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NOTE

pH Metric Studies on Some Binary Complexes of Dysprosium(III) and Ytterbium(III) with Ligands Containing N,N-Donor Atoms

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The present paper describe pH-metric study on formation constant of binary complexes of dysprosium [Dy(III)] and ytterbium [Yb(III)] with amines has been carried out at constant temperature 30 ± 0.1 ºC. The ionic strength μ = 0.2 M dm^{-3} was held constant was held constant using $NaClO_4$ as an electrolyte. Various factors influencing the formation and stabilities of binary complexes have been discussed.

Key Words: pH-Metric, Dy^{3+}, Yb^{3+}, Binary complexes, Diamines.

Lanthanide complexes are well known in the field of biochemistry, medicinal chemistry and pharmacology[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 formation, stabilities and reactivities of these complexes is a very active and challenging field of research[3,4].

The amines were obtained from E. Merck (AR grade) other reagents used were sodium perchlorate (Fluka), perchloric acid (Baker analyzed) and sodium hydroxide (BDH AnalR grade). Metal and acid contents of the solution under analysis are determined by acid-base titration[5] and complexometric titration[6].

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 potentiometic studies. μ pH meter was calibrated with buffer solution and calibration was checked intermittently. All potentiometric titrations were carried out at 30 ± 0.1ºC using carbonate free NaOH following the procedure[7,8]. Irving rossotti titration technique[8,9] was used for determination of binary formation constants.

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Ethylene diamine, 1,2-diamino propane, 1,3-diamino propane, N,N-diethyl ethylene diamine, N,N-dimethyl ethylene diamine all are bidentate ligands. The base strength of N,N-diethyl ethylenediamine is higher amongst diamines used. It is observed that proton ligand stability constant value are in the same order as reported earlier.

The proton ligand formation constant values are some as reported. The proton ligand formation constant value are in the order of

N,N-diethyl ethylene diamine > N,N-dimethyl ethylene diamine >
1,2-diamino propane > ethylene diamine > 1,3 diamino propane

Metal ligands stability constant value for N,N-dimethyl ethylene diamine are higher than N,N-diethyl ethylenediamine although proton ligands stability constant for N,N-diethyl ethylenediamine is higher than N,N-dimethyl ethylenediamine. The steric hinderance due to presence of two-C_2H_5 groups on two chelating nitrogen atoms of N,N-diethyl ethylenediamine has lowered the value of binary stability constants of M $\rightarrow$ N,N-diethylethylene diamine than M $\rightarrow$ N,N-dimethyl ethylene diamine.

Besides the basicity of the ligands size of metal ion and charge/size ratio also plays an important role in determine the value of metal ligand stability constant. The ionic size and charge/size ratio of lanthanide ions (Dy and Yb) are given in Table-1.

TABLE-1

Atomic no.	Symbol	Ionic radii Å	Decrease in size Å	Charge M^{3+} ionic size	Decrease in charge M^{3+} ionic size
66	Dy	0.908	0.015	3.3040	0.0537
70	Yb	0.858	0.011	3.4965	0.0443

TABLE-2
N, pL, log β_2, log K_1, logK_2, DATA OF Dy(III)
ETHYLENEDIAMINE SYSTEM AT 30 ± 0.1 ºC

n	pL	log β_2	log K_1	log K_2
1.25	4.009	8.05	4.38	3.67
1.51	3.975	8.00	4.27	3.73
1.53	3.952	7.92	4.22	3.69
1.54	3.929	7.82	4.18	3.64
1.64	3.900	7.58	4.14	3.44
1.60	3.886	7.51	4.10	3.41
1.65	3.866	7.11	4.08	3.03

Average values for log β_2 = 7.56 ± 0.26; log K_1 = 4.12 ± 0.09;
log K_2 = 3.38 ± 0.23

Lanthanide(III) ions from stable complexes and the order of the stability is expects with respect to the electronic configuration size and ionic potential of tripositive ions.

In present study, the order is followed by log K_1 values for dysprosium complexes as expected with respect to ligands basicity (Table-2). In other cases there is deviation in the order of metal ligands stability constant (Table-3), this may be due to combined effect of steric factor, size of lanthanide ions and charge/size ration of lanthanide ion.

TABLE-3
BINARY METAL LIGANDS FORMATION CONSTANT OF VARIOUS AMINES OF TEMPERATURE 30 ± 0.1 ºC AND IONIC STRENGTH μ: 0.2 M dm^{-3} ($NaClO_4$)

Ligand	Dy(III)	Yb(III)
Ethylene diamine	$\log K_1 = 4.12$ $\log K_2 = 3.38$	$\log K_1 = 4.56$ $\log K_2 = 3.49$
1,2-Diamino propane	$\log K_1 = 4.64$ $\log K_2 = 4.06$	$\log K_1 = 4.70$ $\log K_2 = 3.67$
1,3-Diamino propane	$\log K_1 = 5.00$ $\log K_2 = 3.79$	$\log K_1 = 4.23$ $\log K_2 = 3.63$
N,N-Diethyl ethylene diamine	$\log K_1 = 5.06$ $\log K_2 = 4.66$	$\log K_1 = 5.25$ $\log K_2 = 4.69$
N,N-Dimethyl ethylene diamine	$\log K_1 = 5.99$ $\log K_2 = 4.76$	$\log K_1 = 5.65$ $\log K_2 = 4.72$

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