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ROLE OF TEMPERATURE ON STABILITY CONSTANTS OF METAL COMPLEXES IN 50% (V/V) WATER-ETHANOL SOLUTION

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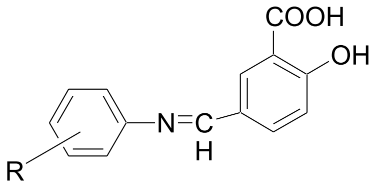
ABSTRACT: Thermodynamic protonation constants of 5-aldehydosalicylic acid-aniline Schiff base, [5ASAA], and o-, m-, p-Toluidine Schiff bases with 5-aldehydosalicylic acid have been determined by Calvin –Bjerrum pH titration technique as used by Irving and Rossotti. The thermodynamic formation constants of the chelates of Cu (II), Co (II), Ni (II), Zn (II), Cd (II) and Mg (II) with these four ligands have been determined at four different temperatures in 50% (v/v) water-ethanol mixture; the stabilities of complexes follow the Irving-William's order.

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-toluidine, m-toluidine and p-toluidine Schiff bases with 5-aldehydosalicylic acid (Scheme –I) and stability constants of their complexes with bivalent metal ions Cu(II), Zn(II), Ni(II), Mg(II), Co(II) and Cd(II) have been determined in 50% (v/v) water-ethanol medium at 15^0C, 25^0C, 35^0C and 45^0C, at an ionic strength of 0.1M ($NaClO_4$). The order of stability constants was found to be in agreement with Irving-Williams order.



R	
H	5ASAA
o-CH_3	5ASAOT
m-CH_3	5ASAMT
p-CH_3	5ASAPT

Scheme I

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[1]. Carbonate free sodium hydroxide, was prepared by the electric method of Vogel[1].

For the first time Schiff bases of 5-aldehydosalicylic acid with aniline, o- , m- , p-toluidene were prepared by refluxing equimolar quantities of said aldehyde with above aniline and substituted anilines in alcoholic medium for about 2 hours[2,3]. 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 metal per chlorates was estimated by complex metric titrations as described by Schwarzenbach[4], by using solutions of Na_2-EDTA and standard sodium hydroxide. Magnesium was estimated by titrating it against standard Na_2-EDTA solution using Erichrome Black T as an indicator. pH- metric titrations were carried out by Following Calvin-Wilson technique[5] as adopted by Irving and Rossotti [6, 7].

The average number of protons ($\tilde{n}_H$) associated with HA; the average number of ligand molecules attached per metal ion (ñ), 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 squire treatment. The stepwise metal ligand stability constants were determined. The values obtained by different methods are in fair agreement. The least squire treatment method has been applied to evaluate the protonation constants of these ligands.

RESULT AND DISCUSSION

The thermodynamic stepwise protonation constants of selected ligands and stepwise formation constants of the corresponding metal-ligand complexes obtained, and summarized in Table 1. In all the metal-ligand titrations, the ñ 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 ñ and pL data. The values of pL at ñ = 0.5 and ñ = 1.5 correspond to the first and second step stability constants respectively [6, 7].

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 the metal complexes, which follow the Irving-Williams 8,16 order: Zn < Cu > Ni > Co = Cd > Mg.

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
5ASAA								
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	1072	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
5ASAOT								
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
5ASAMT								
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
5ASAPT								
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 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+2 can be attributed to steric hindrance preventing the formation of a squire planar structure [9]. The log K1 and log K2 values of the M+2 complexes of the present ligands with the corresponding complexes with salicylic acid [10], 5-Sulfosalicylic acid [11], 2- hydroxyl-3-methyl salicylic acid [12] and 3- aldehydosalicylic acid- aniline Schiff base [13], indicate similar mode of coordination, it is by carboxyl ate-O and Phenol ate-O atoms leaving the Schiff-base N- atom uncoordinated.

Table 2.Thermodynamic functions of 5-aldehydosalicylic acid –Aniline and its related compounds (ML1 and ML2) at 25^{o}C.

Reagent		**Cu(II)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**	**Zn(II)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**
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
ASAOT	**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
5ASAMT	**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
5ASAPT	**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)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**	**Co(II)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**
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
ASAOT	**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
5ASAMT	**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
5ASAPT	**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)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**	**Mg(II)** **$-\Delta G^o$**	**$-\Delta H^o$**	**$-\Delta S^o$**
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
ASAOT	**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
5ASAMT	**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
5ASAPT	**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

The value of pK^H 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.

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

The free energy change were calculated from the relationship

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

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

The values changes in ΔG^o , ΔH^o and ΔS^o accompanying complexation reactions have been calculated at 25oc with the help of the above equation. For the Copper – ligand complexation -ΔG^o values lies in the range of 40.80 Kj/mole to 69.62 Kj/mole. The negative values (Table 2) of ΔG^o show that the complexation reactions tend to proceeds spontaneously and the metal chelates are thermodynamically stable. The negative values of ΔH^o indicate that the metal- ligand bonds are fairly strong and complexation reactions are exothermic in nature and this also explains the de4crease in the value of log K with the rise in temperature.

In the present work the negative value of ΔS^o were observed which indicates favorable conditions for chelate formation14,15 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 effect.

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