) lowering in pH in comparison with the binary versus ternary systems. (ii) non-appearances of solid phase during the titration.

A perusal of these results indicates that the values of $\log k_{MAB}$ (Ln(III)-IMDA-3,5-DNSA) are higher than those of $\log K_{MA}$ or $\log K_{MB}$ system, indicating more stability of ternary systems. The ligand stability constants for different Ln(III) ions show an increasing trend as $La < Ce = Pr < Nd \leq Sm < Gd < Dy < Er < Yb$, according to lanthanide contraction. Anomalous behavior of cerium ion is probably due to tendency of cerium towards quadrivalency. The metal — ligand stability constants also indicate a break at or near Gd(III) ion. This may due to either half-filled arrangement ($4f^7$) of Gd(III)ion or change in ionic radii centering at Gd(III)ion, which can allow a change in coordination number of the cation. A comparison of metal ligand stability constants indicates that ternary complexes (1:1:1) are more stable than binary complexes (1:1). Metal ligand stability constants for Ln (III)-IMDA systems are higher than Ln (III)- 3,5-DNSA systems for binary complexes due to steric hinderances caused by large groups of 3,5- DNSA but for ternary complexes Ln (III)- IMDA-3,5-DNSA systems metal ligand stability constants are higher due to extended exocyclic conjugation caused by two nitro groups of 3,5-dinitrosalicylic acid. The negative values of ΔG^0 indicate that the driving tendency of the complexation reaction is favourable and the reaction tends to proceed spontaneously.

Acknowledgement

The authors are thankful to Prof. S.N. Dubey, Chairman, Department of Chemistry Kurukshetra University Kurukshetra and Prof. J.K. Nepal. Department of Chemistry C C S H A U, Hisar for constructive comments and suggestions in order to improve the manuscript. One author, Dr. T.S. Saini is grateful to the university Grants Commission, New Delhi, for financial assistance in the form of minor research project.

References

- [1]. Ramamoorthy, S. and Santappa, M.; Bull. Chem. Soc. Japan, 1971, 1775.
- [2]. Thakur, P.; Pathak, P. N.; Gedris, T.; Choppin, G. R.; J. Solution Chem. **2009**, 38 (3), 265–287.
- [3]. Räsänen, M.; Rosenberg, J.; Lukkari, J.; Haapakka, K.; Kankare, J.; Takalo.; J. Lumin. **2017**, 187, 471–478.
- [4]. Szabó, Z.; Vallet, V.; Grenthe, I.; Dalt. Trans. **2010**, 39 (45), 10944–10952.

- [5]. Tyagi, S.; Kumar, R.; Singh, U. P.; J. Chem. Eng. Data **2005**, 50 (2), 377–382.
- [6]. Leggett, C. J.; Jensen, M. P.; J. Solution Chem. **2013**, 42 (11), 2119–2136.
- [7]. Shen, C. Q.; Yan, T. L.; Wang, Y. T.; Ye, Z. J.; Xu, C. J.; Zhou, W.; J. Lumin. **2017**, 184, 48–54.
- [8]. Pallagi, A.; Bajnóczi, É. G.; Canton, S. E.; Bolin, T.; Peintler, G.; Kutus, B.; Kele, Z.; Pálinkó, I.; Sipos, P.; Environ. Sci. Technol. **2014**, 48 (12), 6604–6611.
- [9]. Azab, H. A.; Al-Deyab, S. S.; Anwar, Z. M.; Ahmed, R. G.; J. Chem. Eng. Data **2011**, 56 (12), 4604–4622.
- [10]. Taha, M.; Khan, I.; Coutinho, J. A. P.; J. Inorg. Biochem. **2016**, 157, 25–33.
- [11]. Çam, T.; Irez, G.; Aydin, R.; J. Chem. Eng. Data **2011**, 56 (5), 1813–1820.
- [12]. Janrao, D. M.; Pathan, J.; Kayande, D. D.; Mulla, J. J.; Sci. Revs. Chem. Commun **2014**, 4 (2014), 11–24.
- [13]. Komiya, M. and Nishikido, Y. et al.; Journal of Solution Chemistry, **2002**, 34, 931.
- [14]. Chakarawarti, Purushottam B.; Chakarawarti, Mukta and Maint, Pramila; J. Indian Chemical Soc., 2000, 77, 85.
- [15]. Gandhi, Leena and Sekhon, B. S.; J. Indian Chemical Soc., **2006**, 83, 221.
- [16]. Misra, S. N. and Mehta, S. B.; Bull. Chem. Soc. Japan, **1991**, 64, 3653.
- [17]. International Conferences on Coordination Chemistry Detroit **1961**, Stockholm **1962**. Culcutta **1979**, Athenes **1986**, Tokyo **1994**,. Cape Town (South Africa) **2004**.
- [18]. Prashant N Bhatt, Pankaj I Bhadani et al Ind. I.Chem., **2007**. 46A, 39.
- [19]. Misra, S. N. and Sommerer, S. O.; Inorg.Chem.Rev., **1992**, 12, 157.
- [20]. Bhatt, P. N.; Mehta, I. P. and Pathak, T. V.; J. Biochem. Biophys., **2004**, 41, 175.
- [21]. Mehta, J. P.; Bhatt, P. N. and Misra, S. N.; J. Solid State Chem., **2003**, 171, 177.
- [22]. Misra, S. N.; Patel, M. C.; Suveerkumar, C. M. and Mehta, P. N.; Ind. J. Biochem. Biophys., **2002**, 39, 66.
- [23]. Indra Devi, M.; Rajmuhon Singh, N. et al.; Spectrochim. Acta. A. Mol. Biomol. Spectrosc., **2006**, 63, 154.
- [24]. Bjerrum, J. “Metal Ammine Formation in Aqueous Solution,” P. Haase and son, Copenhagen, **1941**.
- [25]. Irving, H. and Rossotti, H. S.; J. Chem. Soc., **1953**, 3397, **1954**, 2904;
- [26]. Chidambaram, M. V. and Bhattacharya, P. K.; J. Inorg. Nucl. Chem., **1970**, 39, 2471.
- [27]. Katkar, V. S. and Munshi, K. N.; Indian J. Chem., **1980**, 24, 336.