ALIPHATIC HYDROXAMIC ACIDS AS CHELATING AGENTS; THE STABILITY OF THEIR PROTON AND METAL COMPLEXES

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Three kinds of aliphatic hydroxamic acids, i.e., acetohydroxamic acid, n-butyrohydroxamic acid, and sorbohydroxamic acid have been prepared as free acids and potassium salts. Their acid dissociation constants and the formation constants of complexes formed by some bivalent metal ions of the first transition element (Mn, Co, Ni, Cu, Zn) with these three chelating agents in aqueous solution have been determined by using potentiometric titration technique at ionic strength of $0.1M$ by sodium perchlorate and at a temperature of $25°C\pm0.1°$. The stability of the transition metal ion complexes with these aliphatic hydroxamic acids is in the order $Mn<Co<Ni<Cu>Zn$, which is in agreement with the Irving and William's rule. The chelating forming properties and the comparison of quality as analytical reagent of these three hydroxamic acids were discussed in terms of the proton displacement constant. Sorbohydroxamic acid is superior in its reactivity and the other respects among the three reagents.

INTRODUCTION

Cupferron, the ammonium salt of nitrosophenylhydroxylamine was first proposed as an analytical precipitant by Bamberger and Baudisch[1]. It reacts with many metal ions to give insoluble or sparingly soluble metal complexes which are readily extracted into organic solvent and has been widely applied in the inorganic analysis. A remarkable weak point of cupferron, however, is its instability. Furthermore, the complexes precipitated by this reagent can not be weighed as such, but must be ignited to the oxide.

Schome[2], by substituting a benzoyl for the nitroso group of cupferron, obtained N-phenylbenzohydroxamic acid that was stable and formed complexes with a variety of metal ions. He introduced it as an analytical reagent which is superior to cupferron. Although this reagent still has a disadvantage of the low solubility in water, it has been found an extensive analytical applications[3-7].

The excellent qualities of N-phenylbenzohydroxamic acid provided a vivid impetus for undertaking a systematic search for better reagents from the family of hydroxamic acids in these two decades[8-10].

In order to evaluate a reagent, it is desirable to have some physicochemical
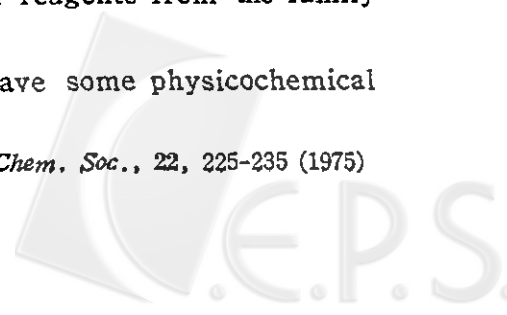
data of reagents and their complexes. In spite of voluminous analytical works on hydroxamic acid, reports of physicochemical studies on formation constants for complexes of these reagent are rather limited. A study of metal complexes of some aliphatic hydroxamic acid was undertaken here.

EXPERIMENTAL

A. Materials

1. Preparation of Aliphatic Hydroxamic Acids:

Three kinds of aliphatic hydroxamic acids have been selected for our investigation. These are acetohydroxamic acid, butyrohydroxamic acid and sorbohydroxamic acid.

The method of Blatt[11] is used to prepare a methyl alcohol solution of the potassium salt of the desired hydroxamic acid, and the free hydroxamic acid is obtained by the method of Wise and Brandt[12]. The procedure is as follows:

One pound of Amberlite IRC-50 resin is charged with $100\,ml$ of $1N$ HCl and washed several times with $300\,ml$ portions of methyl alcohol. The acid charged resin is then mixed with the above methyl alcohol solution of the potassium salt and allow to stand for one half hour.

During this time the slurry is stirred intermittently and the apparent pH is checked. If the solution is not acidic, more charged resin should be added to remove the basic constituents.

The resin is filtered with suction and washed. The combined filtrate and washings are reduced to dryness or a thick sirup under vacuum at room temperature. The residue is recrystallized from ethylacetate. The precipitation is aided by reducing the volume or by the addition of pertroleum ether.

The desired compounds are prepared as follows:

(a) Acetohydroxamic Acid

The compound was synthesized from ethylacetate and hydroxylamine-hydrochloride (Products of wako pure Chemical Co. Ltd., Japan). Acetohydroxamic acid was obtained as a white needle shaped crystals with m. p. of 87-88°, which is in accordance with the literature[13].

(b) n-Butyrohydroxamic Acid

Ethylbutyrate was synthesized from butyric acid and absolute ethylalcohol by conventional esterification method. n-Butyrohydroxamic acid was prepared from this ethylbutyrate (b. p. 119-120°) and hydroxylamine-hydrochloride. The compound is extremely difficult to crystallize and it is often obtained as a thick sirup. The same result is obtained by Inoue and Yukawa[13]. All attempts to isolate n-butyrohydroxamic acid in the solid state, reported m. p. 42°[12] were failed. For the purpose of our investigation, the potassium salt was alternatively used. Potassium-butyrohydroxamate was prepared from ethylbutyrate and hydroxylamine-hydrochloride by

Blatt's method. The crystals were recrystallized from ethyl-alcohol, washed with ether, and dried in air.

The purity of the potassium-butyrohydroxamate was checked against standard perchloric acid, using Bromocresol green as indicator. For the study of stability of metal complex, equivalent of perchloric acid were added to the potassium-butyrohydroxamate to convert into free acid.

(c) Sorbohydroxamic Acid

The starting material, ethylsorbate has been prepared from sorbic acid (Chisso Corporation, Japan) and absolute ethanol using an ordinary esterification method. Ethylsorbate was purified by distillation under reduced pressure (b. p. 87-89°, 18 mm). Sorbohydroxamic acid was obtained as a white scale with m. p. of 122-123°C (m. p. 120°[14], m. p. 133-5°[15], m. p. 145-6°[16]).

All of these three reagents formed blood red colored complexes with ferric ions and this is the characteristic reaction of hydroxamic acid. Among these complexes, ferric sorbohydroxamate gives deepest coloration which is almost of violet red color.

2. Perchlorates of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} were obtained from the G. F. Smith Chemical Co. U. S. A. and stock solutions of these metal ions were standardized by EDTA titration.

3. All other chemicals used in the experiment were of analytical reagent grade.

B. Instrument

All pH of the solution were measured by Radiometer Titrator equipped with saturated calomel (Type K 401) and glass (Type G 202B) electrodes. The electrodes were checked against Beckman standard buffer solutions (pH 4.00 and 7.00) before and after the titration. The titration curves were recorded with Radiometer Titrigraph SBR 2 and 1 ml syringe Buret Unit, SBU 1 carrying out in a thermostatically controlled condition at 25°C$\pm$0.1°. An inert atmosphere was maintained by bubbling nitrogen through and above the solution during titrations.

C. Physico-Chemical Study of Reagents and their Metal Chelates

The Calvin-Bjerrum pH-titration technique as described by Rossotti[17] was employed for the determination of acid dissociation constants of chelating agents and the stability constants of metal chelates.

The experimental method consisted for potentiometric titration of the hydroxamic acid in the absence of and in the presence of metal ion being investigated. The ionic strength was maintained constant by using 0.1M NaClO$_4$ as a supporting electrolyte. The titrations were carried out using 4:1 ratio for hydroxamic acid to metal ion concentration. All measurements were carried out at 25°C$\pm$0.1°.

The following mixtures were prepared.

(a) $4 \times 10^{-3}M$ HClO$_4$, $4 \times 10^{-3}M$ chelating reagent and 0.1M NaClO$_4$ solution.

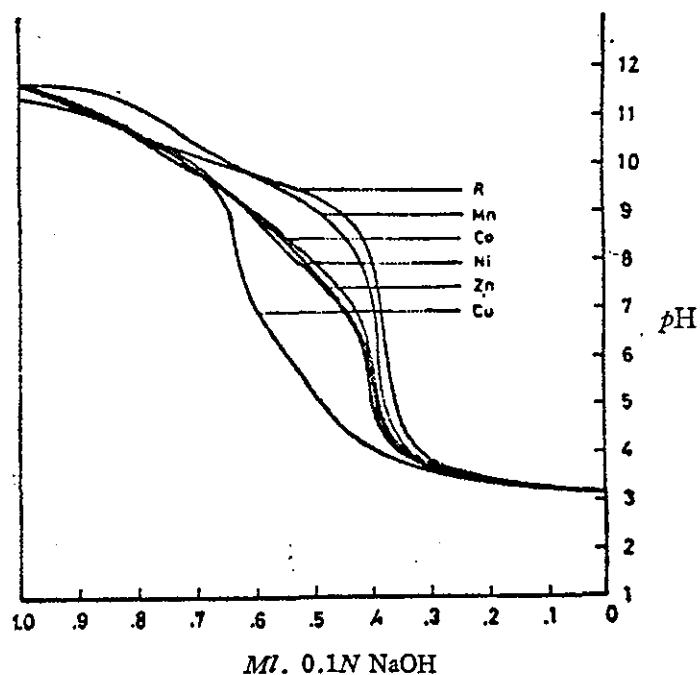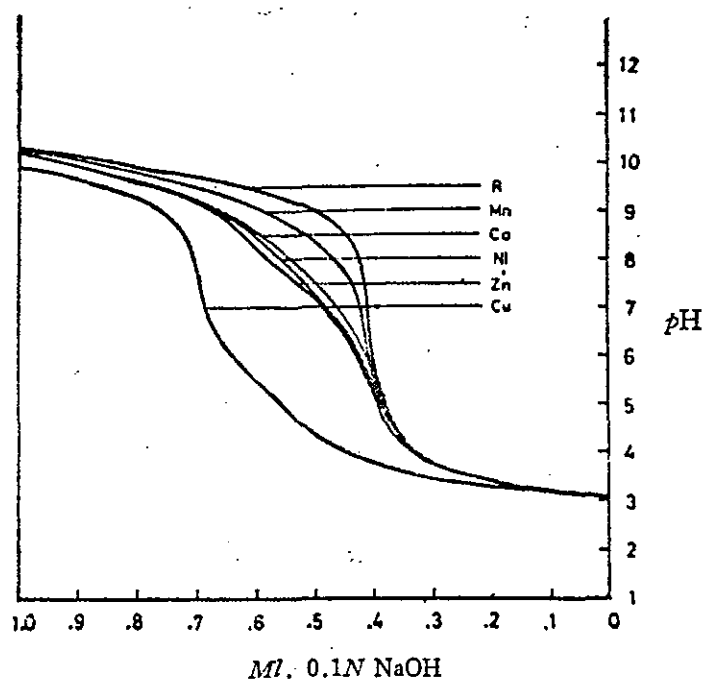(b) mixture (a)+$1 \times 10^{-3}M$ transition metal ion.
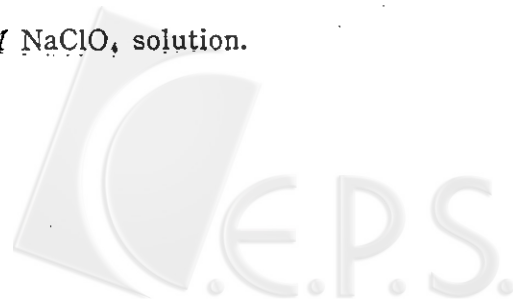
Fig. 1. Potentiometric titrations of acetohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with $0.1005N$ NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{2+}}=1\times10^{-3}M$ $T_{RL}=4\times10^{-3}M$

Fig. 3. Potentiometric titrations of butyrohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with $0.1005N$ NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{2+}}=1\times10^{-3}M$ $T_{HL}=4\times10^{-3}M$
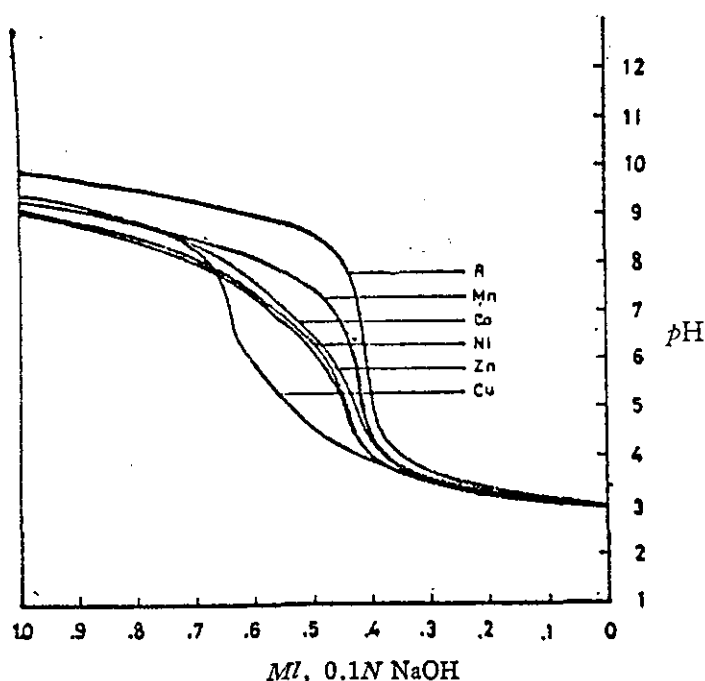
Fig. 5. Potentiometric titrations of sorbohydroxamic acid with known amount of HClO₄ in the absence and presence of metal ions with $0.1005N$ NaOH, at $25°C±0.1°$, $\mu=0.1$.
$T_{M^{2+}}=1\times10^{-3}M$ $T_{RL}=4\times10^{-3}M$

The appropriate mixtures of the solution (a) and (b) were titrated with a carbonate-free standard NaOH solution and the pH changes were recorded against the volume of NaOH added. The titration curves are shown in Figs. 1, 3 and 5.
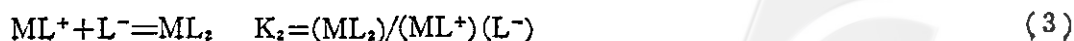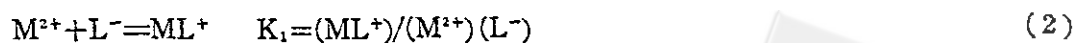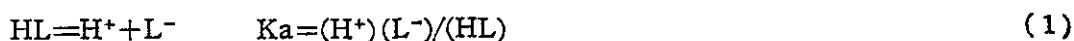
D. Calculations

1. The acid dissociation constants of these hydroxamic acids were calculated from the experimental points in the buffer regions of the titration curves in absence of metal ions by using the following equation.

$$Ka=\frac{(H^+)\{(H^+)+(Na^+)-(A)-(OH^-)\}}{T_{RL}-\{(H^+)+(Na^+)-(A)-(OH^-)\}}$$

where all the terms in round brackets are concentrations in moles per liter, T_{RL} is the analytical concentration of the reagent and (A) represents the total moles of perchloric acid per liter added at the beginning of the titration.

2. The chelate formation constants were calculated from 4:1 titration curves (Figs. 1, 3 and 5) by an adaptation of Calvin and Wilson's[19] method.

Consider the bidentate chelate:

$$HL=H^++L^- \qquad Ka=(H^+)(L^-)/(HL) \tag{1}$$

$$M^{2+}+L^-=ML^+ \qquad K_1=(ML^+)/(M^{2+})(L^-) \tag{2}$$

$$ML^++L^-=ML_2 \qquad K_2=(ML_2)/(ML^+)(L^-) \tag{3}$$

where M^{2+} represents any of the divalent metal ions employed, HL represents hydroxamic acid, if T_{HL} represents the total concentrations of hydroxamic acid species, $T_{M^{2+}}$ represents the total concentration of metal ion species, (Na^+) represents the concentration of base added and (A) represents the same meaning as before, the following relationships hold for solutions of hydroxamic acid and metal ion.

$$T_{HL}=(HL)+(L^-)+(ML^+)+2(ML_2) \tag{4}$$

$$T_{M^{2+}}=(M^{2+})+(ML^+)+(ML_2) \tag{5}$$

$$(ML^+)+2(M^{2+})+(Na^+)+(H^+)=(ClO_4^-)+(OH^-)+(L^-) \tag{6}$$

$$(ClO_4^-)=(A)+2T_{M^{2+}} \tag{7}$$

The resulting expression is

$$(L^-)=\frac{Ka}{(H^+)}\{(T_{HL}+(A)-(Na^+)-(H^+)+\frac{Kw}{(H^+)}\} \tag{8}$$

The average number of moles of ligand, L^-, bound per mole of metal ion present is designated by $\bar{n}$, and is given by the expression

$$\bar{n}=\frac{(ML^+)+2(ML_2)}{T_{M^{2+}}} \tag{9}$$

$$\bar{n}=\frac{1}{T_{M^{2+}}}\{(Na^+)-(A)+(H^+)-\frac{Kw}{(H^+)}-\frac{Ka}{(H^+)}[T_{HL}+(A)-(Na^+)-(H^+)+\frac{Kw}{(H^+)}]\} \tag{10}$$

values of $\bar{n}$ obtained from equation (10) are plotted vs. pL^-, the logarithm of $(L^-)^{-1}$. The value of pL^- at $\bar{n}=0.5$ is equal to log K_1, and the value of pL^- at $\bar{n}=1.5$ is taken as equivalent to log K_2. Bjerrum formation curves for these complexes are shown in Figs. 2, 4 and 6.
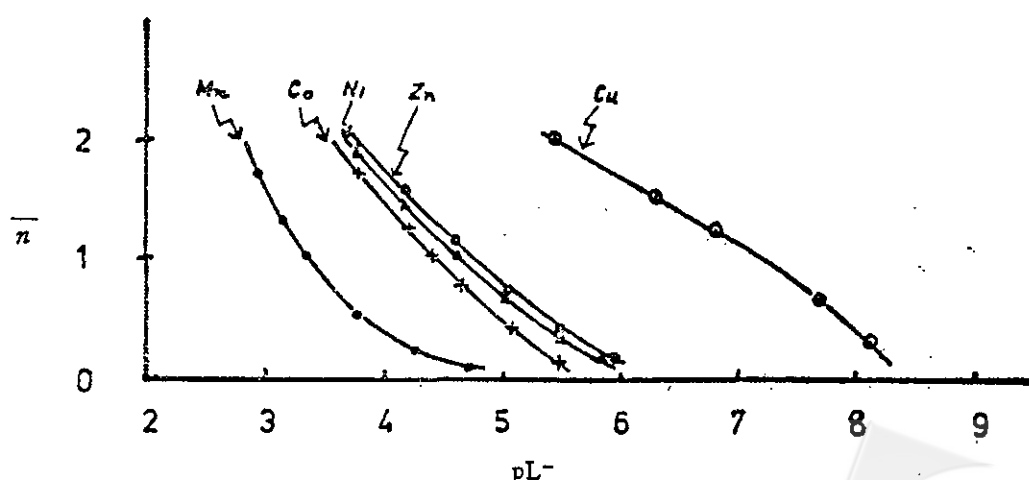

Fig. 2. Bjerrum formation curves for acetohydroxamic acid complexes with some of the bivalent metal ions [25°C].
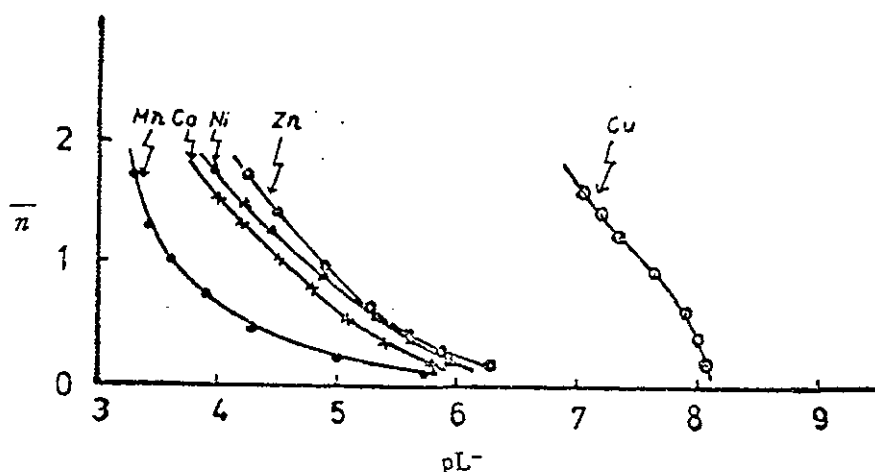
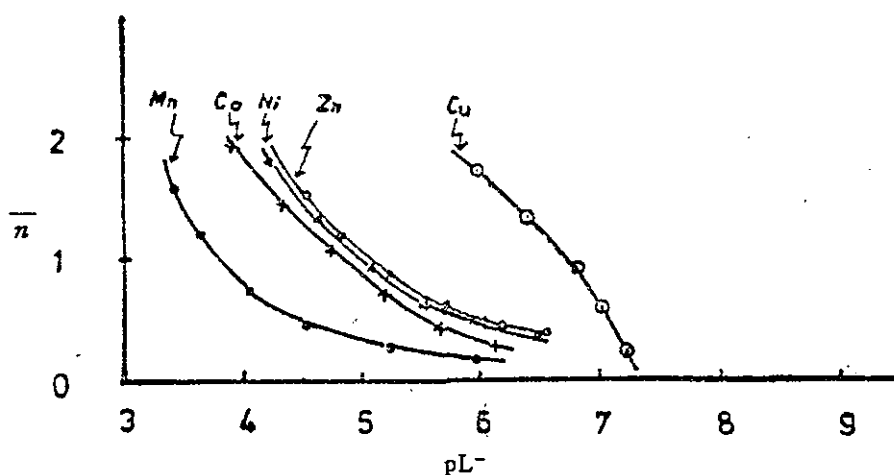Fig. 4. Bjerrum formation curves for butyrohydroxamic acid complexes with some of the bivalent metal ions [$25^\circ C$].

Fig. 6. Bjerrum formation curves for sorbohydroxamic acid complexes with some of the bivalent metal ions [$25^\circ C$].

RESULT AND DISCUSSION

The result of physico-chemical studies for the reagents and their metal complexes are summarized in Table 1, Table 2 and Table 3. The acid dissociation constants of these three kinds of aliphatic hydroxamic acids are approximately of the same magnitude, the influence of the length of aliphatic side chain is very small. It has been pointed out that the introduction of ethylenic unsaturation causes a moderate increase in the strength of a carboxylic acid[19]. The inductive effect is illustrated in the Table 4. The very little drop in pKa for sorbohydroxamic acid may be the reflection of the presence of a conjugated system of double bond between the side chain and the carbon atom of carbonyl group.

The relative stabilities of metal complexes formed by bivalent elements of the first transition series with a wide variety of ligand follow a trend. Irving and

Table 1. Stability constants [given as the logarithms] of some bivalent metal complexes of acetohydroxamic acid determined potentiometrically at $25°C \pm 0.1°$ and ionic strength 0.1 in water

Metal complexes of hydroxamate	pK^a	$\log K_1$	$\log K_2$	$\log \beta_2$
	9.35^a [at $20°C$]			
	9.40^b [at $25°C$]			
	9.40			
Cu		7.90^a	—	—
		7.90	6.40	14.30
Zn		5.40^a	4.20^a	9.60^a
		5.37	4.21	9.58
Ni		5.30^a	4.00^a	9.30^a
		5.30	4.12	9.42
Co		5.10^a	3.80^a	8.90^a
		5.01	4.00	9.01
Mn		4.00^a	2.90^a	6.90^a
		3.80	3.05	6.85

a Reference [22]   b Reference [12]

Table 2. Stability constants [given as the logarithms] of some bivalent metal complexes of butyrohydroxamic acid determined potentiometrically at $25°C \pm 0.1°$ and ionic strength 0.1 in water

Metal complexes of hydroxamate	pK_a	$\log K_1$	$\log K_2$	$\log \beta_2$
	9.48^a			
	9.46			
Cu		7.95	7.15	15.10
Zn		5.45	4.42	9.87
Ni		5.40	4.20	9.60
Co		5.18	4.01	9.19
Mn		4.23	3.35	7.58

a Reference [12]

Table 3. Stability constants [given as the logarithms] of some bivalent metal complexes of sorbohydroxamic acid determined potentiometrically at $25°C \pm 0.1°$ and ionic strength 0.1 in water

| Metal complexes of hydroxamate	pK_a	$\log K_1$	$\log K_2$	$\log \beta_2$
	$9.90^{a,b}$			
	8.80			
Cu		7.10	6.23	13.33
Zn		5.98	4.52	10.50
Ni		5.93	4.50	10.43
Co		5.54	4.30	9.84
Mn		4.50	3.51	8.01

a Reference [14]   b Reference [15]

Table 4. Dissociation constant of some aliphatic carboxylic acid in water at $25°C^a$

Acid	Formula	$10^5 \times K_a$	pK_a
Acrylic	$CH_2=CH—COOH$	5.56	4.25
Propionic	$CH_3—CH_2—COOH$	1.33	4.88
Vinylacetic	$CH_2=CH—CH_2—COOH$	1.62	4.36
trans-Crotonic	$CH_3—CH=CH—COOH$	2.03	4.69
n-Butyric	$CH_3—CH_2—CH_2—COOH$	1.50	4.82
Allylacetic	$CH_2=CH—CH_2—CH_2—COOH$	2.11	4.68
n-Valeric	$CH_3—CH_2—CH_2—CH_2—COOH$	1.38	4.86
Sorbic	$CH_3—CH=CH—CH=CH—COOH$	1.73^b	4.76
n-Hexoic	$CH_3—CH_2—CH_2—CH_2—CH_2—COOH$	1.32	4.88

a Reference [19]   b Reference [23]

Williams[20] concluded that the order of stability holds the following series:

Mn<Fe<Co<Ni<Cu>Zn.
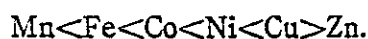
The results obtained for the ligands of these three aliphatic hydroxamic acid also clearly follow the order of Irving-William series as it is shown in Table 1, Table 2 and Table 3. The stability of the nickel (II) and zinc (II) complexes of each of the reagents in Table 1, Table 2 and Table 3 are essentially identical indicating

that these reagents behave in accord with other 5-membered ring forming chelating agents having two oxygen donor atom[21].

The extent of metal chelate formation depends not only on the value of the formation constant but also on the concentration of the free ligand species which in turn depends on the acid dissociation constant of the ligand. The comparison may be made in terms of the proton displacement constant, K_{pd}, which is the product of the overall formation constant, β_n, and the acid dissociation constant K_a raised to the nth power, where n is the number of ligand in the chelate.

For the complex formation of bivalent metal complex, the reaction and the K_{pd} may be expressed as follows:

$$M^{2+}+2HL=ML_2+2H^+$$
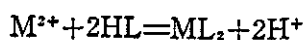
$$K_{pd}=\beta_2 \cdot K_a^2$$

Under this consideration, sorbohydroxamic acid generally have the largest K_{pd} values than others except in the case of copper sorbohydroxamate. Accordingly, it may be said that sorbohydroxamic acid has the highest reactivity and is the best as analytical reagent among the three hydroxamic acids studied. This conclusion is well supported by the observation made by Bass and Yoe[8] for the complexes formed by vanadium with some of the aliphatic hydroxamic acids.

ACKNOWLEDGEMENT

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