

**TEMPERATURE EFFECT ON SOLUTION STABILITY CONSTANTS OF  
METAL COMPLEXES WITH SCHIFF BASES DERIVED FROM 5-  
ALDEHYDOSALICYLIC ACID – ANILINE AND ITS RELATED COMPOUNDS**

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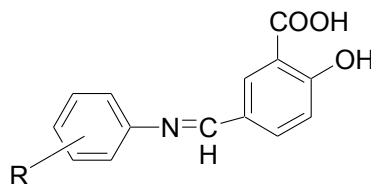
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**ABSTRACT:** Thermodynamic protonation constants of 5-aldehydosalicylic acid Schiff base with aniline and related compounds such as o-chloro aniline, o-nitro aniline, o-anisidine, o-toluidine and with 7-amino-4-methyl coumarin have been determined by Calvin-Bjerrum pH titration technique as used by Irving and Rosssotti. The solution stability constants of their complexes with bivalent metal ions Cu(II), Zn(II), Ni(II), Co(II), Cd(II) and Mg(II) with these ligands have been determined at four temperature in 50% water-ethanol mixture at an ionic strength of 0.1M (NaClO<sub>4</sub>). The order of solution stability constants was found to be Zn < Cu > Ni > Co = Cd > Mg which is in agreement with Irving – William's order. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  have been calculated for the various complex equilibrium. The Copper chelates found to be more stable than Zn and Ni chelates due to difference in their configurations. Cu(II) forms square planar complex while Zn(II), Ni(II) form a tetrahedral or octahedral complex. The log K value for Zn chelate is found to be higher as compared to that of Ni chelate in case of above said all reagents used for investigation.

**Key words:** 5-aldehydosalicylicacid-aniline, Thermodynamic stability constants.

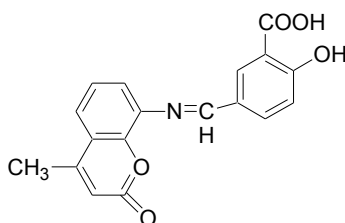
**INTRODUCTION**

The proton-ligand stability constants of 5-aldehydosalicylic acid Schiff base with aniline and related compounds such as o- chloro aniline, o- nitro aniline, o- anisidine, o- toluidine (Scheme 1) and with 7- amino-4-methyl coumarin (Scheme 2) and stability constants of their complexes with bivalent metal ions Cu(II), Zn(II), Ni(II), Co(II),Cd(II) and Mg(II) have been determined in 50% (v/v) water- ethanol medium at 15°C, 25°C, 35°C and 45°C, at an ionic strength of 0.1M (NaClO<sub>4</sub>). The order of stability constants was found to be in agreement with Irving – Williams order.



R	Reagent
H	5ASAA
o-Cl	5ASAOCA
o-NO <sub>2</sub>	5ASAONA
o-OCH <sub>3</sub>	5ASAOA
o-CH <sub>3</sub>	5ASAOT

(Scheme 1)



(Scheme 2)

(5-aldehydosalicylic acid with 7-amino-4-methyl coumarin Schiff base)

## Experimental

All the chemicals including metal salts, sodium hydroxide, perchloric acid, potassiumbiphthalate, and borax, EDTA etc., used were of analytical grade. Ethyl alcohol was purified by the method as described by the Vogel<sup>1</sup>. Carbonate free sodium hydroxide, was prepared by a standard method<sup>1</sup>. 5-aldehydosalicylic acid<sup>2</sup>, 7-amino-4-methyl Coumarin<sup>3,4</sup> and Schiff base compounds of 5-aldehydosalicylic acid with aniline and related derivatives (Scheme 1) were prepared by refluxing equimolar quantities of said aldehyde with above aniline and substituted anilines in alcoholic medium for about 2 hours as adopting the published standard procedures<sup>5</sup> and the Schiff base compound with 7-amino-4-methyl Coumarin was prepared using standard method<sup>6</sup>.

Compounds	Nomenclature	Abbreviation
I.	N - [2-hydroxy 5-carboxy benzylidene] Aniline	(5ASAA)
II.	N-[2-hydroxy5-carboxybenzylidene]O- Chloro aniline	(5SAOCA)
III.	N - [2-hydroxy 5-carboxy benzylidene] O- Nitro aniline	(5ASAONA)
IV.	N - [2-hydroxy 5-carboxy benzylidene] O-Anisidine	(5ASAOA).
V.	N - [2-hydroxy 5-carboxy benzylidene] O-Toluidine	(5ASAOT)
VI.	N-[2-hydroxy5-carboxybenzylidene]7-Amino-4-methylCoumrin	(5ASAAMC)

The Schiff bases thus prepared were more or less strongly colored and insoluble in water, but soluble in 50% (v/v) water-ethanol solvent medium and other organic solvents. They are recrystallised before use, and the purity was checked by elemental analysis, M.P. and IR spectra.

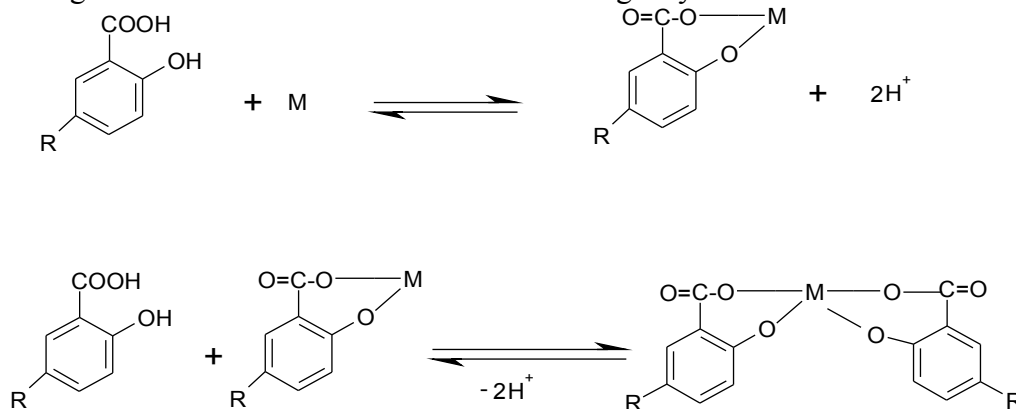
The concentration of metal ions in each of the metalperchlorates of Cu, Zn, Co, Cd and Mg was estimated by complex metric titrations as described by Schwarzenbach<sup>7</sup>, by using solutions of Na<sub>2</sub>-EDTA and standard sodium hydroxide. Magnesium was estimated by titrating it against standard Na<sub>2</sub>-EDTA solution using Erichrome Black T as an indicator. pH- meter (Digital) Model 335, systronics with combined electrodes were used over the entire pH range 0 to 14 reroducibility was within 0.01 pH units.

The medium of titration was 50:50 percent water-ethanol (v/v) mixtures. NaClO<sub>4</sub> was added to maintain constant ionic strength<sup>8</sup>. The pH metric titration were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solution, by following Calvin- Wilson technique<sup>9</sup> as adopted by Irving and Rossotti<sup>10,11</sup>.

The average number of protons ( $\bar{n}_H$ ) associated with HA (proton-ligand stability), the average number of ligand molecules attached per metal ion ( $\bar{n}$ ) (metal-ligand stability) and the free ligand exponent (pL) were calculated adopting the Irving-Rossotti technique. By applying various computations methods like half integral value, average value and least square treatment. The stepwise metal ligand stability constants were determined. The values obtained by different methods are in fair agreement. The least square treatment method has been applied to evaluate the protonation constants of these ligands.

## RESULT AND DISCUSSION

The thermodynamic stepwise protonation constants of selected six ligands and stepwise formation constants of the corresponding metal-ligand complexes obtained, as summarized in Table 1. In all the metal-ligand titrations, the  $\bar{n}$  values steadily increase with pH from 0.25 to 1.98 indicating the formation of 1:2 metal-ligand complexes as the highest complexes in these systems. The metal-ligand stability constants are obtained from analysis of average ligand number  $\bar{n}$  and pL data. The values of pL at  $\bar{n} = 0.5$  and  $\bar{n} = 1.5$  correspond to the first and second step stability constants respectively <sup>10, 11</sup>. The selected ligands react with metal ions in the following ways:



The metal-ligand curves of Zinc, Nickel, Cobalt, Cadmium and Magnesium follow the same path as Copper titrations and they depart at very low pH of the solution. For all chelating agents the relative positions of the metal curve indicate the relative stabilities of metal complexes, which follow the Irving-Williams <sup>12,13</sup> order: Zn < Cu > Ni > Co = Cd > Mg.

The enormously higher log K value for the Copper chelate is due to enhanced stabilization arising from John-Teller effect. The relatively low values of Mg<sup>+2</sup> can be attributed to steric hindrance preventing the formation of a square planar structure <sup>14</sup>. The log K<sub>1</sub> and log K<sub>2</sub> values of the M<sup>+2</sup> complexes of the present ligands with the corresponding complexes with salicylic acid <sup>15</sup>, 5-Sulfosalicylic acid <sup>16</sup>, 2-hydroxyl-3-methyl salicylic acid <sup>17</sup> and 3-aldehydosalicylic acid-aniline Schiff base <sup>18</sup>, indicate similar mode of coordination, it is by carboxylate-O and Phenolate-O atoms leaving the Schiff-base N-atom uncoordinated.

The value of pK<sup>H</sup> and log K at higher temperature indicates that the temperature increases the acidity of metal complexes. The enthalpy of complexation was determined by Van't Hoff equation.

$$d \log K / dT = \Delta H^\circ / 2.303 RT^2$$

The free energy change were calculated from the relationship

$$-\Delta G^\circ = 2.303 RT \log K \text{ and}$$

$$\Delta S^\circ = [\Delta H^\circ - \Delta G^\circ/T]. \text{ Or } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The values changes in  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  accompanying complexation reactions have been calculated at 25°C with the help of the above equation. For the Copper – ligand complexation  $-\Delta G^\circ$  values lies in the range of 40.80 KJ/mole to 69.62 KJ/mole. The negative values of  $\Delta G^\circ$  (Table 2) show that the complexation reactions tend to proceed spontaneously and the metal chelates are thermodynamically stable. The negative values of  $\Delta H^\circ$  indicate that the metal-ligand bonds are fairly strong and complexation reactions are exothermic in nature and this also explains the decrease in the value of log K with the rise in temperature.

**Table 1. Thermodynamic stability constants of complexes of 5-aldehydosalicylic acid –aniline and related compounds at different temperature.**

Cation	LogK1 15°C	25°C	35°C	45°C	LogK2 15°C	25°C	35°C	45°C
<b>5ASAA</b>								
H+	12.94	12.85	12.76	12.68	4.11	4.05	4.01	3.94
Cu+2	11.96	11.50	11.21	10.72	7.52	7.15	6.78	6.41
Zn+2	9.32	8.99	8.68	8.31	4.89	4.58	4.27	3.96
Ni+2	9.22	8.80	8.45	8.10	4.78	4.55	4.32	4.08
Co+2	8.84	8.50	8.16	7.86	5.07	4.73	4.40	4.08
Cd+2	8.79	8.47	8.18	7.91	4.42	4.14	3.86	3.63
Mg+2	6.31	5.94	5.58	5.26	4.34	3.98	3.62	3.29
<b>5ASAOCA</b>								
H+	13.25	12.98	12.71	12.44	3.67	3.58	3.49	3.40
Cu+2	11.32	10.74	10.22	9.87	8.82	8.37	7.83	7.29
Zn+2	9.36	8.90	8.44	8.01	7.86	7.38	6.91	6.42
Ni+2	7.89	7.46	7.03	6.60	5.59	5.12	4.65	4.21
Co+2	7.74	7.21	6.70	6.19	6.14	5.89	5.64	5.40
Cd+2	8.25	7.82	7.39	6.95	6.51	6.04	5.57	5.10
Mg+2	4.82	4.41	3.98	3.56	3.63	3.39	3.15	2.91
<b>5ASAONA</b>								
H+	12.99	12.81	12.63	12.45	3.97	3.75	3.61	3.43
Cu+2	12.67	12.20	11.73	11.26	8.58	8.22	7.86	7.54
Zn+2	9.32	8.99	8.68	8.37	7.93	7.60	7.27	6.94
Ni+2	8.01	7.73	7.47	7.22	5.74	5.47	5.23	5.05
Co+2	8.81	8.44	8.15	7.85	7.05	6.61	6.30	5.94
Cd+2	9.11	8.79	8.49	8.20	7.50	7.16	6.90	6.62
Mg+2	6.77	6.43	6.05	5.67	3.50	3.33	3.16	2.99
<b>5ASAOA</b>								
H+	13.70	13.39	12.95	12.75	2.70	2.47	2.24	7.01
Cu+2	11.42	10.88	10.34	9.80	9.40	8.91	8.42	7.93
Zn+2	9.28	8.69	8.11	7.52	8.34	7.79	7.24	6.99
Ni+2	7.82	7.54	7.26	6.98	5.74	5.32	4.90	4.48
Co+2	8.11	7.51	6.91	6.31	6.06	6.55	5.48	5.21
Cd+2	8.59	8.08	7.57	7.06	6.84	6.32	5.80	5.28
Mg+2	5.65	4.97	4.29	3.61	3.92	3.55	3.18	2.81
<b>5ASAOT</b>								
H+	12.90	12.65	12.44	12.18	3.89	3.71	3.55	3.37
Cu+2	11.93	11.36	10.79	10.22	8.32	7.84	7.33	6.88
Zn+2	9.38	8.80	8.22	7.64	7.86	7.43	7.00	6.57
Ni+2	7.53	7.20	6.87	6.54	5.52	5.29	4.51	4.27
Co+2	8.18	7.70	7.25	6.79	6.65	6.27	5.53	5.21
Cd+2	8.64	8.11	7.64	7.07	7.03	6.56	6.17	5.67
Mg+2	6.42	6.03	5.64	5.25	3.32	3.15	2.98	2.81
<b>5ASAAMC</b>								
H+	13.57	13.28	13.04	12.48	3.91	3.62	3.39	3.09
Cu+2	12.20	11.60	11.00	10.40	8.52	8.05	7.58	7.11
Zn+2	9.45	8.98	8.51	8.03	8.05	7.53	7.01	6.49
Ni+2	7.96	7.60	7.24	6.88	5.42	5.06	4.70	4.34
Co+2	8.49	8.01	7.53	7.05	6.80	6.32	5.84	5.36
Cd+2	8.91	8.36	7.81	7.26	7.21	6.64	6.04	5.52
Mg+2	6.86	6.47	6.08	5.69	3.89	3.63	3.37	3.11

The complex formation is favored by negative enthalpy and by positive enthalpy and by positive entropy changes. It is very difficult to predict the contribution of these terms because the salvation of the constituents of the complex also must be considered in general. According to William<sup>19</sup> the entropy term is usually favorable when ligand is anionic, and is generally unfavorable in the case of neutral ligands.

**Table 2. Thermodynamic functions of 5-aldehydosalicylic acid –Aniline and its related compounds (ML1 and ML2) at 25°C.**

Reagent		Cu(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	Zn(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
5ASAA	ML1	65.62	88.54	76.91	51.30	61.98	35.84
	ML2	40.80	66.37	85.81	26.13	53.57	92.08
ASAOCA	ML1	61.28	95.96	116.38	50.78	85.59	116.81
	ML2	47.76	91.91	148.15	42.11	79.95	126.98
5ASAONA	ML1	69.62	86.78	57.58	51.30	59.32	26.91
	ML2	46.90	64.52	59.13	43.37	57.47	47.32
5ASAOA	ML1	62.08	101.35	131.78	49.59	104.17	183.15
	ML2	50.84	87.21	122.05	44.45	95.24	170.44
5ASAOT	ML1	64.82	100.00	118.05	50.21	102.8	176.48
	ML2	44.74	90.23	152.65	42.40	76.53	114.53
5ASAAMC	ML1	66.17	105.93	132.36	51.24	92.59	138.76
	ML2	45.93	84.75	130.27	42.97	83.89	137.32
Reagent		Ni(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	Co(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
5ASAA	ML1	50.21	66.47	54.56	48.50	60.24	39.40
	ML2	25.96	43.48	58.79	26.99	56.60	39.40
ASAOCA	ML1	42.57	81.78	131.41	41.14	90.36	165.17
	ML2	28.22	75.89	156.61	33.61	46.88	44.53
5ASAONA	ML1	44.11	49.02	16.48	48.16	66.67	62.11
	ML2	31.21	43.42	42.65	37.72	56.82	64.09
5ASAOA	ML1	43.02	76.02	110.74	42.85	107.14	215.74
	ML2	30.36	51.02	69.33	32.92	52.45	65.54
5ASAOT	ML1	41.08	72.73	106.21	43.94	88.24	148.66
	ML2	30.19	61.32	104.46	35.98	84.16	161.68
5ASAAMC	ML1	43.37	64.04	72.72	45.71	90.48	150.24
	ML2	28.87	63.56	116.41	36.06	82.71	156.54
Reagent		Cd(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	Mg(II)- $\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
5ASAA	ML1	48.33	52.63	14.43	33.89	62.50	96.01
	ML2	23.62	48.87	84.73	22.71	61.40	129.83
ASAOCA	ML1	44.62	77.35	109.83	25.16	79.79	183.32
	ML2	34.47	83.33	163.96	19.34	45.11	86.48
5ASAONA	ML1	50.16	53.57	11.44	36.69	79.63	130.67
	ML2	40.86	52.17	37.95	19.00	32.61	4 5.67
5ASAOA	ML1	46.11	96.15	167.92	28.36	65.66	125.17
	ML2	36.06	87.38	172.22	20.36	64.87	140.70
5ASAOT	ML1	46.28	91.46	151.61	34.41	72.65	128.32
	ML2	37.43	78.95	139.33	17.97	30.70	41.38
5ASAAMC	ML1	47.70	105.26	193.15	36.91	71.09	114.64
	ML2	37.89	96.77	197.58	20.71	48.31	92.62

In the present work the negative  $-\Delta S^\circ$  values were observed which indicates favorable conditions for chelate formation<sup>20,21</sup>. In case of the transition type Cu(II) ion the increase in stability resulting from chelation is distributed about equally between entropy and enthalpy terms. It is learnt that the increase in stability resulting from chelation is due to the entropy factor, where, the equal values of  $\Delta H^\circ$  is seen in certain metal complexes. Table 2 of the reagents 5-aldehydosalicylic acid with aniline Schiff base and related compounds, the entropy factor can be noticed in few metal ions with few ligands in complexation.

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## Conclusions

The different types of metal complexes in solution of same ligand have been obtained by pH titration technique. This paper describes the equilibrium study regarding the complex formation of Schiff bases derived from the condensation of 5-aldehydosalicylic acid and aromatic primary amines and 7-amino-4-methyl coumarin with some bivalent metal ions.

These Schiff bases exhibit identical modes of coordination like salicylic acid and their equilibrium study were investigated for the first time. The ligands act as monobasic bidentate OO-donor (carboxylic oxygen and phenolic oxygen of 5-aldehydosalicylic acid involved in coordination) forming monometallic compounds of the type  $[M(LH)_2]$  in between the pH range 2 to 11 in 50% (v/v) water-ethanol medium.

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