INFLUENCE OF IONIC STRENGTH OF MEDIUM ON COMPLEX EQUILIBRIA OF LANTHANUM (III) AND NEODIMIUM (III) WITH SUBSTITUTED SCHIFF'S BASES

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Abstract:

The interactions of metal ions with Ligand (L5) and Ligand (L6) at various ionic strength in 70% DMF-water mixture is investigated by Calvin-Bjerrum pH-metric technique at 28 ± 10C. The ionic strength data were used to study the correct mechanism of complexation reaction. The thermodynamic properties of electrolyte solutions can be studied from long range interaction forces and short range interactions between ions and solvent molecules.

Keywords:

DMF - Dimethyl Formamide Ligand (L5) - 2 – Hydroxy -3-bromo-5-chloro-1-(α-para nitro phenyl imino) ethyl benzene Ligand (L6) - 2 – Hydroxy -3-bromo-5-chloro-1-(α-meta nitro phenyl imino) ethyl benzene

Introduction:

Debye and Huckel have given a theory of ion-ion interaction of dilute solution according to which the mean activity coefficient log (f±) of an electrolyte dissociating into cations of valency Z1 and anions of valency Z2 is given by –

log⟦f ± = - ⟧ (A|Z_1 Z_2 | √(μ))/(1+Ba √(μ)) ....(1)

Where the constants 'A' and 'B' involve the absolute temperature and the dielectric constant of the medium and 'a' is defined as the distance of closest approach of the ions. An equation due to Guntelberg1 for aqueous solution assumes to form –

log⟦f ± = - ⟧ (A|Z_1 Z_2 | √(μ))/(1+ √(μ)) ....(2)

The long range ions pairs not considered by Bjerrum have been discussed in a careful analysis of the whole theory by Fuoss and Krovs2. Equation (2) gives a pair representation of the behavior of a number of electrolytes up to μ = 0.1 M3. At every low value of √μ i.e. in every dilute solutions, the term Ba √μ will ultimately become negligible as compared to unity and equation (1) will be reduced to –

$\log f \pm = - A|Z_1 Z_2| \sqrt{\mu}$ .... (3)

This is Debye-Huckel limiting law according to which log f ± approaches linearly in the square root of concentration at high dilutions. Jaganathswami and Linaith4 have reported the information constants of bivalent metal chelates with some substituted chalcones. Narwade et al5 have studied the stability constants of Th(IV) complexes with some substituted pyrazolines. Ali-Asgar et al6 have investigated the metal-ligand stability constants of Cu(II) chelates with some substituted isoxazolines at different ionic strength. Sondewale et al have studied metal ligand stability constants of Cu(II)-complexes with O-Amino=Benzene-Sulphonic acid in different percentages of methanol-water mixture Mahajan have studied stability constants of Pr(III), UO_2(II) complexes with some substituted sulphonic acids. Bandopadhy et al7 have studied proton-ligand stability constants of its complexes with lanthanides (III) in various mixed aqueous solvents. In view of analytical applications, it was an interest to know the physio-chemical properties and influence of ionic strengths on complex equilibria.

Material and Method:

In present investigation, the dependence stability constants on the ionic strength of the medium was examined by taking fixed concentrations of metal nitrates and perchloric acid using pH-metric titrations. The system has been studied at 0.02 M, 0.04 M, 0.06 M, 0.08 M, 0.1M ionic strengths by varying the concentrations of sodium perchlorate. In addition to sodium perchlorate, the titrating system contains ions from perchloric acid, metal nitrate and sodium hydroxide. The total ionic strength of the medium is calculated by following expression –

$\mu = \frac{1}{2}\Sigma C_i z_i^2$ .... (4)

Where C_i and Z_i are the concentration and valency of the ith ion respectively.

Result and Discussion:

The stability constants for the following systems were determined at 0.02 M, 0.04 M, 0.06 M, 0.08 M, 0.1 M ionic strength. 1. pK Values of (i) Ligand (L5) and (ii) Ligand (L6) 2. Log K Values of (i) La (III) – Ligand (L5) (ii) Nd (III) - Ligand (L5) (iii) La (III) – Ligand (L6) (iv) Nd (III) - Ligand (L6) This pK and log K values for various systems at various ionic strengths are presented in Table 1, 2 and 3. It may be inferred from the experimental data that an increase in the ionic strength of the system causes decrease in the pK and log K values. Gudadhe et al8 have obtained stability constants of Cu(II) – 1- (2-hydroxy-5methyl phenyl)-3-phenyl-1, 3-propandeione t various ionic strengths. Gupta9 have determined the stability constants of transition metal complexes with salicylamide at various ionic strengths in 75% methanol-water mixture. The values of stability constants have been found to increase with decreasing ionic strength. Fazlur Rahman et al10 have determined the stability constants of different metal complexes with substituted acetophenone oxime at various ionic strength in 75% dioxane-water mixture. The values of stability constants have been found to increase with increasing ionic strength. Recently Agrawal et al11 have obtained stability constants of metal complexes of substituted methyl-5-carboxylates at various ionic strengths.

Table – 1

Proton-Ligands Stability Constants at Various Ionic strengths.

Ionic Strength	$\sqrt{\mu}$	$\frac{\sqrt{\mu}}{1\ \sqrt{\mu}}$	$\frac{\sqrt{\mu}}{1\ \sqrt{\mu}} - 0.03\mu$	pK	
				Ligand (L_5)	Ligand (L_6)
0.02	0.1414	0.1238	0.0813	5.30	5.55
0.04	0.2000	0.1666	0.1066	4.96	5.15
0.06	0.249	0.1967	0.1232	4.65	4.80
0.08	0.2888	0.2204	0.1355	4.30	4.35
0.10	0.3162	0.2402	0.1453	4.12	4.24

Table – 2

Metal-Lignd Stability Constants at Various Ionic Strengths.

Ionic Strength	La(III) – Ligand (L_5)		Nd(III) – Ligand (L_5)	
μ	log K_1	Log K_2	log K_1	Log K_2
0.02	4.0515	3.9525	3.5518	3.3665
0.04	3.9505	3.8115	3.4703	3.3160
0.06	3.8100	3.6985	3.3365	3.2000
0.08	3.7520	3.5515	3.2005	3.1010
0.10	3.5752	3.4655	3.1055	3.0102

Table – 3

Metal-Lignd Stability Constants at Various Ionic Strengths.

Ionic Strength	La(III) – Ligand (L_6)		Nd(III) – Ligand (L_6)	
μ	log K_1	Log K_2	log K_1	Log K_2
0.02	4.2505	4.1206	3.9552	3.8105
0.04	4.0552	3.9550	3.8100	3.6999
0.06	3.9505	3.8550	3.7550	3.6550
0.08	3.8051	3.7513	3.6990	3.5800
0.10	3.7575	3.6422	3.6115	3.5202

Conclusion:

An increase in the ionic strength of the system causes decrease in the pK and log K values.

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