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Study the thermodynamics of complex formation of Rare earth metal ions with substituted thiazole Schiff bases in mixed solvent media

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Abstract

The Schiff bases derived from substituted aminothiazole i.e.2-4-Diamino thiazole and R-Substituted salicylaldehyde (R-5-CH_3 and 5-Cl) or 2-hydroxy-1-naphthaldehyde i.e. $(5MS)_2DT$, $(5CS)_2DT$ and $(HN)_2DT$ and Rare earth metal ion La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Ho^{III}, Dy^{III} and Yb^{III} Nitrate Salts.

The stability constants of lanthanide metal ion complexes in mixed solvent media in ethanol-water 50:50 (v/v) at different ionic strength $\mu = 0.05, 0.1, 0.15$ and 0.2 M ($NaClO_4$) and at different temperature (35 ^{0}C and 45 ^{0} C) using Bjerrum pH metric technic as adopted by Irving Rossotti.

The formation constants are determined by Half-Integral method. The stability constants of Rare earth metal (III) ion complexes have been to proportional to their ionic strength. The thermodynamic parameter (ΔH, ΔG and ΔS) were determined. The negative free energy change (ΔG) in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The positive values of ΔS Indicates the reactions are entropically favoured.

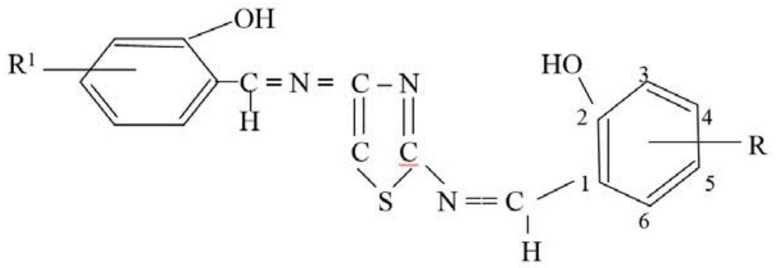
Keywords: Thiazote, Schiff base, Rare earths, Formation constant, Thermodynamic parameter**.**

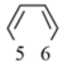
1. Introduction

In continuation of our earliest work [1-3] deals with the stability constants of Schiff bases and their transition metal (Co^{II}, Ni^{II}, Cu^{II} and Zn ^{II}) complexes. The Schiff base derived from substituting amino thiazole i.e. 2-aminothiazole. 2-4-diaminothazole and 2-4-diamino-5-chloro thiazole and 0-hydroxy aldehyde i.e. (5-CH_3, 5-Cl and 2-hydroxy-1-nathaldehydes). The review reveals that no work on stability constants of Schiff base and their rare earth metal complexes, hence on interest is taken to study the Schiff base and rare earth. Metal complexes in the present investigation. An attempt has been made to study the stability constant, effect of ionic strength and thermodynamic parameter of the Rare earth metal complexes. The Schiff bases derived from 2-4 diamino thiazole and 0-hydroxy aldehyde i.e. (5-CH_3, 5-Cl and 2-hydroxy-1-naphthaldehyde) and rare earths. La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Ho^{III}, Dy^{III}, Yb^{III}.

2. Materials and methods

All chemicals are A.R. grade. The Schiff bases were prepared by condensation of 2-4 diaminothiazole and 5-methylsalicylaldehyde, 5-Chloro salicylaldehyde and 2-hydroxy-1-naphthaldehyde i.e. $(5 MS)_2DT$, $(5CS)_2$ DT and $(HN)_2$ DT respectively. The structure I, II and III.



Sr. No.	Schiff base	$R = R^1$
I	$(5MS)_2$ DT	5 - CH_3
II	$(5CS)_2$ DT	5 - Cl
III	$(HN)_2$ DT	 5 6

I. *$(5MS)_2$ DT: [N-bis (5-methylsalicylindine) 2-4 diaminothiazole]*
II. *$(5CS)_2$ DT: [N-bis (5-Cholorosalicylindine) 2-4 diaminothiazole]*
III. *$(HN)_2$ DT: [N-bis (2-hydroxy-1-naphthalidine) 2-4 diaminothiazole]*

The fresh solutions of *$(5MS)_2$ DT, $(5CS)_2$ DT, $(HN)_2$ DT* were prepared in double distilled ethanol and always used. Stock solution of rare earth (Nitrate) salts were prepared in double distilled air-free water and their strength were formed in ethanol - water (50:50%) (v/v) at different ionic strength (µ) = 0.05, 0.1, 0.015 and 0.2 M ($NaClO_4$) and also at different temperature (35 and 45^0C) using Bjerrum pH, metric technic as adopted by Irving and Rossotti. The pH-metric titrations were performed against standard alkali (NaOH) solution as under.

1. *Acid titration: A Mixture [2ml 0.2 M $HClO_4$ + 1ml 0.1 M $NaClO_4$+17 ml distilled water + 20 ml ethanol]*
2. *Schiff base titration: A mixture [2ml 0.2 M $HClO_4$ + 1ml 0.1 M $NaClO_4$+10 ml ligand solution + 17 ml distilled water + 10ml ethanol]*
3. *Metal-Ligand titration: A mixture [2ml 0.2 M $HClO_4$ + 1ml 0.1 M $NaClO_4$+10 ml ligand solution + 2 ml metal ion solution + 15ml distilled water + 10 ml ethanol]*

The titrations were carried out in an inert nitrogen atmosphere using an Elico-4T-120pH meter with combined glass electrode. The pH meter was calibrated with standard buffer and the readings were corrected as per literature [4].

From titration curves at different pH values different sets of n^- values were determined of the corresponding free ligands (L) were calculated. The formation curves were drawn and found to be normal. The values of stepwise stability constant logk, and $logk_2$ of these complexes were determined at $n^- = 0.5$ and $n^- = 1.5$ from the formation curves. At each temperature average values of overall stability constant (logk) were plotted against ionic strength for the metal-ligand system and the values of thermodynamic stability constant (logk) at zero ionic strength were calculated by extrapolation.

The thermodynamic stability constants, the values of (ΔG^0) were calculated at 35 and 45 ^0C using relation free energy change

$$\Delta G^0 = 2.303 \text{ RT } logk^0$$

Enthalpy (H^0) $[1/T_2 – 1/T_1] = -2.303 (logk^0 T – (log k^0) T_1]$

and Entropy (ΔS^0) = $\Delta H^0 - \Delta G^0 / T$

3. Result and Discussion

Proton-ligand stability constant (PK) values of the ligands $(5MS)_2$ DT, $(5CS)_2$DT, and $(HN)_2$DT, were calculated using Half-Integral Method**.** The values are summarized in table 1.

The ligand posses two pK value due to dissociable proton of the two phenolic – OH group. The protonation of imino nitrogen (HC=N) does not take place in the pH range under study. The pK values of ligands follows the trend: ligand $(5MS)_2$ DT > $(5CS)_2$DT > $(HN)_2$DT, and it is explained on the grounds of basic nature of azomethine nitrogen and phenolic oxygen [5-7].

The ligand $(5CS)_2$ DT exhibit higher proton-ligand stability constant values than the ligand $(HN)_2$DT and this may be due to the presence of the Cl group in the aromatic ring. Cl behave as an electron releasing group due to a mesomeric effect (+ M) rather than (–I) effect (inductive effect). Hence electron density on phenyl ring increases and azomethine nitrogen and phenolic oxygen become more basic.

The ligands $(5MS)_2$ DT posses methyl group at meta position with respective to azomethine group. Due to (+I) effect of methyl group, electron density over phenyl ring increases and azomethine nitrogen and phenolic oxygen become more basic. Hence the ligand posses higher stability constant values.

Thus (+I) effect of methyl and stronger (+M) of halogen group present in the phenyl ring in the series of the Schiff base support the trend proposed for proton-ligand stability values.

4. Metal – Ligand stability constants

The titration curves of acid, ligands and the metal ions are studied. The metal ion curve shows departure from ligand curves at pH much lower than the pH of hydrolysis of metal ion and therefore the liberation of proton is due to chelation[7-9]. The metal ligand stability constants were determined by using Half Integral Method and values are summarized in table 2.

The order of stability constant for the trivalent Rare earth complexes have no regular trends that is in many cases no order is apparent [10-14].

Few observations were made for Rare earth complexes, were the increasing stability constants with increasing atomic number up to Tb^{III} and Yb^{III} [15-16] respectively.

In present observation complexes of Rare earth trivalent metal (iii) ions and Schiff bases I, II and III shows increasing in stability from La^{III} to Yb(III) in agreement with increasing Lewis acidity of the metal ions. The order of stability constant of Rare earth complexes with Schiff bases I, II and III has been found to be as follows.

$La^{III} < Pr^{III} < Nd^{III} < Gd^{III} < Ce^{III} > Sm^{III} < Tb^{III} < Dy^{III} < Ho^{III} < Yb^{III}$. The Gd^{III} has a low value of stability constant then Sm^{III} indicates the Gadolinium break. The Ce^{III} cerium show higher value due to the partial conversion of Ce^{III} to Ce^{III}.

The value of stability constants are decreased with increasing ionic strength which is an agreement with dehye-Hukel equation.

To study the effect of temperature on complexation observed that the value of proton-ligand and metal-ligand decreases with increasing temperature suggesting that low temperature is favorable for complexation. These results are good agreement with pitzer and Garge [16-17].

The thermodynamic parameters (ΔH, ΔG and ΔS) have been calculated and are summarized in Table 2. The ΔG and ΔH values are negative, the ΔG free energy change in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The ΔS values are positive. The positive values of ΔS indicates that entropy effect is found to be predominant over enthalpy effect.

Table 1: Stability constant of Rare earth trivalent metal ion in mixed solvent media ethanol – water (50:50) ($NaClO_4$) at different ionic strength 25 ^{0}C±1.

Sr. No.		Proton-Ligand and metal-ligand stability constant, Ionic strength (μ) – ($NaClO_4$) PK and log K			
		0.05M	**0.1M**	**0.15M**	**0.2M**
1) LH, PK$_1$,	I	8.95, 11.85	8.80, 11.55	8.66, 11.43	8.51, 11.23
PK$_2$	II	8.65, 11.52	8.40, 11.22	8.16, 11.04	8.01, 10.92
	III	8.38, 11.41	8.20, 11.10	8.03, 10.95	7.95, 10.88
2) La^{III}	I	7.10	6.55	6.25	5.90
	II	7.46	7.07	6.74	6.34
	III	7.92	7.51	7.21	6.84
3)Ce^{III}	I	7.35	6.95	6.65	6.26
	II	7.75	7.35	7.05	6.71
	III	8.16	7.80	7.42	7.05
4) Pr^{III}	I	7.24	6.82	6.50	6.16
	II	7.62	7.20	6.91	6.62
	III	8.04	7.63	7.33	6.98
5) Nd^{III}	I	7.35	6.98	6.71	6.36
	II	7.87	7.47	7.16	6.82
	III	8.21	7.86	7.55	7.16
6) Sm^{III}	I	7.40	7.05	6.74	6.34
	II	7.80	7.42	7.11	6.77
	III	8.22	7.85	7.56	7.21
7) Gd^{III}	I	7.30	6.90	6.61	6.32
	II	7.70	7.33	7.02	6.75
	III	8.11	7.72	7.42	7.14
8) Tb^{III}	I	7.45	7.06	6.76	6.36
	II	7.86	7.42	7.12	6.78
	III	8.28	7.91	7.61	7.27
9) Ho^{III}	I	7.52	7.12	6.81	6.41
	II	7.96	7.52	7.23	6.86
	III	8.31	7.90	7.63	7.31
10) Dy^{III}	I	7.55	7.05	6.76	6.35
	II	7.96	7.56	7.27	6.83
	III	8.36	7.94	7.66	7.32
11) Yb^{III}	I	7.58	7.27	7.01	6.64
	II	7.99	7.62	7.32	6.94
	III	8.40	8.01	7.68	6.30

Table 2: Metal ligand stability constants of Rare earth trivalent metal ion in mixed solvent media ethanol - water (50:50) (v/v) at ionic strength 0.1 M $NaClO_4$ and their thermodynamic parameters.

Cation	Log^{K}			-ΔG KJ Mol^{-1}			ΔS JK Mol^{-1}			-ΔH KJ Mol^{-1}	
	25 ^{0C}	35 ^{0C}	45 ^{0C}	I	II	III	I	II	III	I	II
La^{III} I	6.55	6.40	6.05	32.60	32.88	27.58	28.22	28.21	44.34	24.19	168.59
II	7.07	6.93	6.59	33.20	35.05	33.87	41.06	43.73	09.65	21.58	36.88
III	7.51	7.35	7.01	38.09	38.41	29.35	31.84	31.85	814.11	28.60	288.24
Ce^{III} I	6.95	6.78	6.44	33.95	34.59	33.13	63.62	63.63	41.72	14.99	46.40
II	7.35	7.14	6.82	36.90	36.08	34.71	109.7	108.8	27.32	69.61	43.36
III	7.80	7.61	7.24	39.20	39.83	37.45	62.2	62.46	120.3	20.59	75.62
Pr^{III} I	6.82	6.61	6.31	33.59	33.96	32.23	37.28	37.27	71.19	22.48	54.87
II	7.20	7.01	6.67	35.79	29.35	34.20	64.11	25.17	376.72	227.60	154.21
III	7.63	7.44	7.06	38.62	39.00	33.92	38.01	38.08	401.28	27.27	161.53
Nd^{III} I	7.98	6.78	6.46	34.03	34.59	33.24	55.95	55.97	30.06	17.35	42.80
II	7.47	7.27	6.92	37.89	37.75	35.01	14.12	14.12	164.33	42.10	87.27
III	7.86	7.65	7.31	39.38	39.99	38.10	60.83	60.84	68.93	21.25	60.02
Sm^{III} I	7.05	6.86	6.51	32.37	34.83	33.50	24.68	20.64	27.79	41.19	42.34
II	7.42	7.22	6.83	37.62	37.23	34.74	38.39	38.60	139.24	49.12	79.02
III	7.85	7.66	7.31	39.35	40.03	38.10	67.55	67.56	72.79	19.22	61.25
Gd^{III} I	6.90	6.71	6.36	33.82	46.09	32.61	53.05	91.16	70.56	18.01	55.05
II	7.33	7.14	6.81	37.02	36.08	34.68	94.36	94.35	75.69	65.14	10.61
III	7.72	7.53	7.19	38.94	39.47	36.86	52.55	52.56	145.56	23.28	83.15
Tb^{III} I	7.06	6.83	6.51	32.82	34.74	33.50	27.44	32.79	18.77	24.64	39.47
II	7.42	7.23	6.83	37.62	37.34	34.74	27.24	27.27	150.59	45.74	82.63
III	7.91	7.81	7.46	39.52	40.55	39.11	102.91	102.9	21.19	8.85	45.85
Ho^{III} I	7.12	6.91	6.55	34.52	34.98	33.69	45.33	45.35	22.38	21.01	40.81
II	7.52	7.33	7.01	38.14	38.26	29.36	12.04	12.04	799.11	34.55	283.48
III	7.90	7.71	7.34	39.50	40.22	38.39	72.11	72.11	66.94	18.01	59.68
Dy^{III} I	7.05	6.84	6.52	32.37	34.77	33.55	23.62	11.98	16.69	39.41	38.86
II	7.56	7.35	7.01	38.32	38.41	29.36	08.79	08.79	124.49	35.70	68.95
III	7.94	7.83	7.49	39.60	41.66	39.27	132.8	104.5	10.81	9.46	42.71
Yb^{III} I	7.27	7.04	6.70	36.53	32.88	34.31	36.39	36.42	34.81	145.08	45.38
II	7.62	7.43	7.03	38.58	38.94	32.15	36.20	36.20	557.70	27.79	215.86
III	8.01	7.83	7.52	34.08	40.61	39.42	42.51	39.01	4.81	160.77	37.89

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