Studies on Stability Constants of Salicylates Derivatives (Part-I)

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Summary: The Job's method of continuous variation was used to study the chelating behavior of salicylic acid with different transition metals. In this regard spectrophotometric measurements for 2-hydro-oxybenzoic acid and 2-hydroxy 4-amino benzoic acid with IB and IIB metals were made. The stability constants of the system, in which 1: 1, 2: 1 (L: M) complexes formed at different pH values were calculated. The measurements also reflect the effects of concerned metals and ligands used for chelation. Between two ligands, 2-hydroxy benzoic acid and 2-hydroxy 4-amino benzoic acid, the later found to form stable complexes than the former.

Introduction

Stability constant is a useful physical entity, which explains the importance and function of various complexes in biological and chemical science. For example some metallic ions of the minerals have a very low value of stability constant. This low value of the stability constant for dietary minerals then makes them easily dissociable even at physiological pH of the body fluids [1]. The important phenomenon, which reduces the concentration of toxic metals (*e.g.* mercury) and saves the life, is the complexation process. Such ligands strongly bind with the metal ion, hence making them unavailable for the body damage available to the body.

Most of the dietary minerals have stability constant less than three. For the compounds with stability constant greater than six, there is almost no release of metal regardless of how lower is the pH of the system. In short stability constant explains the barrier responsible for the release of the blockage of different metallic ions. There exists a relationship between the basic strength of the chelating group, as measured by the dissociation constant and the stability of the complex it forms. This work is also supported by our previous published work [2-8].

Results and Discussion

2-Hydroxy benzoic acid formed 1: 1 and 2: 1 ligand metal complex with copper (II) chloride at pH 5.5 and 8.0 respectively and shown in Fig. 1 while 2-hydroxy-4-amino benzoic acid showed complex with copper (II) chloride at pH 6.0 and 8, and reported in Fig. 2 respectively 2-hydroxy benzoic, 2-hydroxy-4-amino benzoic acid. Formed complex with silver nitrate and depicted in Fig. 3 and 4 respectively. 2-hydroxy benzoic acid formed complex with zinc (II)

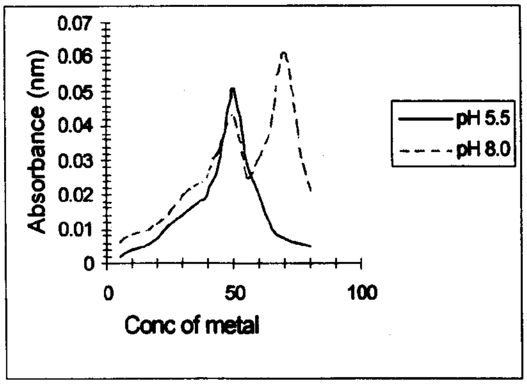

Fig. 1: Reaction of 2-hydroxy benzoic acid with copper (II) chloride.

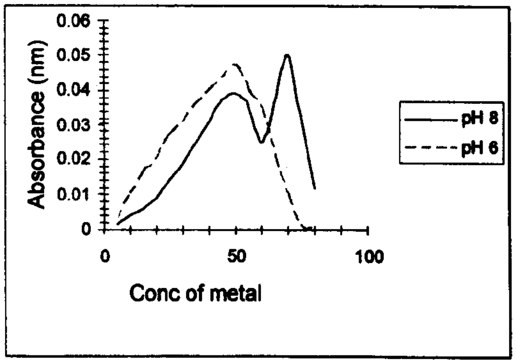

Fig. 2: Reaction of 2-hydroxy-4-amino benzoic acid with copper (II) chloride.

chloride in 1: 1 And 2; 1(L: M) at pH 5.5 and 8.0 respectively and reported in Fig. 5. The Fig. 6 depicts complex formation of 2-hydroxy 4-amino benzoic acid with zinc (II) chloride at pH 6.2 and 8.0 respectively. The complex formation 2-hydroxy

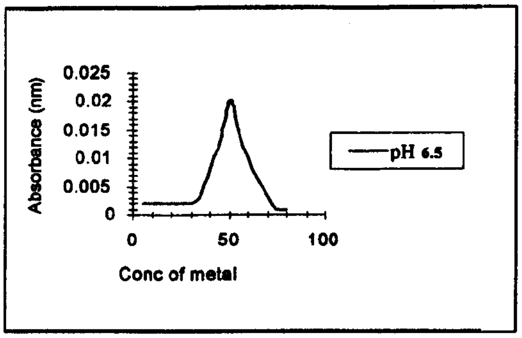

Fig. 3: Reaction of 2-hydroxy benzoic acid with silver (I) nitrate.

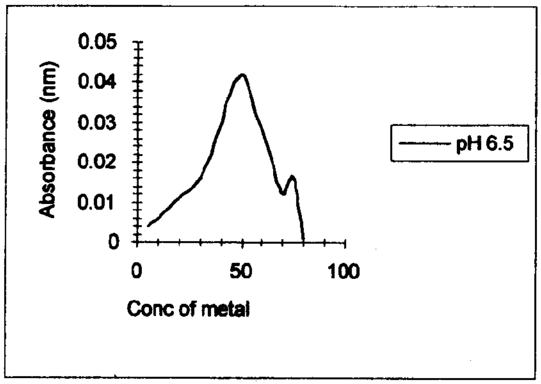

Fig. 4: Reaction of 2-hydroxy-4-amino benzoic acid with Silver (I) nitrate.

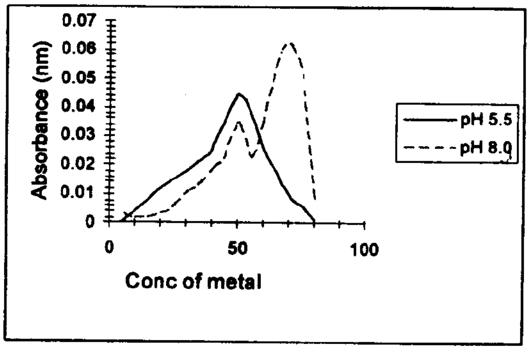

Fig. 5: Reaction of 2-hydroxy benzoic acid with Zinc (II) chloride.

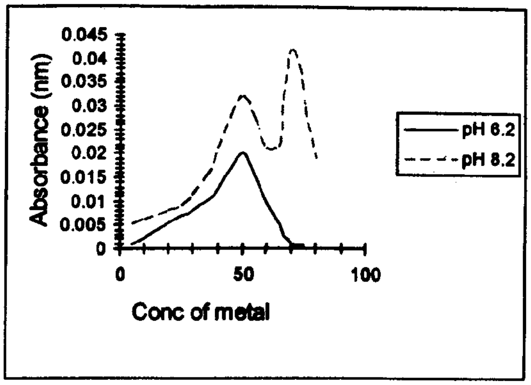

Fig. 6: Reaction of 2-hydroxy-4-amino benzoic acid with zinc (II) chloride.

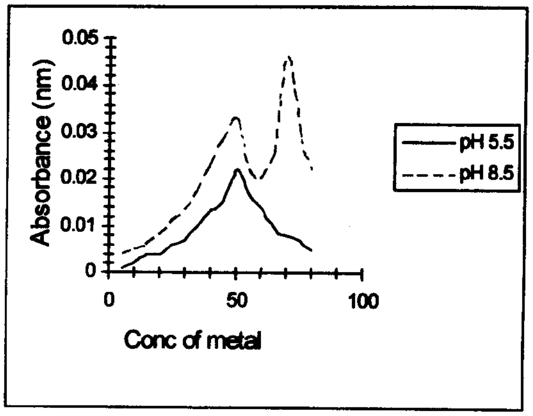

Fig. 7: Reaction of 2-hydroxy benzoic acid with cadmium (II) chloride.

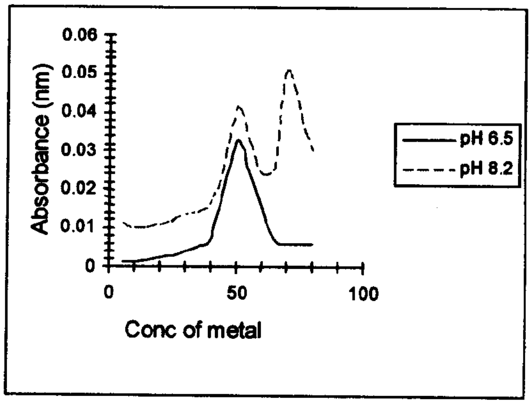

Fig. 8: Reaction of 2-hydroxy-4-amino benzoic acid with cadmium (II) chloride.

Table-1: Stability constants of 2-hydroxybenzoic acid and 2-hydroxy -4-aminobenzoic acid with copper (II) chloride.

Ligand	Metal	pH	$K_f = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$	L:M
2-hydrox-benzoic acid	Copper (II) Chloride	5.5 8.0	9.3×10^5 4.4×10^5 and 6.7×10^5	1: 1 and 2: 1
2-hydroxy-4-amino benzoic acid	Copper (II) Chloride	6.0 8.0	9.7×10^5 3.6×10^5 and 7.7×10^5	1: 1 and 2: 1

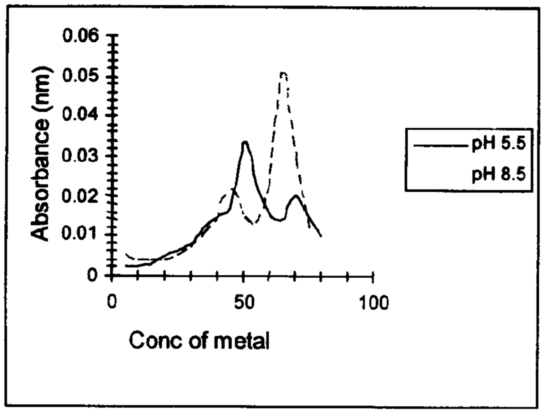

Fig. 9: Reaction of 2-hydroxy benzoic acid with mercury (II) acetate.

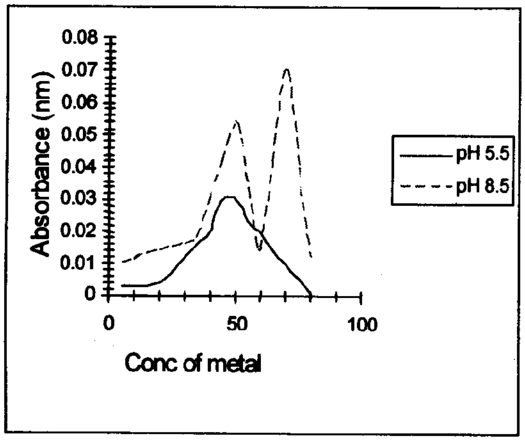

Fig. 10: Reaction of 2-hydroxy-4-amino benzoic acid with mercury (II) acetate.

Table-2: Stability constants of 2-hydroxybenzoic acid and 2-hydroxy -4-aminobenzoicacid with silver (I) nitrate.

Ligand	Metal	pH	$K_f = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$	L: M
2-hydrox-benzoic acid	Silver (I) Nitrate	5.5	3.5×10^5	1: 1
2-hydroxy-4-amino benzoic acid	Silver (I) Nitrate	6.5	4.2×10^5	1: 1

Table-3: Stability constants of 2-hydroxybenzoic acid and 2-hydroxy-4-aminobenzoic acid with zinc (II) chloride.

Ligand	Metal	pH	$K_f = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$	L: M
2-hydro-xbenzoic acid	Zinc (II) chloride	65 8.0	4.2×10^5 $3.0 \times 10^5$and 8.0×10^5	1: 1 and 2: 1
2-hydroxy-4-amino benzoic acid	Zinc (II) Chloride	6.0 8.0	9.7×10^5 3.6×10^5 and 7.7×10^5	1: 1 and 2: 1

Table-4: Stability constants of 2-hydroxybenzoic acid and 2-hydroxy-4-aminobenzoic acid with Cadmium (II) chloride.

Ligand	Metal	pH	$K_f = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$	L: M
2-hydrox-benzoic acid	Cadmium (II) Chloride	5.5 8.0	3.57×10^5 7.6×10^5 and 6.6×10^5	1: 1 and 2: 1
2-hydroxy-4-amino benzoic acid	Cadmium (II) Chloride	5.5 8.0	6.3×10^5 $7.5 \times 10^5$and 3.7×10^5	1: 1 and 2: 1

benzoic acid with cadmium (II) chloride at pH 5.5 and 8.0 is given in Fig. 7 similar trend of complex formation for 2-hydroxy 4-aminobenzoic acid with cadmium (II) chloride reported in Fig. 8. 2-hydroxy benzoic acid formed complex with mercury (II) acetate, the presence of 1: 1 and 2: 1 complex was noted. At pH 5.5 and 8.5 respectively, shown in Fig. 9. Fig. 10 depict the complex formation of 2-hydroxy

Table-5: Stability constants of 2-hydroxybenzoic acid and 2-hydroxy-4-aminobenzoic acid with mercury (II) acetate.

Ligand	Metal	pH	$Kf = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$	L: M
2-hydrox-benzoic acid	Mercury (II) Acetate	5.5 8.5	2.37×10^5 3.7×10^5 and 1.5×10^5	1: 1 and 2: 1
2-hydroxy-4-amino benzoic acid	Mercury (II) Acetate	5.5 8.5	5.1×10^5 5.6×10^5 and $\times 10^5$	1: 1 and 2: 1

4-amino benzoic acid with mercury (II) acetate at pH 7.2 and 8.5 respectively.

Experimental

To Study the complex formation in solution, Job [9] developed the method of continuous variation. This method makes use of any measurable additive property of two species. Any complex formed by the two species must give a value for the separate species. The simple application of the method involves an equilibrium of type A + nB = ABn, where A represents a metal, B a co-ordinating group and ABn, a complex. Solutions are prepared in which the mole fractions of the components are varied and the total number of moles of both is kept constant. If there is no complexing, the plot of extinction coefficient or absorbance against mole fraction is a straight line. But if a complex is formed, the plot deviates from linearity. The deviation is maximum at mole fraction corresponding to the composition of complex. When the deviation is plotted against the mole fraction, the maximum point gives the desired composition.

UV/ VIS Spectrophotometer (Lamda 1 Perkin Elmer) was used for the determination of absorbance required for Job's Method. The stock solutions of ligands (1×10^{-4} M) and metals salts (1×10^{-4}M) were prepared according to the requirement of Job's method. In series of flasks the sum of the number of moles of ligand plus sum of number of the moles of metal were kept constant. The pH values were adjusted and their absorbance was measured λ_{max}, where neither the metal nor the ligand absorbs but only the complex absorbs. The stoichiometry of various complexes was determined by plotting absorbance against various concentrations of ligand and metal. The plots were made at different pH values of the reaction mixtures (Fig. 3-10). These graphs were used to calculate the stability constants of various complexes by using the following formula.

$$Kf = \frac{\frac{A}{A_{ex}} C_M}{(C_M \frac{A}{A_{ex}} C_M)(C_{complex} - \frac{A}{A_{ex}} C_M)}$$

In the present case, this method has been applied to determine the stability constants of the systems in which the complex, either 1: 1 or 2: 1 (L: M) is formed at different pH values. This procedure is supported by Vosburgh and Cooper [10], who applied it for a system in which three complexes were formed.

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