Asian Journal of Chemsitry Vol. 8, No. 3 (1996), 346–352

Spectrophotometric Determination of Stabilities of 2-Furo- and 2-Furanacrylohydroxamic Acid Chelates of Fe(III): A Comparative Study†

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2-Furohydroxamic acid [FHA] and 2-furanacrylohydroxamic acid [FAHA] from blue coloured complexes with Fe(III) at pH 2. The metal-ligand ratios of the complexes are found to be 1 : 3 for both the systems. Beer's law is obeyed over the range of 0–40 ppm and 0–110 ppm for Fe-FHA and Fe-FAHA systems respectively. Yatsimirskii's and Leden's methods are adopted to determine the step-wise stability constants of both the systems. The results reveal that an introduction of double bond between functional grouping increases the molar absorptivity, λ_{max}, step-wise and overall stability constants of the system. The overall stability constant of the Fe-FAHA system is approximately ten times greater than that of Fe-FHA system.

INTRODUCTION

Hydroxamic acids are versatile reagents in analytical chemistry[1–7], and are widely used in the analysis of trace metals[8, 9]. Tandon and Bhattacharya studied several nitrogen and carbon substituted hydroxamic acid chelates of vanadium(V)[10–12]. The effect of various substituents in the hydroxamic acid on the stabilities of its several chelates reveals that the metal ligand stability constants are in accordance with that of the basicity of the ligands[13–18]. The role of heterocyclic hydroxamic acids as analytical reagents has received considerable interest in recent times. However, some more light should be thrown on the stability of heterocyclic hydroxamic acid chelates so as to make them useful in the analytical chemistry. Agrawal and Dallali[19] have determined the thermodynamic stability constants of substituted 2-furo and 2-thenohydroxamic acid chelates of alkaline earth metals.

Our earlier report deals with the spectrophotometric determination of the stability of 3-(2-furanyl)-2-propenohydroxamic acid chelates of uranium(VI) and vanadium(V)[20]. We further reported the effect of conjugation on the stabilities of the metal chelates from the comparative study of 2-furo- and 2-furanacrylohydroxamic acid chelates of vanadium(V)[21]. In continuation of our earlier work, the present work deals with the spectrophotometric determination of the stability

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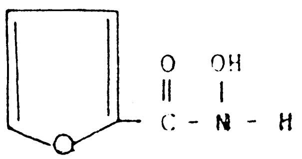
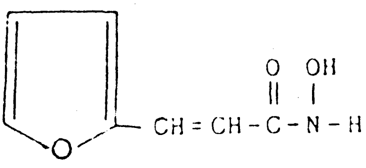
†Paper presented in "30th Annual Convention of Chemists", Calcutta, India, Dec. 22–24, 1993.

of 2-furo-[I] and 2-furanacrylohydroxamic acid [II] chelates of Fe(III) at pH 2 in 30% ethanol-water medium.



(I)



(II)

EXPERIMENTAL

All the chemicals were of reagent grade unless otherwise specified. The ligands were prepared following the procedure adopted by Blatt[22]. A stock solution of ligands (0.1 M) was prepared by dissolving them in absolute ethanol and lower concentrations were obtained by dilution with absolute ethanol. A stock solution of iron(III) (0.1 M) was prepared from ferric alum and it was standardised using standard procedure[23]. Solutions of other concentrations were obtained from these solutions by dilution with double distilled water. Buffer solution of pH 2 was prepared by dissolving 20 mL of conc. HCl and 14.9 g of potassium chloride in one litre distilled water.

The pH was measured with an ITL digital pH/MV meter (model DPH-14), having a glass electrode. A spectrophotometer (model UVIDEC 340) was used for absorbance measurements.

RESULTS AND DISCUSSION

Stoichiometry of the complexes: 2-Furo- and 2-furanacrylohydroxamic acids form stable blue coloured complexes with iron(III), buffered at pH 2. The maximum absorption occurs at 525 nm, for Fe(III)-FHA, and at 530 nm for Fe(III)-FAHA system. Job's, mole-ratio, and slope-ratio methods indicate the metal-ligand ratio to be 1 : 3 for both the systems. All the absorption values were measured against to the identical condition of the reagent blank.

Conformity to Beer's law: The optimum condition of the systems by Beer's law and Ringbom's methods was found to be 0–40 ppm, 20–40 ppm for Fe-FHA and 0–110 ppm, 15–80 ppm for Fe-FAHA. The molar-extinction coefficient and relative error coefficients are found to be 4.933×10^3 dm^3 mol^{-1} cm^{-1} and 0.04 for Fe-FHA and 6.241×10^3 dm^3 mol^{-1} cm^{-1}, and 0.03 for Fe-FAHA systems respectively.

Determination of stability constants: Yatsimirskii's method[24]

Stability constants of Fe(III)-FHA and Fe(III)-FAHA were evaluated by the Yatsimirskii's method using mole-ratio technique. A series of different subsidiary functions f_1, f_2 and f_3 were calculated and the values are reported in Table-1. The functions f_1, f_2 and f_3 have been plotted against free ligand concentration of ligand [L]. The intercept values a_1, a_2 and a_3 were calculated by using the linear regression and an exponential curve analysis. The intercept values are

TABLE-1
YATSIMIRSKII'S METHOD

[Iron] = [FHA] = 0.0025 M
[Iron] = [FAHA] = 0.002 M
Temperature = 30 ± 0.1°C

Buffer 5 mL of pH 2
Final volume = 25 mL
Metal taken = 2.5 mL

ε_{max} Fe-FHA = 4.933×10^3 $dm^3\ mol^{-1}\ cm^{-1}$
ε_{max} Fe-FAHA = 6.241×10^3 $dm^3\ mol^{-1}\ cm^{-1}$

System	Absorbance	Total ligand conc. (Mol/dm^3) $T_L \times 10^4$	Equilibrium ligand conc. (Mol/dm^3) $[L] \times 10^4$	Molar extinction coefficient $\bar{e} = A/C_M \times 10^{-3}$	$Y = 1/[L] \times 10^{-4}$	$f_1 = \bar{e}/[L] \times 10^{-7}$	$f_2 = \frac{f_1 - a_1}{[L]} \times 10^{-10}$	$f_3 = \frac{f_2 - a_2}{[L]} \times 10^{-13}$	$g_1 = \frac{\bar{e} - b_1}{1/[L]}$	$g_2 = \frac{g_1 - b_2}{1/[L]} \times 10^4$
Fe-FHA	0.371	5.8	3.5439	1.484	0.2821	0.4187	—	—	–0.7569	1.4622
	0.395	6.2	3.7980	1.580	0.2633	—	—	—	–0.7747	1.4995
	0.408	6.6	4.1189	1.632	0.2428	0.3962	—	—	—	—
	0.438	7.0	4.3365	1.752	0.2306	—	—	—	–0.8100	1.5590
	0.440	7.2	4.5243	1.760	0.2210	0.3690	—	—	–0.8415	—
	0.461	7.8	4.9966	1.844	0.2001	0.3690	–0.2644	—	–0.8873	—
	0.484	8.2	5.2567	1.936	0.1902	0.3683	–0.2527	0.3646	—	—
	0.506	8.6	5.5230	2.024	0.1810	0.3664	–0.2438	0.3631	–0.8814	—
	0.529	9.0	5.7831	2.116	0.1729	0.3658	–0.2338	—	—	—
	0.551	9.4	6.0493	2.204	0.1653	0.3643	–0.2262	0.3608	—	—
Fe-FAHA	0.459	4.32	2.1139	2.295	0.4731	1.0857	–1.1954	—	–0.0880	—
	0.536	4.96	2.3838	2.680	0.4195	1.1243	—	—	–0.0901	—
	0.558	5.28	2.5980	2.790	0.3849	1.0739	–1.0181	1.0520	–0.0953	—
	0.597	5.76	2.8906	2.985	0.3459	1.0327	–1.0576	—	–0.1004	0.8591
	0.615	5.92	2.9641	3.075	0.3374	1.0374	–1.0155	0.9308	–0.1003	0.8842
	0.620	6.00	3.0200	3.100	0.3311	1.0265	–1.0328	0.8563	–0.1015	—
	0.675	6.56	3.3157	3.375	0.3016	1.0179	—	—	–0.1023	0.9244
	0.722	7.20	3.7298	3.612	0.2681	0.9678	–0.9934	0.7989	–0.1063	—
	0.783	8.00	4.2366	3.915	0.2360	0.9241	–0.9779	0.7399	–0.1078	0.9468

Fe(III)-FHA systems	Fe(III)-FAHA system
$a_1 = 5.01 \times 10^6$	$a_1 = 1.34 \times 10^7$
$a_2 = -4.44 \times 10^9$	$a_2 = -1.29 \times 10^{10}$
$a_3 = 3.91 \times 10^{12}$	$a_3 = 1.65 \times 10^{13}$

Similarly, the functions $\bar{e}$, g_1 and g_2 were calculated and plotted against reciprocal of free ligand concentration [1/L] and extrapolated to zero reciprocal of free ligand concentration. An exponential curve and linear regression analysis were employed to calculate the intercepts b_1, b_2 and b_3. The intercept values are

Fe(III)-FHA systems	Fe(III)-FAHA system
$b_1 = 3.62 \times 10^3$	$b_1 = 6.46 \times 10^3$
$b_2 = -1.17$	$b_2 = -1.30$
$b_3 = 2.07 \times 10^{-4}$	$b_3 = 1.16 \times 10^{-4}$

The relationships between the stability constants and the intercepts are as folows.

$$\lim_{[L] \to 0} f_1 = a_1 = e_1\beta_1 \tag{1}$$

$$\lim_{[L] \to 0} f_2 = a_2 = e_2\beta_2 - e_1\beta_1^2 \tag{2}$$

$$\lim_{[L] \to 0} f_3 = a_3 = e_3\beta_3 - e_1\beta_1^3 \tag{3}$$

and introducing $Y = [1/L]$

$$\lim_{Y \to 0} e = b_1 = e_3 \tag{4}$$

$$\lim_{Y \to 0} g_1 = b_2 = (e_2 - e_3)\beta_2/\beta_1 \tag{5}$$

$$\lim_{Y \to 0} g_2 = b_3 = (e_1 - e_3)\beta_1/\beta_3 - (e_2 - e_3)(\beta_2/\beta_3)^2 \tag{6}$$

The above equations were solved to get a second-degree equation in β_1.

$$[a_1b_2^2 - a_1b_1b_3]\beta_1^2 - [b_1^3 + a_1b_1b_2]\beta_1 + [a_3b_2^2 + a_1b_1^2 - a_3b_1b_3 - a_2b_1b_2] = 0$$

By solving the quadratic equations value of β_1 can be readily calculated. The calculated logarithm values of K_1, K_2 and K_3 are listed in Table-3.

Leden's method[25]

Series of subsidiary functions ψ_1, ψ_2 and ψ_3 were calculated from the degree of complex formation (ϕ) and the calculated values are presented in Table-2. The functions were plotted against equilibrium ligand concentration [L]. The overall stability constants can be directly obtained as the intercepts on the ordinate from these plots.

Table-3 reveals the comparative account of stabilities of Fe(III)-FHA and

TABLE-2
LEDEN'S METHOD

[Iron] = [FHA] = 0.0025 M
[Iron] = [FAHA] = 0.002 M
Temperature = 30 ± 0.1°C

Buffer 5 mL of pH 2
Final volume = 25 mL
Metal taken = 2.5 mL

ε_{max} Fe-FHA = 4.933×10^3 dm^3 mol^{-1} cm^{-1}
ε_{max} Fe-FAHA = 6.241×10^3 dm^3 mol^{-1} cm^{-1}

System	Absorbance	Total ligand conc. (Mol/dm^3) $T_L \times 10^4$	Equilibrium ligand conc. (Mol/dm^3) $[L] \times 10^4$	Equilibrium metal conc. (Mol/dm^3) $[M] \times 10^4$	Degree of complex formation $\Phi = C_M/[M]$	$\psi_1 = \frac{\phi - 1}{[L]} \times 10^{-3}$	$\psi_2 = \frac{\psi_1 - \beta_1}{[L]} \times 10^{-6}$	$\psi_3 = \frac{\psi_2 - \beta_2}{[L]} \times 10^{-9}$
Fe-FHA	0.248	4.20	2.6919	1.9973	1.2517	0.9350	1.9501	3.7281
	0.309	5.00	3.1209	1.8736	1.3343	1.0711	2.1181	3.7534
	0.336	5.40	3.3567	1.8189	1.3744	1.1155	—	—
	0.371	5.80	3.5439	1.7480	1.4302	1.2140	2.2685	3.7302
	0.395	6.20	3.7980	1.6993	1.4712	1.2406	—	—
	0.438	7.00	4.3365	1.6122	1.5507	1.2700	—	—
Fe-FAHA	0.597	5.76	2.8906	1.0435	1.9166	3.1709	6.0268	9.1569
	0.620	6.00	3.0200	1.0067	1.9867	3.2676	6.0877	8.9662
	0.675	6.50	3.3157	1.9185	2.1775	3.5507	6.3996	9.1073
	0.722	7.20	3.7298	0.8432	2.3117	3.6777	—	—
	0.755	7.52	3.8912	0.7904	2.5304	3.9330	6.4356	—

Fe(III)-FAHA systems determined by Yatsimirskii's and Leden's methods. From Table-3, it is inferred that the values of the stability constants obtained by Leden's method are somewhat lower than that of Yatsimirskii's method. The values obtained from the Leden's method cannot be trusted since only few data are available to calculate the values of equilibrium metal concentration [M] where excess of metal is not present. The order of stepwise stability constants of Fe(III)-FHA and Fe(III)-FAHA complexes, according to Yatsimirskii's method, are

$$K_1 > K_2 > K_3,$$

which is in accordance with statistical factors.

TABLE-3

COMPARATIVE ACCOUNTS OF Fe-FHA AND Fe-FAHA COMPLEXES AT 30 ± 0.1°C

Method	System	Wave-length	Molar extinction coefficient $\varepsilon \times 10^3$ dm^3 mol^{-1} cm^{-1}	log K_1	log K_2	log K_3	log β_3
Yatsimirskii's	Fe-FHA	525	4.933	3.45	3.37	3.26	10.08
	Fe-FAHA	530	6.241	3.88	3.70	3.50	11.08
Leden's	Fe-FHA	525	4.933	2.61	3.36	3.60	9.57
	Fe-FAHA	530	6.241	3.07	3.46	3.43	9.96

It is evident from the results that an introduction of double bond between furan ring and $-\overset{\overset{\displaystyle O}{\|}}{C}-$ group in the hydroxamic acid increases the stepwise and overall stability constants of the complexes. This is in line with our earlier work on the stability of 2-furo- and 2-furanacryclohydroxamic acid chelates of vanadium(V)[21] where it has been noted that an introduction of double bond between furan ring and $-\overset{\overset{\displaystyle O}{\|}}{C}-$ functional grouping of hydroxamic acid increases the overall stability constants, λ_{max}, Beer's law validity and molar extinction coefficients of the systems. Tandon and Bhattacharya[26] also reported that the introduction of double bond between phenyl ring and $-\overset{\overset{\displaystyle O}{\|}}{C}-$ grouping of hydroxamic acid caused increase of wavelength, molar absorptivity and Sandell's sensitivity. In general, an introduction of $-CH{=}CH-$ group in between R— and $-\overset{\overset{\displaystyle O}{\|}}{C}-$ grouping of hydroxamic acid, is expected to increase in Beer's law optimum, wavelength, molar absorptivity, Sandell's sensitivity and stability of metal-chelate of the system.

In the present study the ligands FHA and FAHA act as uninegative bidentate ligands. The composition of the chelate may be depicted as $[Fe(HR)_3]$.

ACKNOWLEDGEMENT

One of the authors (V.T.) gratefully thanks Prof. (Late) S. Govindasamy, Department of Chemistry, Annamalai University, for critical suggestions during the course of study.

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(*Received*: 21 February 1995; *Accepted*: 15 December 1995) AJC-1053