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## Synthesis characterisation and stability constants of lanthanide (III) ion complexes of schiff base and their chemical speciation

**Dr. Tekale AS****Abstract**

The proton-ligand and metal ligand stability constant of 2,4 Diamino thiazole with R-substituted salicylaldehyde (R-5-SH<sub>3</sub> and 5-Cl) or 2-hydroxy-1-Nathanlyde ie, (5 mS)<sub>2</sub> DCT, (5 CS)<sub>2</sub> DCT and (HN)<sub>2</sub>DCT and lanthanide (III) ion complexes have been determined in ethanol-water (v/v) medium at different ionic strength ( $\mu$ )=0.2,0.15,0.1 and 0.05 m NaClO<sub>4</sub> and different temperatures 35 °C and 45 °C. The effect of dielectric constant on stability has also been studied at different percentages of solvent and variation in different solvent system.

The stability constants of the complexes are found to decrease with increasing ionic strength which is in agreement with Debye-Huckel equation. The stability of complexes containing an O-H or O-M link increases with increasing organic content of the solvent due to decrease in dielectric constant of the bulk solvent.

The thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) were calculated and over all free energy, enthalpy and entropy changes at room temperature. The negative free energy change (G) in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The positive values for S indicates the complexation reaction are entropically favored under the experimental condition.

**Keywords:** Synthesis characterisation, stability constants, lanthanide (III) ion, schiff base

**Introduction**

In our earlier communication <sup>[1-3]</sup> we have reported the stability constant of transition metals (Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup>) and Schiff bases derived fro 4-(P-bromophenyl)-2-amino thiazole and 2,4 Diamino-5-chlorothiazole and 2,4-Diamino thiazole with R-substitued slicylaldehyde. The literature survey reveals that no PH-metric work has been done on the lanthenide complexes of above Schiff bases so present study was undertaken to determine the stability constants of lanthanide with above Schiff bases at various ionic strengths, different temperatures and different percentage of solvent, in different solvent system.

**Experimental**

All chemicals are AR grade. The Schiff bases were prepared by condensation of 2,4 Diamino-5-chlorothiazole and 5-methyl salicylaldehyde, 5-chlorosalicylaldehyde and 2-hydroxy-1-napthaldehyde, ie, (MS)<sub>2</sub>DCT, (CS)<sub>2</sub>DCT and (HN)<sub>2</sub>DCT respectively. The structure I, II and III.

The titrations were carried out in nitrogen atmosphere using Elico-4T-120 PH- meter coupled with combined glass electrode. The PH meter was calibrated with standard buffer and readings were corrected as per literature<sup>4</sup>. The method of BJerm and calvin as modified by Irving and ROSotti has been used to determine the PK and logK values. The measurements were made at 25 °C, 35 °C and 45 °C also the measurements were made at ionic strength  $\mu$ =0.1 m (NaCl)<sub>4</sub> in 25:75 ethanol-water medium. The PH-metric titrations were performed against standard alkali (NaOH) as under

1. **Acid titration:** A mixture [2 ml 0.2 m HNO<sub>3</sub> + 1 mL 0.1 m NaClO<sub>4</sub> + 27 distilled water + 10ml ethanol]
2. **Schiff base titration:** A mixture (2 ml 0.2 HNO<sub>3</sub> + 1 ml 0.1 m NaClO<sub>4</sub> + 5 ml ligand solution + 27 distilled water + 5 ml ethanol]
3. **Metal ligand titration:** A mixture (2 ml 0.2 HNO<sub>3</sub> + 1 ml 0.1 m NaClO<sub>4</sub> + 5 ml ligand solution + 2 ml metal ion solution]

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complexation. The negative free energy change ( $\Delta G$ ) in each case indicates that the complexation is spontaneous.

The enthalpy changes are exothermic. The positive values for  $\Delta S$  indicates that entrop effects is found to be predominant over enthalpy effect.

Generally, the stability of the complexes containing with an O-H or O-M link increases with increasing organic content of the solvent due to decrease in dielectric constant of the bulk solvent [8, 10-12]. The dielectric constant decrease the ion-ion interaction involving the proton (or metal-ion) and the anionic oxygen donor of the ligand increases to a greater extent that the ion-dipole interaction between the proton (or metal ion) and the solvent molecules.

In a used composition, stability constant of metal complexes follow the trend 30%Et-OH>30%MeOH>30%DMF.

The high values of stability constant in ethanol is progressive of hydrogen bonding in water [12], ie, hydrogen bonded structure is less prevalent in ethanol than methanol and least in DMF.

The metal-ligand titration curve describe from the acid dissociation curve in the pH range 4.7 to 7 indicates that the complexation takes place in the pH range. The maximum value of n- is found 1.2 in all complexes which indicates that the lanthanide forms 1:1 complexes.

**Table 1:** Stability constants of lanthanide (III) ion in ethanol-water medium at different ionic strength

Sr. No.		Stability constant logK, Ionic strength ( $\mu$ ) (NaCl) <sub>4</sub>			
		0.05 m	0.1 m	0.15 m	0.2 m
1	H+ I	9.18,11.85	8.86,11.60	8.7,11.44	8.51,11.20
	pk <sub>1</sub> pk <sub>2</sub> II	9.44,11.40	9.125,11.10	9.012,10.95	8.81,10.74
	III	9.41,11.45	9.025,11.05	8.84,10.90	8.63,10.68
2	La(III) I	7.12	6.35	6.25	5.85
	II	7.50	6.60	6.50	6.10
	III	8.04	7.55	6.05	6.55
3	Ca(III) I	7.22	6.55	6.44	5.05
	II	7.63	7.14	6.99	5.58
	III	8.09	7.62	7.46	7.06
4	pr(III) I	7.30	6.54	6.43	6.03
	II	7.18	7.05	6.91	6.52
	III	8.15	7.65	7.53	7.02
5	Sm(III) I	7.50	6.71	6.60	6.42
	II	7.91	7.10	7.10	6.62
	III	8.28	7.55	7.34	7.03
6	Gd(III) I	7.12	6.30	6.20	5.81
	II	7.40	6.60	6.51	5.11
	III	7.92	7.13	7.01	6.62
7	Tb(III) I	7.35	6.66	6.56	6.15
	II	7.47	6.72	6.60	6.21
	III	7.803	7.60	7.48	7.08
8	Ho(III) I	7.42	6.71	6.59	6.20
	II	7.55	6.86	6.75	6.35
	III	8.09	7.42	7.31	6.92
9	Dy(III) I	7.48	6.73	5.61	6.23
	II	7.61	6.81	5.96	5.62
	III	8.11	7.35	7.22	6.77
10	Yb(III) I	7.54	6.84	6.72	6.31
	II	7.68	7.05	6.94	6.63
	III	8.16	8.52	8.41	8.03

**Table 2:** Stability constants of lanthanide (III) ion complexes of schiff bases in ethanol-water medium at ionic strength  $\mu=0.1$  m NaClO<sub>4</sub> at different temperatures 25 °C, 35 °C and 45 °C and thermodynamic parameters

Sr. No		LogK			- $\Delta G$ KJ MOL <sup>-1</sup>			- $\Delta H$ KJ MOL <sup>-1</sup>		$\Delta S$ JK MOL <sup>-1</sup>		
		25 °C	35 °C	45 °C	I	II	III	I	II	I	II	III
1	La(III) I	6.35	5.80	5.15	37.5	29.94	53.33	57.45	32.46	0.0669	0.0081	0.0090
	II	6.60	6.15	5.85	38.24	39.24	30.76	25.45	78.31	0.0429	0.1268	0.149
	III	7.55	7.05	6.70	41.69	36.23	31.27	40.52	65.52	0.0039	0.0983	0.107
2	Ce(III) I	6.55	6.06	5.65	35.94	35.78	31.46	43.87	15.31	0.0266	0.0653	0.0507
	II	7.14	6.66	6.03	45.10	35.54	33.50	70.74	29.63	0.0860	0.0200	0.0130
	III	7.62	7.12	6.72	41.92	45.55	37.26	29.84	34.75	0.04053	0.053	0.078
3	Pr(III) I	6.54	6.01	5.63	35.99	35.65	31.55	29.39	8.95	0.1892	0.086	0.0715
	II	7.05	6.49	6.14	36.18	36.28	41.60	36.83	24.29	0.0011	0.389	0.054
	III	7.65	7.12	6.73	41.27	45.55	37.23	30.69	79.68	0.03550	0.1108	0.130
4	Nd(III) I	6.62	6.09	5.72	35.64	29.01	31.20	48.62	20.41	0.0436	0.027	0.0341
	II	7.07	6.56	6.16	35.34	35.95	41.23	72.99	24.29	0.0246	0.036	0.0532
	III	7.41	6.92	6.65	42.42	34.71	37.53	42.29	67.34	0.0004	0.1059	0.0937
5	Sm(III) I	6.71	6.20	5.86	35.31	83.52	30.73	23.40	72.95	0.0411	0.1117	0.132
	II	6.10	6.55	6.09	34.45	36.00	30.61	30.98	54.21	0.0116	0.0591	0.055
	III	6.55	7.04	6.72	41.69	38.52	37.26	36.06	11.40	0.0195	0.088	0.0813

6	Gd(III) I	6.30	6.81	6.41	37.45	35.03	38.75	18.05	13.20	0.0651	0.0708	0.0803
	II	6.60	6.08	5.74	35.73	29.30	32.20	36.58	15.09	0.0028	0.046	0.0538
	III	7.13	6.61	6.24	35.28	35.74	40.16	44.84	18.09	0.0014	0.057	0.0882
7	Tb(III) I	6.66	6.14	5.76	35.49	40.27	31.05	28.18	77.47	0.0245	0.120	0.1459
	II	6.72	6.13	5.80	35.27	40.46	30.92	31.11	79.90	0.0139	0.128	0.1540
	III	7.60	7.11	6.82	41.46	46.76	36.92	30.83	83.62	0.0356	0.119	0.1468
8	Ho(III) I	6.71	6.21	5.84	41.01	39.23	30.79	22.14	72.66	0.0633	0.108	0.131
	II	6.86	6.32	5.92	34.88	38.16	30.05	17.96	55.14	0.0557	0.097	0.1109
	III	7.40	6.93	5.61	42.42	34.44	31.63	56.30	36.46	0.0465	0.0033	0.0183
9	Dy(III) I	6.73	6.11	5.73	35.29	40.89	31.16	34.40	18.37	0.0027	0.132	0.1578
	II	6.10	6.58	5.25	34.50	30.77	33.98	43.08	16.32	0.0287	0.046	0.0547
	III	7.35	6.66	6.22	42.88	30.44	40.39	53.38	21.30	0.0352	0.0296	0.0287
10	Yb(III) I	6.84	6.31	5.29	34.93	38.24	30.55	10.08	65.76	0.0827	0.089	0.1107
	II	7.05	6.52	5.15	36.23	36.92	35.33	42.56	20.54	0.0212	0.052	0.455
	III	7.52	8.01	7.66	41.89	53.25	43.56	38.34	57.34	0.0103	0.071	0.0433

**Table 3:** Stability constants of lanthanide (III) ion complexes of schiff bases. In different percentage of solvent and in various solvent system at ionic strength  $\mu = 0.1$  M NaClO<sub>4</sub> at temperature 25 °C $\pm$ 1C

Sr. No.	Cation	Different percentage of solvent ethanol			Different solvent system	
		Et-OH 30%	Et-OH 35%	Et-OH 40%	Me-OH 30%	DMF 30%
1	La(III) I	6.32	6.51	6.81	5.22	5.10
	II	6.61	6.87	7.10	5.50	5.38
	III	7.41	7.40	7.70	6.06	6.00
2	Ce(III) I	6.42	6.70	7.05	5.30	5.20
	II	6.83	7.05	7.30	5.71	5.60
	III	7.29	7.56	7.87	6.20	6.11
3	Pr(III) I	6.34	6.62	7.93	5.25	5.13
	II	6.81	6.98	7.25	5.72	5.61
	III	7.35	7.57	7.80	6.26	6.17
4	Nd(III) I	6.65	6.92	7.24	5.55	5.50
	II	6.90	7.15	7.42	5.52	5.75
	III	7.34	7.62	7.91	6.23	6.13
5	Sm(III) I	6.65	6.90	7.20	5.53	5.41
	II	6.98	7.24	7.55	5.80	5.74
	III	7.50	7.71	7.96	6.39	6.30
6	Gd(III) I	6.36	6.62	6.90	5.27	5.18
	II	6.66	6.62	7.24	5.60	5.52
	III	6.98	7.24	7.55	5.91	5.87
7	Tb(III) I	6.45	6.63	6.94	5.63	6.30
	II	6.61	6.86	7.10	5.56	5.41
	III	7.23	7.55	7.77	5.16	6.05
8	Ho(III) I	6.63	6.91	7.17	5.60	5.50
	II	6.67	6.98	7.32	5.63	5.52
	III	7.29	7.62	7.92	6.20	6.09
9	Dy(III) I	6.61	6.92	7.31	5.52	5.41
	II	6.82	7.10	7.42	5.75	5.68
	III	7.33	7.62	7.92	6.29	6.18
10	Yb(III) I	6.74	6.99	7.52	5.68	5.59
	II	6.77	7.05	7.36	5.71	5.60
	III	7.38	7.65	7.97	6.37	6.29

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