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NOTE

Equilibrium Studies on Some Binary Complexes of La(III), Ce(III), Pr(III) and Nd(III) with Ligands Containing N-N Donor Atoms

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The present paper describes a potentiometric study on formation constants of binary complexes of inner transition "4f" metal ions La(III), Ce(III), Pr(III) and Nd(III) with amines such as ethylenediamine, N-N-dimethyl ethylenediamine, N-N-diethyl ethylenediamine, 1,2-diaminopropane and 1,3-diaminopropane carried out at constant temperature 30 ± 0.1°C and ionic strength $\mu = 0.2$ M dm^{-3} ($NaClO_4$). Various factors influencing the formation and stabilities of binary complexes have been discussed.

Lanthanide complexes are well known in the field of biochemistry, medicinal chemistry, pharmacology and physiology[1]. The ligands containing functional groups identical with those present in enzymes, *viz.*, —COOH, —NH_2, —CONH— etc. are very important for many analytical and biological reactions[2]. The complexes of Ni(II) with 1,3-diaminopropane as ligand have been studied using computer programme[3].

The amines were obtained from E. Merck (AR grade). Other reagents used were sodium perchlorate (Fluka), perchloric acid (Baker analysed) and sodium hydroxide (BDH AnalaR grade). Metal and acid contents of the solution under analysis are determined by acid-base titration[4] and complexometric titrations[5]. Ionic strength was maintained at 0.2 M dm^{-3} with the use of sodium perchlorate. 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 ± 0.1°C using carbonate-free NaOH following the procedure[6, 7].

Irving-Rossotti titration technique[7, 8] was used for determination of binary formation constants.

The proton ligand and metal ligand formation constants of ligands and trivalent lanthanone ions with amines were calculated by measuring the magnitude of the proton displacement during titration of ligand in absence and in presence of metal ions against standard sodium hydroxide, respectively. The proton ligand and

binary metal ligand formation constants are presented in Table-1. The proton-ligand formation constant values are same as reported earlier[9]. The metal-ligand formation constant values are in the order of

N,N diethyl ethylenediamine > N,N dimethyl ethylenediamine
> 1,2-diaminopropane > Ethylene diamine > 1,3-diaminopropane

The order is explained in terms of the basicities of ligands. 1,3-Diaminopropane forms a six-membered chelate ring while all other ligands form a five-membered chelate ring in coordination with lanthanone (III) ions. So complexes of 1,3-diaminopropane are least stable; lower pK_1^H values of 1,3-diaminopropane indicate least basicity in this group of amines. The proton ligand formation constant values confirm the above given order. The base strength of N-N-diethyl ethylenediamine is higher than N,N-dimethyl ethylenediamine but steric hindrance of two $—C_2H_5$ groups on two chelating nitrogen atoms has lowered the value of binary formation constant of M → N,N-diethyl ethylenediamine than M → N,N-dimethyl ethylenediamines.

Besides, basicity of ligand, size of the metal ion and charge/size ratio also play an important role in values of binary formation constant values[10]. The overall formation constant values for ethylenediamines and 1,2-diaminopropane are found to be in accordance with the order La > Ce > Pr > Nd as expected with respect to electronic configuration, size and ionic potential for tripositive ions. The proton ligand formation constant values for ethylenediamine and 1,2-diaminopropane are nearly same. In some cases there is deviation in the order of metal ligand formation constants. This may be due to combined effect of basicity along with steric hindrance due to $—C_2H_5$ groups or $—CH_3$ groups present in such ligands.

TABLE-1
BINARY METAL LIGAND FORMATION CONSTANTS OF VARIOUS AMINES AT TEMPERATURE 30 ± 0.1°C AND IONIC STRENGTH $\mu = 0.2$ M dm^{-3} ($NaClO_4$)

Metal(III) ions	Ligand				
	ethylene diamine	N,N-dimethyl ethylene-diamine	N,N-diethyl ethylene-diamine	1,2-diamino-propane	1,3-diamino-propane
La	3.70	5.02	4.21	3.75	3.02
Ce	3.67	5.20	4.49	4.35	3.23
Pr	4.26	4.99	4.38	4.53	3.53
Nd	3.98	5.03	4.09	4.42	3.61

Minimum deviation = ± 0.05 units

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