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The study of stability constants and thermodynamic parameters of transition metal complexes of substituted aminothiazole schiff bases

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Abstract

Stability constants of transition metal complexes of 5-methyl-4-phenyl-2-aminothiazole and R-Substituted salicylaldehyde (R-H, 4CH₃ and 5-Br) i.e. N-(Salicylidene)-5-methyl-4-phenyl-2-aminothiazole (SMPAT), N-(4-methylsali-cylidene) 5-methyl-4-phenyl-2-aminothiazole (4MSMPAT) and N-(5-Bromosalicylidene)5-methyl-4-phenyl-2-aminothiazole. (5BSMPAT) has been determined in ethanol-water 75:25 (v/v) medium at different ionic strength. I = 0.1, 0.08, 0.06 and 0.04 M (NaNO₃) and at different temperature (35 and 45^oC) using Bjerrum PH – metric technique as adopted by Irving-Rossoti.

The formation constants (logβ_n) have been calculated using Bjerrum half integral n and graphical method. The stability constants of metals Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with SMPAT, 4MSMPAT and 5BSMPAT have been found to be proportional to their ionic strength and inversely proportional to the temperature. (-ΔH) and (-ΔG) values shows spontaneous and exothermic reactions respectively between the metal and ligand. (ΔS) values observed in all cases.

Keywords: Schiff base, stability constant and thermodynamic parameter

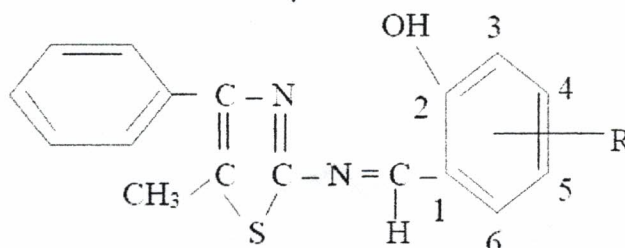
1. Introduction

Great researcher's like Bjerrum [1], Calvin [2], Irving-Rossotti [3], Martin [4] and Schwarzenbach [5] have made good contribution in the field stability constants of organic ligands and their metal complexes. Lot of work on metal complexes with organic ligands in aqueous or mixed solvents (ethanol-water, methanol-water or dioxane-water etc) and various methods are also available in the literature for calculation of stability constants.

The researcher mainly attracts towards Schiff bases in organic coordinating ligands due the reason of their strong ability to form complexes with transition metals and rare earth [6]. In our earlier communication [7] we have reported the metal (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) complexes of Schiff bases derived from 4-(P-Bromophenyl)-2-aminothiazole and R substituted salicylaldehyde. The complexes possess 1:2 stoichiometry and octahedral geometry and are found to be thermally stable. The Cu^{II} and Zn^{II} complexes exhibit good antibacterial activity against s. typhi.

In continuation of our earlier studies on complex formation of some transition metals with thiazole Schiff base [8]. The effect of ionic strength on stability constants and thermodynamic parameters of transition metal complexes with 5-methyl-4-phenyl-2-aminothiazole and R-substituted salicylaldehyde (R-H, 4-CH₃ and 5-Br) i.e.

1. N-(Salicylidene)-5-methyl-4-phenyl-2-aminothiazole (SMPAT)
2. N-(4-methylsali-cylidene) 5-methyl-4-phenyl-2-aminothiazole (4MSMPAT)
3. N-(5-Bromosalicylidene)-5-methyl-4-phenyl-2-aminothiazole. (5BSMPAT)



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Schiff base	R
3MPAT	H
4MSMPAT	4-CH ₃
5BSMPAT	5-Br.

2. Experimental

Fresh solution of SMPAT, 4MSMPAT & 5BSMPAT, prepared in double distilled ethanol, was always used. Stock solutions of metal salts (cobalt nitrate, Nickel nitrate copper nitrate and zinc nitrate) were prepared in double distilled air-free water and their strength were determined by usual method. Analar grade reagents were used. The study has been performed in ethanol-water 75.25% (v/v) at different temperature (35 and 45°C) at ionic strengths $I = 0.1, 0.08, 0.06$ and 0.04m (NaNO_3) using Bjerrum PH-metric technique were performed against standard alkali (NaOH) solution as under.

1. Acid Titration: A Mixture [2ml 0.2 M HNO_3 + 1ml 0.1 M NaNO_3 + 17 ml distilled water + 20 ml ethanol] was titrated against standard alkali (NaOH).
2. Schiff base titration: A Mixture [2ml 0.2 M HNO_3 + 1ml 0.1 M NaNO_3 + 10 ml ligand solution + 17 ml distilled water + 10 ml ethanol] was titrated against standard alkali (NaOH).
3. Metal-Ligand titration: A Mixture [2ml 0.2 M HNO_3 + 1ml 0.1 M NaNO_3 + 10 ml ligand solution + 2 ml metal ion solution + 15 ml distilled water + 20 ml ethanol] was titrated against standard alkali (NaOH).

The titrations were carried out in nitrogen atmosphere at different temperature using Elico-4T-120PH-Meter with combined glass electrode. The PH-meter was calibrated with standard buffer and the reading were corrected as per literature [9].

From titration curves at different PH values different sets of n values were determined and the corresponding free ligands (L) were calculated. The formation curves were drawn and found to be normal. The values of stability constant $\log k_1$, & $\log k_2$ of these complexes were determined at $n = 0.5$ and 1.5 from the formation curves. At each temperature average values of stability constants (Log K) were plotted against ionic strength for each metal-ligand system and the values of thermodynamic stability constant ($\log k$) at zero ionic strength were calculated by extrapolation.

The thermodynamic stability constants, the values (ΔG^0) were calculated at 35 and 45°C using the relation.

3. Free energy change

$$\Delta G^0 = -2.303 RT \log k^0$$

$$\text{Enthalpy } (\Delta H^0) [1/T_2 - 1/T_1] = -2.303 [(\log k^0) T_2 - (\log k^0) T_1] \text{ and Entropy } (\Delta G^0) = \Delta H^0 - \Delta G^0/T$$

4. Result and Discussion

The pH metric titration⁵ alone at different temperatures and different ionic strengths showed almost identical natural of the curves. Proton-ligand stability constant (pk) values of

the ligands 4MSMPAT and $(5\text{CS})_2\text{DCT}$ were calculated using. Half Integral and Graphical Method the ligands contains two pk value due to dissociable proton of the phenolic-OH group. The protonation of imino nitrogen ($\text{CH}=\text{N}$) does not take place in the pH range under study. The pk values of ligand follow the trend: 4MSMPAT > 5BSMPAT > SMPAT. It is explain on the grounds of basic nature of azomethine nitrogen and phenolic oxygen [10-13].

The ligand (4MSMPAT) posses methyl group at para position with respective to azomethine group. Due to effect of methyl group, electron density over phenyl ring increases and azomethine nitrogen and phenolic oxygen becomes more basic. Hence 4MSMPAT posses higher stability constant. In 5BSMPAT the *Br.* behave as electron releasing group due to (mesomeric effect) + M rather than - I effect (inductive effect). Hence electron density on phenyl ring increases and azomethine nitrogen and phenolic oxygen becomes basic.

5. Metal – Ligand stability constants

The titration curves of acid, ligands and the metal ions are studied. The metal ion curve show 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 [14-16]. The metal ligand stability constants were determined by using Half Integral & Graphical Method and the values are summarized in table 1.

The order of stability of Schiff base complexes follows trend: $\text{Zn} > \text{Co} > \text{Ni} > \text{Cu}$ and it is found to be in accordance with the order suggested by Irving and Williams [17].

To study the effect of temperature on complexation, we have chosen Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes of a representative Schiff bases 4MSMPAT and 5BSMPAT for the determination of metal-ligand stability constant at 35 and 45°C in ethanol-water (75:25%) medium and at constant ionic strength $\mu = 0.1\text{ M}$ (NaNO_3). The values of the metal-ligand stability constants are summarized in Table 1. As the temperature increases, the value of metal-ligand stability constant decreases suggesting that low temperature is favorable for complexation. The average values of stability constants were found to decrease with increasing ionic strength in all the cases and exhibited a decreasing trend with increasing temperature [18].

The thermodynamic parameters (ΔH , ΔG and ΔS) have been calculated and are summarized in Table 2. The $\log K$ values decrease with increase in temperature for complexation. The negative values of ΔG in all the cases showed spontaneous reaction between the metals and the ligands. Negative values of ΔH showed the exothermic nature of the metal-ligand interaction. Positive values of ΔS were observed in all. The ΔH , ΔG values are negative, while ΔS values are positive. The positive values of ΔS indicate that entropy effect is found to be predominant over enthalpy effect [12].

Table 1: Stability constants of bivalent transition metal complexes of 4MSMPAT and (5CS) 2DCT in ethanol-water 50:50% (v/v) medium at different ionic strength at 25°C + 0.5°C.

Metalion	Stability Constant	Ionic Strength (u)			
		0.04M	0.06M	0.08M	0.01M
4MSMPAT	pk	--	--	--	11.17
Zn-4MSMPAT	log k ₁	6.56	6.61	6.65	6.69
	log k ₂	5.47	5.53	5.58	5.62
	log β ₂	12.03	12.14	12.23	12.31
Co-4MSMPAT	log k ₁	6.52	6.58	6.61	6.67
	log k ₂	5.48	5.52	5.55	5.61
	log β ₂	12.00	12.10	12.16	12.28
Ni-4MSMPAT	log k ₁	6.50	6.48	6.54	6.64
	log k ₂	5.44	5.5	5.53	5.55
	log β ₂	11.94	11.98	12.07	12.19
Cu-4MSMPAT	log k ₁	6.44	6.47	6.51	6.55
	log k ₂	5.42	5.44	5.48	5.53
	log β ₂	11.86	11.91	11.99	12.08
5BSMPAT	pk	--	--	--	11.02
Zn-5BSMPAT	log k ₁	6.52	6.57	6.61	6.66
	log k ₂	5.51	5.46	5.59	5.63
	log β ₂	12.03	12.12	12.20	12.29
Co-5BSMPAT	log k ₁	6.48	6.51	6.66	6.60
	log k ₂	5.47	5.50	5.55	5.62
	log β ₂	11.95	12.01	12.21	11.92
Ni-5BSMPAT	log k ₁	6.44	6.47	6.51	6.55
	log k ₂	5.42	5.44	5.48	5.54
	log β ₂	11.86	11.91	11.99	12.09
Cu-5BSMPAT	log k ₁	6.40	6.45	6.56	6.53
	log k ₂	5.41	5.43	5.47	5.49
	log β ₂	11.81	11.88	11.97	12.02
SMPAT	pk	--	--	--	10.90
Zn-SMPAT	log k ₁	6.43	6.48	6.53	6.57
	log k ₂	5.42	5.37	5.50	5.51
	log β ₂	11.85	11.85	12.03	12.08
Co-SMPAT	log k ₁	6.39	6.42	6.47	6.51
	log k ₂	5.36	5.40	5.44	5.52
	log β ₂	11.75	11.82	11.92	12.03
Ni-SMPAT	log k ₁	6.34	6.37	6.42	6.45
	log k ₂	5.30	5.32	5.37	5.43
	log β ₂	11.64	11.69	11.79	11.88
Cu-SMPAT	log k ₁	6.31	6.35	6.45	6.48
	log k ₂	5.32	5.32	5.38	5.42
	log β ₂	11.63	11.67	11.83	11.90

log k₁ values are calculated by using Bjerrums half integral and graphical method.

Table 2: Stability constants of bivalent transition metal complexes of 4MSMPAT and 5BSBPAT in ethanol-water 75:25 (v/v) medium at ionic strength I = 0.1M NaNO₃ at different temperature, with overall free energy, enthalpy and entropy change at temperature = 25 + 0.5°C.

4MSMPAT												
S. No.	Cation	Log k ₁			-ΔG (kJ mol ⁻¹)			-ΔH (kJ mol ⁻¹)		-ΔS (JK ⁻¹ mol ⁻¹)		
		25°C	35°C	45°C	I	II	III	I	II	I	II	III
1.	Zn ^{II}	6.74	6.50	6.10	38.69	37.92	36.90	68.48	55.32	98.13	99.07	60.07
2.	Co ^{II}	6.72	6.40	6.05	38.51	38.61	36.80	68.71	64.35	45.40	88.40	88.80
3.	Ni ^{II}	6.69	6.38	6.04	38.63	37.70	36.26	68.72	62.67	97.36	98.84	84.42
4.	Cu ^{II}	6.60	6.35	6.01	38.29	37.80	38.42	52.66	33.17	48.17	48.19	66.72
5BSBPAT												
S. No	Cation	Log k ₁			-ΔG (kJ mol ⁻¹)			-ΔH (kJ mol ⁻¹)		-ΔS (JK ⁻¹ mol ⁻¹)		
		25°C	35°C	45°C	I	II	III	I	II	I	II	III
1.	Zn ^{II}	6.71	6.39	6.05	38.65	37.85	36.85	68.44	55.32	98.05	99.09	59.97
2.	Co ^{II}	6.65	6.37	6.02	38.59	38.48	36.74	68.64	64.27	45.29	8.55	88.68
3.	Ni ^{II}	6.60	6.30	5.97	38.60	37.75	36.37	66.65	62.62	97.27	98.75	84.27
4.	Cu ^{II}	6.58	6.28	5.95	38.35	37.35	38.36	52.47	33.08	48.07	48.08	66.65

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