A Solution Study of Complex Formation of Some Diamines with Lanthanones

J.J.VORA^{*}, D.R.PATEL[¶], ASHA D. PATEL, KANU PATEL[§],
SANGITA SHARMA, LAXMAN S. BHUTADIYA[#] and SUNIL B. VASAVA

Department of Chemistry,
Hemchandracharya North Gujarat University, Patan-384 265, Gujarat, India.
[¶]Municipal Arts & Science College, Mehsana-384 002, Gujarat, India.
[§]Shri M.P. Pandya Science College, Lunavada, Gujarat, India.
[#]Sheth M.N. Science College, Patan-384 265, Gujarat.

jabali_vora@hotmail.com

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Abstract: To study the metal ligand equilibrium in aqueous solution, the well known Irving-Rossotti titration method was used. The temperature selected is $30 \pm 0.1^{\circ}\text{C}$ at ionic strength 0.2 M (NaClO_4) which was maintained constant through out the work. The binary metal complex (ML_2) formation was studied. The metals selected are Sm^{3+} , Gd^{3+} , Dy^{3+} and Yb^{3+} . The diamine ligands taken are ethylenediamine, 1,2 diamino propane, 1,3 diamino propane, *N-N* diethyl ethylenediamine and *N-N*-dimethyl ethylenediamine. Factors that affected the stability of the complexes are size and ionic potential of lanthanone ions, basicity of ligands, ring size and steric effect of ligands.

Keywords: Lanthanone ions, Diamines, Equilibrium study

Introduction

The chemistry of lanthanones has been extensively reviewed^{1,2}. During last 15 years, the lanthanone(III) complexes have been extensively used for medical diagnostic methods like MRI (magnetic resonance imaging)^{3,4}. Complexes of lanthanones in solid state were studied for their photo chemical and thermal properties⁵. Lanthanones have been employed as aids to the separation, preparation and purification of molecular cells in immunoassay in histochemistry⁶. Complexes of lanthanones with nitrogen donor ligands of weak basicity are well known^{7,8}. Europium complexes with 1,10-phenanthroline were studied for their formation, bonding characteristics and important photochemical properties⁹. Amino acids are well known chelating agents, their importance in biological system and in industry has earned attention of chemists for their metal complexes¹⁰⁻¹³. During past several decades, diamines and their derivatives are studied for important applications as stable complexes in fields like biotechnology, environmental science and biochemistry, etc¹⁴⁻¹⁶.

In the present study, an attempt has been made to determine the stability constants of binary complexes of Sm(III), Gd(III), Dy(III) and Yb(III) with some diamines. Various factors influencing the formation and stabilities of binary complexes have been discussed.

Experimental

All the reagents used were of A.R. grade. Lanthanone trivalent metal nitrates (Aldrich) were used. The amines (E-Merck) perchloric acid (Baker Analyzed), sodium perchlorate (Fluka) and sodium hydroxide (BDH Analar Grade) were used.

All the solutions for the equilibrium study were prepared in conductivity water. Perchloric acid and sodium hydroxide were standardized by acid-base titration¹⁷, while metal nitrate solutions were standardized by complexometry method¹⁸. Systronics μ pH system 361 with readability ± 0.01 was used for potentiometric studies. μ pH meter was calibrated with buffer solutions and calibration was checked intermittently.

All potentiometric titrations were carried out at $30 \pm 0.01^\circ\text{C}$ by using carbon dioxide free sodium hydroxide solution¹⁹. The proton ligand and metal ligand stability constants are calculated using EXCEL computer program on the basis of literature method²⁰.

Result and Discussion

The formation constants of the binary complexes formed due to interaction of trivalent lanthanone(III) ions with diamines *i.e.* *N-N* diethyl ethylenediamine, *N-N* dimethyl ethylenediamine, 1,3 diamino propane and 1,2 diamino propane were calculated by measuring the magnitude of the shift in pH observed during the titration of the ligand in absence and in the presence of metal against standard sodium hydroxide solution²¹. The proton ligand and metal ligand stability constants are presented in the Table 1.

Ethylenediamine, 1,2 diaminopropane, 1,3 diaminopropane, *N-N* diethyl ethylenediamine and *N-N* dimethyl ethylenediamine are bidentate ligands. The basicity of *N-N* diethyl ethylenediamine is highest among the diamines used. It is observed that proton ligand stability constant values are of the same order as reported earlier²².

Proton ligand stability constants are in the following order.....*N-N* diethyl ethylenediamine > *N-N* dimethyl ethylenediamine > 1,2 diamino propane > ethylenediamine > 1,3 diamino propane.

Metal ligand stability constant value for *N-N* dimethyl ethylenediamine are higher than *N-N* diethylethylenediamine although proton ligand stability constant for *N-N* diethyl ethylenediamine is higher than *N-N* dimethyl ethylenediamine. The steric hinderance due to present of two $-\text{C}_2\text{H}_5$ groups on two chelating nitrogen atoms of *N-N* diethyl ethylenediamine has lowered the value of binary stability constants of M(III) *N-N* diethylethylenediamine than M(III) *N-N* dimethyl ethylenediamine.

Besides the basicity of the ligand, size of metal ion and charge/size ratio also plays an important role in determining the value of metal ligand stability constant. Lanthanones(III) form stable complexes and the order of the stability are expected²³ with respect to the electronic configuration, size and ionic potential of tripositive ions. In present study, this order is followed by $\log K_1$ values for Gadolinium and Dysprosium complexes as expected with respect to ligand basicity. In other cases, there is deviation in order of metal ligand stability constants. This may be due to combined effect of steric factor, size of lanthanone ion and charge/size ratio of lanthanone ion²⁴.

Table 1. Proton-ligand and metal–ligand stability constants of lanthanone(III) ions at temperature $30 \pm 0.1^\circ\text{C}$. Ionic strength $\mu = 0.2 \text{ M dm}^{-3}$ (NaClO_4).

Metal Ligand	pk_1^{H}	pk_2^{H}	Sm		Gd		Dy		Yb	
			$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$
Ethylene diamine	9.77	7.04	4.44	3.54	4.22	3.84	4.12	3.38	4.56	3.49
1,2 diamino propane	9.85	6.97	4.68	3.67	4.44	4.10	4.64	4.05	4.70	3.67
1,3 diamino propane	9.56	8.19	4.22	3.69	4.59	3.51	5.00	3.79	4.23	3.63
<i>N-N</i> diethyl ethylene diamine	10.51	7.09	4.33	3.54	4.68	4.21	5.06	4.66	5.25	4.69
<i>N-N</i> dimethyl ethylene diamine	9.89	6.73	5.05	3.87	5.68	4.54	5.99	4.76	5.65	4.72

Conclusion

All the diamines selected were found to form complexes in solution state under the experimental conditions. Their order of stabilities is explained on the basis of basic character of ligands, size of metal ion, steric effects *etc.* The study also suggests the possibility of the formation of complexes in solid state.

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