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THERMODYNAMICS STUDY OF FORMATION OF ZINC COMPLEXES CARRYING NOVEL SCHIFF BASES IN MIXED SOLVANT MEDIA

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Abstract : The proton-ligand and metal-ligand stability constants of novel Schiff bases 4-hydroxy-3-(1-((5-substitutedphenyl)-1,3,4-thiadiazol-2-yl)imino)ethyl)-2H-chromen-2-one with transition metal ion Zn (II) ions using a pH metric titration technique in 80%(v/v) ethanol-water mixture at three different temperatures 25°C, 35°C & 45°C at an ionic strength of 0.1M $NaClO_4$ were determined. The Calvin-Bjerrum method as modified by Irving-Rossotti has been employed to determine metal-ligand stability constant logK values. The thermodynamic parameters such as, Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) associated with the complexation reactions were calculated.

***Keywords*:** stability constant, transition metal ion, Schiff bases, pH metric titration, thermodynamic parameter etc.

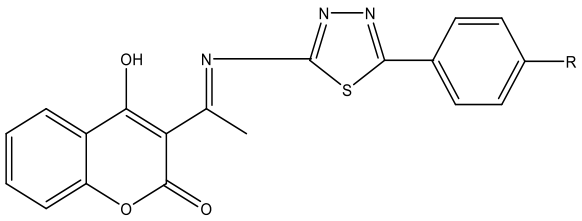
1. INTRODUCTION

pH metric titration a powerful electro-analytical technique due to its easy set up and reliability for determination of stability constants. Several d-block elements form complexes owing to incomplete d orbitals. Organic ligands with donor atons like N, O or S form complexes with these metal ions. Schiff base metal complexes are important class of coordination compounds due to their enormous applications. In the present investigation, we have selected series of seven schiff bases as ligands.

After a review of literature survey and in continuation of our earlier work with complexation of schiff bases and medicinal drugs[1-10], it was thought of interest to study the effect of temperature on thermodynamic parameters such as Gibb's free energy change ΔG, enthalpy change ΔH and entropy change ΔS of complexes of seven schiff bases with transition metal ion Zn^{2+} pH metrically in 80% (v/v) ethanol-water mixture.

2.SYNTHESIS OF SCHIFF BASES

All seven schiff bases were synthesised by reported methods[11-12]. The compounds 3-acetyl-4-hydroxy-2H-chromen-2-one and 2-amino thiadiazole derivatives were the intermediates for preparing novel Schiff bases 4-hydroxy-3-(1-((5-substitutedphenyl)-1,3,4-thiadiazol-2-yl)imino)ethyl)-2H-chromen-2-one. The ketone, 3-acetyl-4-hydroxychromen-2-one was prepared from 4-hydroxy coumarin and acetic acid in presence of $POCl_3$ refluxed for 30 minutes[13]. The aromatic amine, 5-(4-substitutedphenyl)-1, 3, 4-thiadiazol-2-amine was prepared by reacting para substituted benzoic acid with thiosemicarbazide in presence of conc. H_2SO_4 and refluxed for 4 hours[14-16]. The Schiff bases were prepared by adding 3-acetyl-4-hydroy chromen-2-one (0.01mole) and 5-(4-substitutedphenyl)-1, 3, 4 thiadiazol-2-amine (0.01mole) in ethanol (50ml) and refluxing the mixture for four hours. After cooling, the product was crystallized from ethanol. The purity of the ligand was checked by usual laboratory techniques i.e. m. p. and TLC. Melting points were determined in open capillaries and are uncorrected. These Schiff bases were characterized by IR, ^{1}HNMR, ^{13}CNMR.



R= -H, -CH_3, NO_2, -F, -Cl, -Br, -I

Fig. 1 *(Molecular formula $C_{19}H_{12}$ O_3N_3SR)*

3. EXPERIMENTAL

3.1 Materials and Solution: Salt of Zinc metal ion, NaOH, $NaClO_4$, $HClO_4$ used were of AR grade and all solutions were prepared in double distilled water free from CO_2. The NaOH solution was standardized against oxalic acid solution and standard alkali solution was again used for standardization of $HClO_4$. The measurements were made at temperatures 25°C, 35°C and 45°C in 80% (v/v) ethanol-water mixture at constant ionic strength (0.1M $NaClO_4$). The thermostat model SL-131 [Adar dutt and Co. India Pvt. Ltd. Mumbai] Narang Scientific Works Pvt. Ltd., New Delhi is used to maintain the temperature constant and the solutions were equilibrated in the thermostat for about 10-15 minutes before titration. The pH measurement was made using a digital Spectralab potentiometric titrator AT 38 C with combined glass electrode consisting of glass and reference electrodes in the single entity. This digital potentiometric titrator has built in voltage stabilizer for ± 10% fluctuations in voltage supply. The instrument has built in temperature compensator having range 0-99^{0}C. The instrument could read pH in the range 0.001-14.000 with an accuracy of 0.0017 pH unit and (0.1mV). Provision of in built three way valves and gas tight burette with Teflon piston with an accuracy of 0.001 mL enabled the required precision during the titration particularly near the equivalence point. The instrument was calibrated at pH 9.18, 7.00 and 4.00 using the standard buffer solutions.

3.2 pH metric procedures: To calculate the protonation constant of the ligand and the formation constant of the complexes with different metal ions, the following sets of solutions were prepared in 80% (v/v) ethanol-water mixture (total volume 50 ml) and titrated pH metrically against standard NaOH solution at temperature 25°C, 35°C and 45°C.

i. Free Acid $HClO_4$
ii. Free Acid $HClO_4$ + Ligand (schiff base)
iii. Free Acid $HClO_4$ + Ligand (schiff base) + Zn^{2+} metal solution

The above mentioned sets prepared by keeping M: L ratio, the concentration of perchloric acid and sodium perchlorate were kept constant for all sets.

3.3Determination of the thermodynamic parameters

Thermodynamic parameters such as Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) for formation of complexes were determined. The change in Gibb's free energy (ΔG) of the ligands is calculated by using the equation $\Delta G = -2.303RT \log K$, where R is ideal gas constant with a value of 8.314 $JK^{-1}mol^{-1}$, K is the dissociation constant for the ligand or the stability constant of the complex and T is absolute temperature in Kelvin.

The change in enthalpy (ΔH) is calculated by plotting *logK vs 1/T* The equation utilized for the calculation of changes in enthalpy is as Slope = - $\frac{\Delta H}{2.303R}$ The evaluation of changes in entropy (ΔS) is done by the equation: ΔS = $\frac{(\Delta H - \Delta G)}{T}$

Table 1: **Proton-ligand stability constant of schiff bases**

Temperature	***Proton-ligand stability constant***	**Schiff bases**						
		S1	S2	S3	S4	S5	S6	S7
25 °C	pK_1	3.2234	3.3961	3.0385	2.9744	3.6355	3.4792	--
	pK_2	4.4968	5.1755	4.7142	3.6138	4.8790	5.3457	4.0972
35 °C	pK_1	3.0782	3.2750	2.9374	2.8893	3.4614	3.3438	--
	pK_2	4.3749	5.0532	4.5991	3.487	4.7013	5.1946	3.9860
45 °C	pK_1	2.9303	3.1228	2.826	2.8061	3.3052	3.1451	--
	pK_2	4.2027	4.8810	4.4339	3.3352	4.5062	5.0035	3.8637

Table 2: **Metal-ligand (Zn-SB) stability constant of schiff bases**

Temperature	25 °C			35 °C			45 °C		
Metal-ligand stability constant → Schiff Bases↓	$logK_1$	$logK_2$	$log\beta$	$logK_1$	$logK_2$	$log\beta$	$logK_1$	$logK_2$	$log\beta$
S_1	3.8523	3.4107	7.2630	3.6612	3.3427	7.0039	3.4938	3.2753	6.7691
S_2	4.0048	3.2166	7.2214	3.8954	3.0454	6.9408	3.6316	2.8533	6.4849
S_3	4.4882	4.2126	8.7008	4.3055	4.0414	8.3469	4.0981	3.8351	7.9332
S_4	3.1837	2.6543	5.8380	3.0763	2.5497	5.6260	2.9733	2.4521	5.4254
S_5	4.3015	3.6197	7.9212	4.0928	3.4159	7.5087	3.8609	3.2312	7.0921
S_6	5.6139	4.3886	10.002	5.3627	4.1872	9.5499	5.0632	3.9326	8.9958
S_7	3.4203	3.0226	6.4429	3.2917	2.9407	6.2324	3.1727	2.8497	6.0224

Table 3: Thermodynamic parameters of shiff base complex formation with zinc metal ion at 25 °C

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	$(KJmol^{-1})$		$(KJmol^{-1})$		$(KJmol^{-1})$	
S_1	21.981	19.461	32.544	12.283	-35.4	24.1
S_2	22.851	18.353	33.853	32.935	-36.90	-48.93
S_3	25.609	24.036	35.362	34.208	-32.70	-34.10
S_4	18.166	15.145	19.090	18.349	-3.10	-10.80
S_5	24.544	20.653	39.944	35.261	-51.70	-49.00
S_6	32.032	25.041	49.906	41.311	-60.00	-54.60
S_7	19.516	17.246	22.470	15.675	-9.90	5.30

Table 4: Thermodynamic parameters of shiff base complex formation with zinc metal ion at 35 °C

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	$(KJmol^{-1})$		$(KJmol^{-1})$		$(KJmol^{-1})$	
S_1	21.591	19.713	32.544	12.283	-35.6	24.1
S_2	22.972	17.960	33.853	32.935	-35.30	-48.60
S_3	24.567	23.060	35.362	34.208	-36.20	-37.40
S_4	17.553	14.548	19.090	18.349	-5.20	-12.80
S_5	23.353	19.491	39.944	35.261	-55.70	-52.90
S_6	30.599	23.892	49.906	41.311	-64.80	-58.50
S_7	18.782	16.779	22.470	15.675	-12.40	3.70

Table 5: Thermodynamic parameters of shiff base complex formation with zinc metal ion at 45 °C

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	(KJmol^{-1})		*(KJmol^{-1})*		*(KJmol^{-1})*	
S_1	21.273	19.943	32.544	12.283	-35.4	24.10
S_2	22.112	17.373	33.853	32.935	-36.90	-48.90
S_3	23.383	21.882	35.362	34.208	-40.20	-41.40
S_4	16.965	3.99	19.090	18.349	-7.10	-14.60
S_5	22.030	18.437	39.944	35.261	-60.10	-56.50
S_6	28.89	22.439	49.906	41.311	-70.50	-63.30
S_7	18.103	16.0260	22.470	15.675	-14.70	2.00

4. RESULTS AND DISCUSSION

Results obtained are analyzed by the computer programme and the stability constant values are calculated. The proton-ligand stability constant is determined by point wise calculation method as suggested by Irving and Rossoti. The proton ligand stability constant pK_a of all seven schiff bases were determined in 80% (v/v) ethanol-water medium at three different temperatures 25 °C, 35 °C and 45 °C and at 0.1M ionic strength (NaClO4). The proton-ligand stability constants of all the schiff bases are presented in **Table 1.** The schiff base S7 has only one pK value where as S1, S2 , S3, S4, S5, and S6 have two pK values. The *n*A value ranges between 0.2 to 1.8 indicates the presence of two pK values whereas the range of *n*A is in between 0.2 to 0.8 shows only one pK value. In the present investigation schiff base selected contains hydroxyl group and azomethine nitrogen as bonding sites. The order of pKa values of seven drugs is as follows. **S6 > S2 > S5 > S3 > S1 > S4 > S7** The above order indicates that S_7 has lowest basicity whereas S_6 has highest basicity.

For the calculation of metal ligand stability constant logK of transition metal ion Zn (II) with schiff bases, point wise and half integral method of Calvin and Bjerrum as modified by Irving and Rossotti has been employed. The $\log K_1$ values calculated by point-wise calculation method and half integral method, indicates simultaneous formation of 1:1 complex. Values of proton-ligand formation number ($\overline{n}_A$) ranging between 0.2 to 0.8 and 1.2 to 1.8 indicates formation of 1:1 and 1:2 complex. The proton-ligand stability constant (pKa) values decrease with increase in temperature i.e. the acidity of the ligands increases[15]. This suggests that the liberation of proton becomes easier at higher temperature.

The order of metal-ligand stability constants for transition metal Zn (II) complexes with schiff bases (**Table 2)** found to be as follows:

S6 > S3 > S5 > S1 > S2 > S7 > S4

The metal-ligand stability of Bromo substituted schiff base is higher, while Fluro substituted Schiff base is lower {$S_6 > S_5 > S_7 > S_4$} and the metal-ligand stability of Nitro substituted schiff base is higher, while unsubstituted schiff base is lower. {$S_3 > S_2 > S_1$}.

The negative ΔG values indicates that both dissociation of the ligand and the complexation process are spontaneous[17]. A decrease in metal-ligand stability constant (logK) with an increase in temperature and the negative values of enthalpy change (ΔH) for the complexation suggests that all the complexation reactions are exothermic, favorable at lower temperature and the metal-ligand binding process is enthalpy driven[18] and metal-ligand bonds are fairly strong.

The positive entropy changes (ΔS) accompanying a given reaction are due to the release of bound water molecules from the metal chelates. The positive value of ΔS is considered to be the principal driving force for the formation of respective complex species. According to Martell and Calvin positive entropy effects was predicted towards an increase in the number of particles after the reaction and positive ΔS

is responsible to give more negative ΔG. The positive values of ΔS in some cases indicate that the entropy effect is predominant over enthalpy effect.The positive ΔS values for some metal complexes indicated that the formation of these complexes was entropy favored, while negative ΔS values for some metal complexes suggesting a highly solvated metal complexes.

5. CONCLUSIONS

Transition metal ion Zn (II) forms 1:1 and 1:2 complexes with all Schiff Bases. The metal-ligand stability constant logK decreases with an increase in temperature. The negative values of change in enthalpy (ΔH) for the complexation suggest that all the complexation reactions are exothermic, favorable at lower temperature. The negative change in free energy (ΔG) values indicates that both dissociation of the ligand and the complexation process are spontaneous. The negative change in entropy (ΔS) values indicated a highly solvated metal complex while positive ΔS values for some metal complexes indicated that the formation of these complexes was entropy favored.

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