Comparative Studies of Stability Constants of Trace Metals Salicylhydroxamic Acid Complexes

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Summary: Salicylhydroxamic acid forms complexes with trace metals such as Fe^{3+}, Cr^{3+}, Mn^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+} and Al^{3+}. The stability constants of these complexes formed have been determined by a potentiometric method. The data obtained were computed with the help of computer program "BEST". The resulted "β" values were compared.

Introduction

Hydroxamic acids are weak organic acids [1] with a wide variety of applications, including uses in extractive metallurgey inhibitors for copper corrosion, anti fungal agents, pharmaceuticals food additives and in nuclear fuel processing. One of the characteristics of hydroxamic acid is there ability to form stable complexes with transition metal ions [2] which form the basis of their usefulness as analytical reagent [3]. Under iron deficient conditions, micro organism secrete low molecular weight iron chelators called siderophores [4]. Some naturally occurring hydroxamic acids serve as iron(III) specific chelators. They are involved in microbial iron transport, their specific function is to solubilize iron from the environment and transport it to the cell [5]. The specificity of hydroxamate siderophores for chelating iron(III), among the physiologically important metal ions and their high stability constants, has led to investigation of their use in the treatment of iron overload in humans caused by β thalassemia [6]. The first hydroxamate type siderophore was discovered by Neilands in 1952 [7]. Salicyl-hydroxamic acid forms stable complexes with trace metals such as Al(III), Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ca(II) and Mg(II) [8]. The affinity of ligand for metal ions may be defined quantitatively in terms of the stability constants of complex. In solution at any pH, we have the following species in equilibrium [9,10].

For interaction of bidentate ligands and metal ions forming octahedral complexes the following stepwise equilibria may be written.

$$M + L \rightleftharpoons ML$$

$$ML + L \rightleftharpoons ML_2$$

$$ML_{+2} \rightleftharpoons ML_3$$

$$ML_{n-1} + L \rightleftharpoons ML_n$$

$$K_n = \frac{[ML]}{[ML_{n-1}][L]} \qquad \beta = \frac{[ML_n]}{[M][L]^n}$$

In certain biological systems metals display more than one valence state. Complexation by any given ligand may favour one state rather than the others and resultant changes in redox potential are again of importance in biochemical reactions [11,12]. Two or more different metals will form complexes of un-equal stabilities with one and same ligand. The stability constant of complexes are also a measure of free energy changes by the relation $-\Delta G = 2.303\ n\ RT\ Log\ \beta$, thus both enthalpy and entropy contribute to the stability of a complex [13-16].

Our motivation for standing this system is twofold. On one hand we wish to evaluate if salicylhydroxamic acid can potentially disturb the trace metals metabolism of minerals other than iron and secondly we wish to find out if salicylhydroxamic acid were used as on analytical reagent for iron(III) as it gives very intensly colored solutions in the pH range 5-7 [17], with approaching those of iron(II)-2,2,bipyridin system, what would be the interfering ions.

Results and Discussion

The data obtained from the experiments are shown in the Figure 1,2, and 3. Following points were found to be observable from these graphs.

1. Fe(III) form most stable complexes with salicylhydroxamic acid having one metal, one ligand and one proton (which can be expressed as 11) at pH 3 and with one metal two ligand no proton (210) at pH 7.

2. Al(III) and Cr(III) also form two types of complexes 1:1 or 110 at pH 3 and 2:1 or 210 at pH 4. Al(III) has higher stability than Cr(III).
3. Among dispositive ions the stability constant of Cu(II) complexes are very high very stable 1:1 and 2:1 complexes at pH 3 and pH and pH 7 respectively are indicated.

4. Ca(II), Mg(II) and Cd(II) do not form complexes with salicylic hydroxamic acid.

5. Co(II) and Ni(II) form complexes at pH 6 which are 2:1.

6. Mn(II) and Zn(II) form complexes at pH 7 which also of 2:1 stoichiometry.

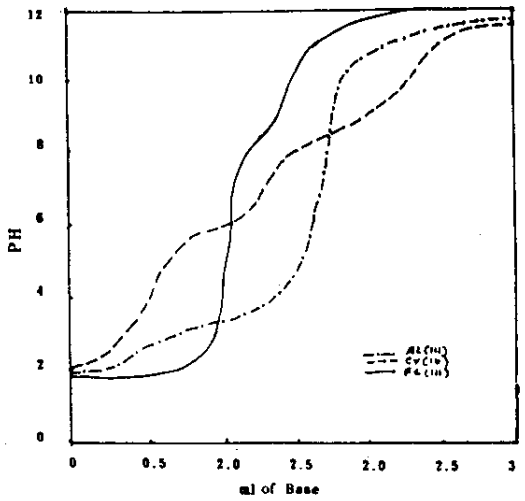

Fig.1: Titration curve of trivalent trace metals (Al, Cr, Fe) complexes with salicylhydroxamic acid.

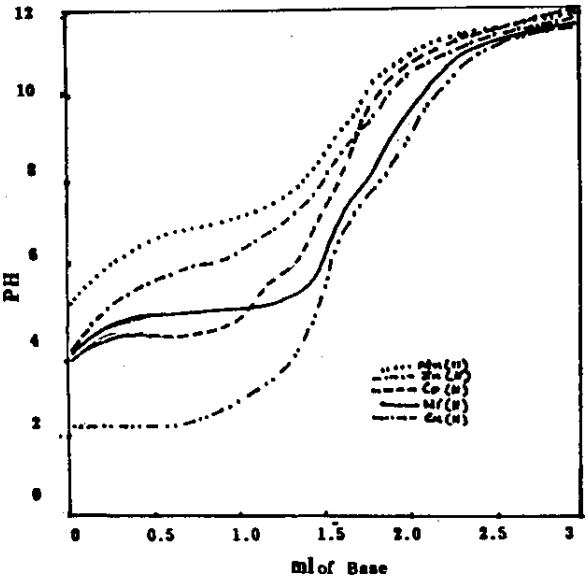

Fig. 2: Titiration curve of blvalent trace metals (Mn, Zn, Co, Ni, Cn) complexes with salicylhydroxamic acid.

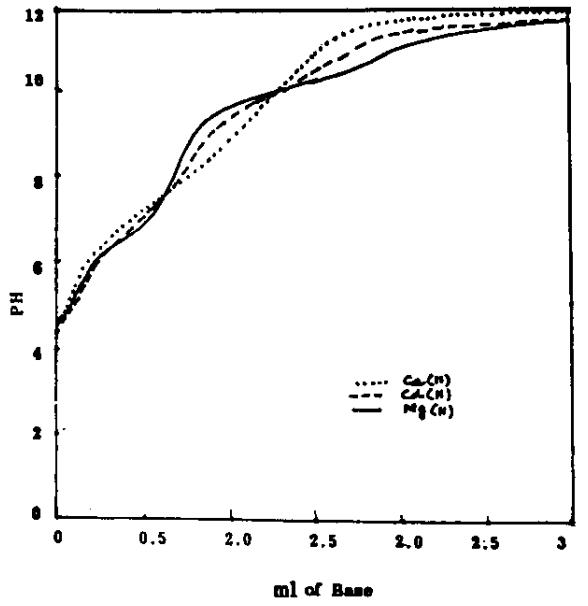

Fig. 3: Titration curve of Ca(II), Cd(II) and Mg(II) complexes of hydroxamic acid.

Published and original data on the stability of complexes formed by bivalent ions of first transition series have been collected. The order of

stability Mn<Co<Ni<Cu>Zn of nearly all this type of complexes irrespective of nature of the co-ordinated ligand or of the number of ligand, molecules involved. A theoretical justification for the stability order follows from consideration of the resprocal of the ionic radii and the second ionization potentials of the metal concerned. The β values of salicylic hydroxamic acid complexes of Mn(II), Co(II), Ni(II),.Cu(II) and Zn(II), which are calculated by computer programe BEST followed the Irving and Williams order of stability. Data are shown in the Table-1. The available data for other hydroxamic acid metal complexes indicate that it has a high affinity for spherically symmetric +3 ions in general. The variation in stability constants among these complexes can readily be explained on the basis of charge to radius ratio of metal ion therefore hydroxamic acid has high affinity for iron(III) in the biological system among other

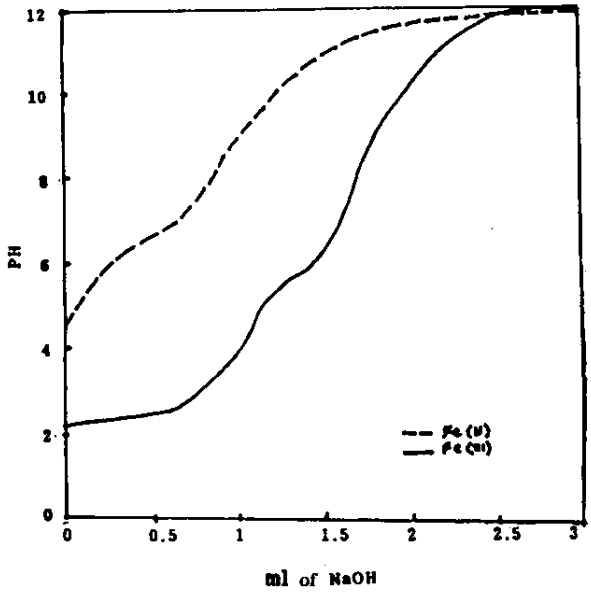

Fig. 4: Comparison of the titration curve of Fe(II) and Fe(III) complexes of hydroxamic acid.

Table-1: Stability Constants of some Divalent Trace Metals

Metals	Glycine		Analine		Hyd. Acid	
	β1	β2	β1	β2	β1	β2
Mn(II)	3.44	6.63	3.04	6.05	3.00	7.73
Co(II)	5.06	8.94	4.82	8.48	3.50	10.43
Ni(II)	6.14	11.15	5.96	10.66	4.10	11.94
Cu(II)	8.47	15.38	8.51	15.37	9.80	18.00
Zn(II)	5.33	9.72	5.21	9.54	3.60	11.90

Table-2: Stability Constants of Trivalent Trace Metal Complexes with Salicylhydroxamic Acid Calculated by "BEST"

Metal	β110	β210	β310
Fe(III)	14.8	24.00	30.15
Al(III)	9.6	17.50	–
Cr(III)	6.6	11.66	–

Table-3: Stability Constants of Different Siderophores and other Ligands with Fe(II) and Fe(III)

Ligands	Fe(II)	Fe(III)
Enterbactin	10.50	52.00
Desferrium B	11.00	30.50
Transferrin	3.20	20.90
EDTA	14.20	25.00
EGTA	11.92	20.50
HDTA	11.00	21.58
CDTA	16.27	27.00
TTHA	7.10	29.40
Oxalic acid	5.15	14.90
Citric Acid	4.40	11.40
Malic Acid	2.50	7.10
Salicyl Hydroxamic Acid	4.80	30.15

biologically available metal ions. In case of salicylic hydroxamic Fe(III) complexes have highest stability constant among tripositive ion.

Fe(II) and Fe(III) were also compared in case of hydroxamic acid, the β values of iron(II) were found to be much lower the Fe(III). These values were found to be comparable with other ligands (Table-3).

Experimental

All reagents used were of AR or equivalent grade and were used without further purification Distilled water was re-distilled and subsequently. passed through a column of cation exchanger (Amberlite resin IRA-401 from BDH chemicals) in order to make it free of cations. To remove CO_2 from water, it was boiled and then cooled in a sealed beaker. This doubly distilled decarbonized and deionized water was used in preparation of all solutions of reagents. For all pH measurements in potentiometric titrations, ORION pH meter model SA 220 was used A 0.05M solution of potassium hydrogen pthalate, which has value 4.01 at room temperature, 25°C was used to calibrate the pH meter.

The titration were carried out in double walled glass cell, fitted with an air tight cork,

having three holes. One for nitrogen purging other for base to be added and third one for the electrode to be dipped in the solution. The temperature of the cell was kept constant throughout the experiment by circulating thermostated water between the two walls.

The pH of the solutions, during titration, was measured with a combination glass electrode upto 001 pH unit. All the titrations were performed at room temperature i.e. 25°C. 20 ml of 0.01M of salicylhydroxamic acid were mixed with 20 ml of 0.01M metal ions solution respectively for each titration and were titrated with 0.1M NaOH solution. The change in pH was noted with the smal increment (0.05 ml) of base added. Equilibrium conditions, determined by a constant meter reading falling with in an interval of less than 0.002 pH unit, was obtained for each experimental point before proceeding with the next step. The solution was stirred with magnetic stirrer constantly. For each meal salicylhydroxamic acid solution these titrations were repeated to minimize the probable error.

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