

Potentiometric Determination of Formation Constants of Metal Ion Complexes with Schiff Bases of 4,5-Dimethyl Salicylaldehyde

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In the present research work an attempt is made to calculate the stability constants of the metal complexes formed with the Schiff-bases of 4,5-dimethyl salicylaldehyde. A potentiometric study has been carried out on metal complexes of Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} with N-[4,5-dimethyl salicylidene] aniline, N-[4,5-dimethyl salicylidene]-4-chloroaniline, N-[4,5-dimethyl salicylidene]-4-methoxyaniline, N-[4,5-dimethyl salicylidene]-4-methylaniline. The stability constants of these reagents and their bivalent metal ion chelates have been determined by Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti at 303 ± 1 K and at ionic strength of 0.1 M in 75 : 25 (v/v) dioxane-water medium. All the synthesized complexes were also screened for their antibacterial activity.

Key Words: 4,5-Dimethyl salicylaldehyde, Stability constants, Potentiometric study.

INTRODUCTION

Most of the common biologically active compounds have structures quite suitable for chelation with metal ions and the studies of various organic compounds have supported the hypothesis that formation of strain-free chelate rings enhances the biological activities. Schiff bases and their metal complexes have been the subject of intensive research due to their novel structural features, interesting spectral and magnetic properties and their industrial and biological importance^{1,2}.

There is considerable interest in coordination chemistry of metal complexes with various Schiff-bases partially due to their capability of acting as multidentate N—N and N—O donor with the formation of mono- and polynuclear complexes³. It is well documented that the biological activity of an active ligand is altered quantitatively on coordination with suitable metal ions. A number of Schiff bases have been reported for their bactericidal, fungicidal, antipyretic, antitumor, antitubercular⁴, anticancer⁵ activities. Large proportions of coordination chemistry of Schiff-bases with transition and non-transition metal ions have been reported^{6,7}.

Extensive data on the stabilities of transition metal complexes in solution is

available with various substituted Schiff bases⁸. However, there is no systematic solution study of the complexes of transition metals with Schiff bases derived from 4,5-dimethylsalicylaldehyde has been reported.

EXPERIMENTAL

All the metal salts used were of AR grade. All the chemicals used except ligand and perchloric acid were of BDH (AR) grade. The perchloric acid used was of E. Merk (GR) grade. 1,4-dioxane (AR grade) was further purified by the standard method of Vogel. Ligands were synthesized by refluxing equimolar quantities of 4,5-dimethyl salicylaldehyde with respective amines in ethanol. The product obtained was repeatedly crystallized to obtain analytically pure sample. The purity was checked by TLC and IR. Structure of all these ligands was confirmed by spectral analysis. The IR spectra of the complexes were recorded using KBr pellets in the region 4000–400 cm^{-1} .

All the titrations were carried out in an inert atmosphere of nitrogen. The temperature of the solution was kept constant at 303 ± 1 K. The experimental details and computational methods are same as described in our earlier publication⁹.

RESULTS AND DISCUSSION

Potentiometric studies have been carried out to study the complexation of ligands (Table-1) with various bivalent metal ions. *viz.* Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} . The dissociation constants of the reagent and the formation constants of their metal chelates have been determined by Calvin-Bjerrum pH titration technique as adopted by Irving-Rossotti¹⁰ at 303 ± 1 K and at the ionic strength 0.1 M in 75 : 25 (v/v) dioxane-water medium. Before taking discussion on proton-ligand stability constants it is necessary to discuss the structure of the parent ligand and its substituted derivatives to get a clear understanding regarding its dissociation character.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS OF SCHIFF-BASES

Medium 75 : 25 (v/v) dioxane-water mixture; Temperature 303 ± 1 K, $\mu = 0.1$ M (NaClO_4)

Ligand No.	Ligands	pK_1^{H}	pK_2^{H}
A	N-[4,5-dimethyl salicylidene] aniline	11.025	3.207
B	N-[4,5-dimethyl salicylidene]-4-chloroaniline	10.899	2.157
C	N-[4,5-dimethyl salicylidene]-4-methoxyaniline	11.264	4.138
D	N-[4,5-dimethyl salicylidene]-4-methylaniline	11.177	3.728

There are two main factors which affect proton dissociation

(1) **Effect of substitution:** The study of dipole moment of organic molecules reveals the fact that each functional group exhibits a permanent electrical effect of either attracting or releasing the electron. A transfer of electrical charges from one part of molecule to other takes place because of inductive and mesomeric effect.

An increase in the acidic strength indicates that the substitution causes an increased tendency for the hydrogen of the acidic group to separate as free proton and decrease in acidic strength denotes a firm binding of proton to the ligand.

(2) **Hydrogen bonding:** The acidic character of the ligand is due to the dissociation of proton from phenolic —OH group. The hydrogen bonding established with the neighboring nitrogen from the azomethine group is the deciding factor for the release of the proton. The strength of the hydrogen bonding mainly governs the release of proton which is affected by the electron environment on the nitrogen atom. With this view in mind, the IR spectra of the ligands are recorded in KBr pellets and it was observed that the phenolic —OH group and the azomethine group ($>C=N$) are kept undisturbed. This group forms the site for the co-ordination complex.

Proton-Ligand Stability Constants

Selected series of ligands has been taken to study the effect of substitution on the basicity of the azomethine nitrogen. The pK_1^H values are found in good agreement with the change in the basicity of the azomethine group (Table-3). The following substituents were selected to study the effect of substitution:

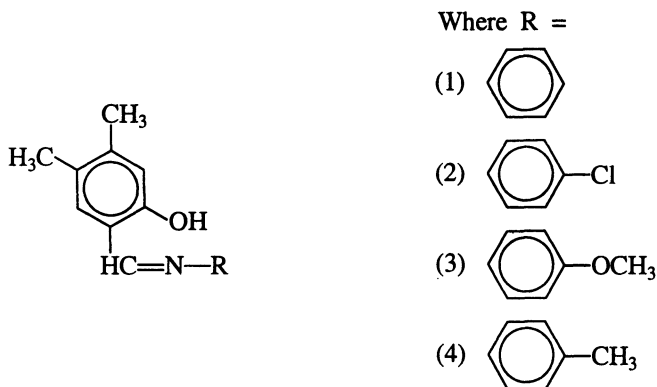
Substituted group	Mesomeric and inductive effect
A —C ₆ H ₅	+M +I
B —Cl	+M -I
C —OCH ₃	+M -I
D —CH ₃	+M +I

The pK_1^H values for various ligands are studied by comparing them with each other. The above substituents show very interesting variation in pK_1^H values of the ligands synthesized. It is found that ligand (C) has the highest pK_1^H value in the series of the ligands selected and ligand (B) has lowest pK_1^H value. These observations may be explained by the simultaneous mesomeric and inductive effects exercised by the substituents.

The pK_1^H value for ligand (A) (11.025) is greater than the ligand (B) (10.899). This is probably due to the —Cl group which exerts (-I effect) thereby decreasing the electron density around azomethine nitrogen. This leads to an increase in the acidic character of phenolic —OH group which lowers the pK_1^H value.

The pK_1^H value for the ligand (C) (11.264) is slightly higher than the ligand (D) (11.177). This is probably due to the strong (+M effect) of oxygen atom with its lone pair of electrons in —OCH₃ group. The (+M effect) of —OCH₃ group in ligand (C) is stronger than the —CH₃ group in ligand (D). As a result the H-bond is weaker in case of ligand (D) and shows lower pK_1^H value as compared to (C).

Further the CH₃ group in ligand (D) shows stronger (+M effect) than C₆H₅ group (ligand-A) and —Cl group (ligand-B); hence it shows higher pK_1^H as compared to the other two (Table-2).

TABLE-2
STRUCTURE OF THE LIGANDS**Metal-Ligand Stability Constants**

All the above compounds were employed as ligands to study their co-ordination behaviour with some bivalent metal ions (Table-3). Metal-ligand stability constants were calculated by Irving-Rossotti's equation. The stability of the metal complexes decreases with the increasing basicity of metals. The weakly basic copper forms stronger complex than the strongly basic metals like Ca^{2+} , Mg^{2+} forming weakest chelates. This suggests that strength of bonding in these chelates depends on the ability of the metal to form the homopolar bonds between the metal and ligand. A comparison would give an idea of the relative strength of the metal-ligand bond in a series of closely related bivalent metal ions (Table-3). It was observed that all the ligands followed Irving-William order of stability constant.

TABLE-3
FORMATION CONSTANTS OF TRANSITION METAL ION WITH SCHIFF BASES

Medium 75 : 25 (v/v) Dioxane-water mixture
Temperature 303 ± 1 K; $\mu = 0.1$ M (NaClO_4)

Ligands	Ca	Mg	Co	Ni	Zn	Cu
(A) Graph	3.45	4.58	5.84	6.29	6.72	9.44
H.I	3.46	4.58	5.85	6.29	6.72	9.40
(B) Graph	3.80	4.39	6.29	6.62	6.67	9.14
H.I	3.81	4.35	6.29	6.62	6.67	9.11
(C) Graph	3.52	4.27	5.95	6.26	7.05	9.34
H.I	3.51	4.28	5.93	6.24	7.05	9.35
(D) Graph	4.07	5.10	6.12	6.42	7.00	9.45
H.I	4.05	5.11	6.12	6.42	6.99	9.45

The order of stability for all the ligands was seen as $\text{Cu} > \text{Zn} > \text{Co} > \text{Ni} > \text{Mg} > \text{Ca}$.

Antibacterial Activity

All the Schiff bases along with parent aldehyde were tested for the antibacterial activity against two Gram-positive and four Gram-negative strains. Ditch plate method was employed for the determination of antibacterial activity of the compound.

Compounds	Organisims					
	1	2	3	4	5	6
4,5-dimethyl salicylaldehyde	+	+	+	+	-	-
N-[4,5-dimethylsalicylidene] aniline	-	-	-	-	-	-
N-[4,5-dimethyl salicy lidene]-4-chloroaniline	-	-	-	-	-	-
N-[4,5-dimethyl salicylidene]-4-methoxyaniline	-	-	-	-	-	-
N-[4,5-dimethyl salicylidene]-4-methylaniline	-	-	-	-	-	-

Legends:

(+) Inhibition

(-) No inhibition

Organisms:

1. *Escherichia coli*
2. *Salmonella typhi*
3. *Salmonella paratyphi*
4. *Corynebacterium diphtheria*
5. *Pseudomonas aeruginosa*
6. *Staphylococcus aureus*

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