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POTENTIOMETRIC STUDY OF BINARY COMPLEXES OF TRANSITION METAL ION CU^{+2} WITH SCIHFF BASE LIGANDS

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ABSTRACT
A new Schiff base ligand synthesized from sulphonamide salicylaldehyde and substituted salicylaldehyde and characterized by elemental analysis, IR spectra, M.P, TLC. The stability constants of Sciff base ligand complexes with transition metal ion Cu^{+2} were determined pH metrically. The stability constants of Schiff base ligands and metals have been calculated.

KEYWORDS: Schiff base ligands, binary complexes, transition metals

INTRODUCTION
Schiff base are the compound containing azomethine group (-HC=N-). They are condensation products of ketones (or) aldehydes (aldehyde and ketones) with primary amines and were first reported by Hugo Schiff in 1864[2]. Formation of Schiff base generally takes place under acids or base catalysis or with heat. The common Schiff base are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids. Schiff base are used as intermediates for the synthesis of amino acids or as ligands for Preparation of metal complexes having a series of different structures.A Schiff base behaves as a Flexi-dentate ligand and commonly co-ordinates through the O atom of the de -pronated phenolic group and the N atom of azomethine group[3]. In Schiff base azomethane nitrogen and other donor atoms like oxygen play a vital role in co-ordination chemistry. Hence an attempt is made to study the interaction of reduced Schiff base with transition of metals of biological interest and to investigate the co-ordination chemistry of such interactions. In the present work we described the synthesis and characterization of reduced Schiff base and its metal complexes[4]. Moreover antibacterial and analgesic activity of reduced Schiff base metal complexes is also evaluated and compared with the standards[5].

MATERIALS AND METHODS

ExperimentalDigital pH meter

An Elico model L1-127 Digital pH meter in conjunction with an Elico combined electrode consisting of glass and reference electrode in the single entity of the type CL-51 B was used for the pH measurements.

Reagents and chemicals

Water-The metal distilled water was redistilled in a glass distillation assembly with potassium permanganate and little potassium hydroxide to remove dissolved CO_2. It is collected in a well stopper bottle and always used a fresh. Its pH was about 6.60 to 6.80.Other solvent, THF was purified as below. Tetrahydrofuran-Ferrous sulphate (A.R.grade) was added in terahydrofuran[6]. It was kept overnight. Next day it was filtered, distilled and stored in a stopper bottle.The solutions of transition metals were prepared in perchloric acid to avoid the possibility of complex formation of metal ions with anions. The metal solutions were prepared by dissolving the corresponding metal nitrates (A.R grade) in a known volume of standard perchloric acid[7].The concentration of metal ions in solutions were estimated by standard procedure[8-10]. All other chemicals like perchloric acid, sodium perchlorate and sodium hydroxide were of A.R.grade, obtained either from B.D.H. (London) or E. Merck Reidal (Germany).The solution were prepared in CO_2 free glass distilled water by taking precautions to avoid errors in their concentrations. Exact normalities were obtained by standard methods.

RESULT AND DISCUSSION

This section also describes the experimental methods used for the synthesis of sulphonamide and it's Schiff bases, Analytical data of these Schiff bases given in before publication[5] For the sake of convenience Schiff bases in the present work are divided into groups.

1) Those which are prepared by salicylaldehyde
2) Those which are prepared by substituted salicylaldehyde i.e.2,4-dihydroxybenzaldehyde

Group A-

R_1-4-(2'-hydroxybenzylidene amino)benzene sulphonamide
R_3-2-methyl-5-(2'-hydroxybenzylidene amino) benzene sulphonamide
R_5-2-methoxy-3-(2'-hydroxybenzylidene amino) benzene sulphonamide

Group B-

R_2-4-(2' 4'-dihydroxybenzylidene amino) benzene sulphonamide
R_4-2-methyl-5-(2' 4'-dihydroxybenzylidene amino) benzene sulphonamide
R_6-2-methoxy-3-(2' 4'-dihydroxybenzylidene amino) benzene sulphonamide

The experimental data obtained from pH metric titration in 50%(v/v) THF-water medium of a representative system is presented in Table 1.1 which includes the titrations of

1. Free $HClO_4$(A) A
2. Free $HClO_4$(A) + ligand (R) A +R
3. Free $HClO_4$(A) + ligand (R)+metal ion (M) A +R+M

The pK_1 and pK_2 values of Schiff bases which represent the dissociation of conjugate azomethine formed in presence of $HClO_4$ group and phenolic –OH respectively have been determined in 50% (v/v) THF –water medium in presence of 0.01 M sodium perchlorate. The ligands R1-R6 have two well separated buffer regions. The observed values show that the substituents in the phenyl ring of amine component of Schiff bases influence the electron density

at azomethine nitrogen and also affect the deprotonation of phenolic –OH group. It seems from the table that high values of pK_1 of R_2, R4 and R_6 than R_1, R_3 and R_5 respectively can be explained on the basis that (4-OH) group in R_2, R4 and R_6 exerts electron withdrawing inductive effect but an electron donating mesomeric effect with the result the electron density on azomethine nitrogen increases and thus increases pK value. The pK_2 values of R_2, R_4 and R_6 are approximately similar or negligibly greater than pK_2 values of R_1, R_3 and R_5 respectively. pK_1 and pK_2 values of R_5 and R_6 are smaller than pK_1 and pK_2 values of R_1,R_3 and R_2,R_4 respectively. This can be explained on the basis that though introduction of electron releasing –OCH_3 group at 2 position increases the basicity of Schiff bases, at the same time the negative contribution of the steric effect, compensates the increased basicity and thus decreases the pK_1 and pK_2 values. The ligands R_2, R_4 and R_6 do not show pK value for (4'-OHgroup) may be more than 12 [12-13]. Because of limitations in potentiometric titrations, mentioned earlier, the value of dissociation constant of –OH in 4th position could not be determined. The protons of –SO_2NH_2 group are dissociable as these are highly acidic which do not dissociate in present conditions.

Table 1.1 Potentiometric Titration data for Cu^{+2}-2 methyl-5-(2'-hydroxybenzylidene amino) benzene sulphonamide (R_3)

Medium-50% (v/v) THF water mixture

ε^{o}= 6.5116 x10^{-3} T^{0}_{L} =2.00 x 10^{-3}m

V^{o}=50 ml μ=0.1 M $NaClO_4$

T^{o}_{M} =4.000 x 10^{-4}M NaOH=0.23255 N

Temp =25^{o}C±0.1

Titration of free acid (A)		Titration of free acid + ligand(A+R)		Titration of free acid + ligand + metal (A+R+M)	
Vol of NaOH	Ph	Vol of NaOH	pH	Vol of NaOH	pH
0	2.51	0	2.61	0	2.64
0.07	2.53	0.16	2.68	0.07	2.67
0.17	2.57	0.31	2.77	0.15	2.70
0.25	2.59	0.39	2.81	0.23	2.74
0.34	2.63	0.54	2.90	0.31	2.78
0.425	2.67	0.61	2.96	0.39	2.83
0.49	2.72	0.67	3.01	0.47	2.88
0.56	2.75	0.79	3.12	0.55	2.93
0.62	2.80	0.91	3.26	0.63	3.00
0.685	2.85	0.97	3.34	0.69	3.06
0.75	2.89	1.10	3.55	0.755	3.12
0.82	2.94	1.14	3.64	0.79	3.16
0.88	2.99	1.16	3.69	0.84	3.19
0.95	3.07	1.18	3.74	0.88	3.23
1.01	3.16	1.215	3.86	0.92	3.30
1.06	3.21	1.235	3.93	0.96	3.34
1.10	3.28	1.25	4.00	1.00	3.40
1.14	3.36	1.27	4.10	1.04	3.46
1.185	3.46	1.29	4.20	1.08	3.54
1.23	3.60	1.31	4.32	1.12	3.63

1.25	3.65	1.33	4.46	1.16	3.74
1.27	3.74	1.35	4.63	1.18	3.79
1.29	3.82	1.37	4.89	1.23	3.91
1.31	3.92	1.385	5.25	1.26	4.06
1.335	4.06	1.40	5.96	1.30	4.28
1.35	4.26	1.42	7.86	1.32	4.58
1.37	4.47	1.44	8.74	1.36	4.81
1.40	4.88	1.46	9.34	1.38	5.09
1.42	5.41	1.49	9.77	1.40	5.44
1.44	6.41	1.51	10.05	1.42	5.79
1.455	8.32	1.54	10.24	1.44	6.10
1.48	10.40	1.56	10.38	1.46	6.39
1.50	11.78	1.58	10.50	1.48	6.71
1.53	12.30	1.60	10.61	1.51	7.10
		1.62	10.70	1.54	7.37
		1.64	10.79	1.56	7.71
		1.66	10.88		
		1.68	10.97		
		1.70	11.07		
		1.72	11.16		
		1.74	11.25		
		1.78	11.47		
		1.81	11.71		
		1.85	11.95		

Table 1.2 Formation constants of Schiff Bases
Temp 25 ^{O}C
Medium-50% (v/v) THF-water mixture μ=0.1M ($NaClO_4$)

No	Ligand	pK_1	pK_2
R1	4-(2,-hydroxybenzylidene amino) benzene sulphonamide	3.30	11.05
R2	4-(2,,4,-dihydroxybenzylidene amino) benzene sulphonamide	3.48	11.16
R3	2-methyl-5-(2,-hydroxybenzylidene amino) benzene sulphonamide	3.18	11.07
R4	2-methyl-5-(2,,4,-dihydroxybenzylidene amino) benzene sulphonamide	3.92	11.16
R5	2-methoxy-3-(2,-hydroxybenzylidene amino) benzene sulphonamide	2.55	10.53
R6	2-methoxy-3-(2,,4,-dihydroxybenzylidene amino) benzene sulphonamide	2.85	10.65

CONCLUSION

In the present work pH metric study was performed to determine stability constants and to asses binary species. The complexes of transition metals with Schiff base ligands shows following order of stability.

pK_1:R_4>R_2>R_1>R_3>R_6>R_5

pK_2:R_2>R_4>R_3>R_1>R_6>R_5

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