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Effect of Conjugation on Formation Constants of Vanadium (V) Complexes

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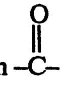
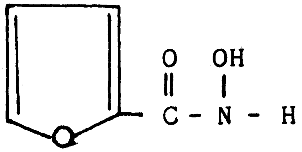
2-Furo- and 2-furanacrylohydroxamic acids (FHA and FAHA) form stable red-orange coloured complexes with vanadium (V). Spectrophotometric measurements have revealed the metal-ligand ratio to be 1 : 4 for both the systems. Stability constants of the complexes have been determined by Yatsimirskii's and Leden's methods and compared. The effect of conjugation on the spectral characteristics and on stability of complexes has been discussed.

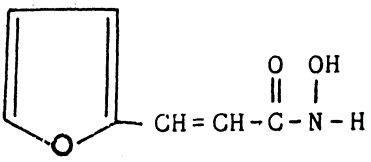
INTRODUCTION

Hydroxamic acids have received considerable attention as analytical reagents for various kinds of metals. From the study of several N-arylhydroxamic acid complexes of V(V), Tandon *et. al.*[1] have found that N-phenylcinnamohydroxamic acid is the most sensitive reagent for spectrophotometric determination of V(V). The effect of various substituents (Cl, Br, NO_2, CH_3) in phenyl ring at carbon atom of the hydroxamic acid on the spectral characteristics of the corresponding V(V) complexes has also been made[2].

Effect of substitutents on the stability of hydroxamic acid complexes of various metals[3–8] has also been studied. comparison reveals that the metal-ligand stability constants are in accordance with that of the basicity of the ligands. Agarwal and Gupta[8] have reported that the introduction of electrophilic substituent like chlorine on N–phenylring of the cinnamohydroxamic acid complexes of V(V) reduces the stability of the complexes and increases selectivity of the reagent. Bag and Chakrabarti[9] proposed a new approach for the evaluation of the step-wise stability constants in solution by two-dimensional extrapolation method by an extension of Yatsimirskii's[10] and Leden's[11] methods. A very few pieces of work have paid attention to determine the formation constants of hydroxamic acid complexes with high metal-ligand ratio[9,12]. This paper deals with the spectrophotometric determination of stability constants of 1 : 4 metal-ligand systems by the extended Yatsimirskii's and Leden's methods. Moreover, the effect of increasing the length of the conjugation by the introduction of side chain double bond (–CH=CH–) between  $\overset{\overset{\displaystyle O}{\|}}{-C-}$ group and R–group of the hydroxamic acid on the stability constants has also not been studied in detail. The authors report here a comparative account of spectral characteristics and stability of 2-furohydroxamic acid (I) (FHA) and 2-furanacrylohydroxamic acid (II) (FAHA) complexes of V(V) at pH 2 in 30% ethanol-water medium at 30 ± 0.1°C.



(I)



(II)

EXPERIMENTAL

Stock solution of vanadium (V) was prepared from AR grade ammoniummeta vanadate and standardised[13] by known procedure. Ligands I and II were prepared following the method of Blatt[14]. Buffer of pH 2 was prepared using known procedure.

Spectrophotometric measurements were made with a UV–visible spectrophotometer, model UV–DEC 340 using, 1 cm quartz glass transmission cells, and an ITL digital pH/Mv meter with glass electrode, model DPH-14 was used for pH measurement.

Vanadium (V) develops a red-orange colour with FHA and FAHA. The maximum absorption of 2-furo- and 2-furanacrylohydroxamic acid complexes of V(V) occurs at 460 and 470 nm respectively. The absorption measurements were carried out in 30% ethanol-water medium at 30 ± 0.1°C after adding 5 ml buffer of pH 2. The total volume was kept as 30 ml for both the systems.

RESULTS AND DISCUSSION

The composition of the complexes determined by Job's methods of continuous variation, slope-ratio and mole-ratio methods indicate the metal-ligand ratio to be 1 : 4 for both the systems. Rowland and Meloan[15] have also reported the same composition for V(V)–FHA system at pH 8. The molar extinction coefficients of V(V)–FHA and V(V)–FAHA complexes calculated from Beer's law plots are found to be 0.8846×10^3 and 2.003×10^3 $dm^3 mol^{-1} cm^{-1}$ respectively.

Stability Constants

According to Yatsimirskii's method, a series of different subsidiary functions f_1, f_2, f_3, f_4, $\bar{e}$, g_1, g_2 and g_3 are constructed from the absorption values measured by mole-ratio technique for both the systems and the values calculated in this manner are reported in Tables 1 and 2. The calculated values of f_1, f_2, f_3 and f_4 have been plotted against free ligand concentration at equilibrium and extrapolated

TABLE 1
V(V)–FHA COMPLEX YATSIMIRSKII'S METHOD

[Metal] = [Ligand] = 0.0145 M
Metal taken = 2.0 ml of 0.0145 M
Temperature 30 ± 0.1°C

Solvent = 30% Ethanol – water
Final volume = 30 ml

Buffer 5 ml of pH 2
Wave length for measurement = 460 nm
$\varepsilon_{max} = 0.8846 \times 10^3$ dm^{3}mol^{-1}cm^{-1}

Absorbance	Total ligand conc. (Mole/dm^3) $C_L \times 10^3$	Equilibrium ligand Conc. (Mole/dm^3) $[L] \times 10^3$	Molar extinction coefficient $\bar{e} = A/C_M$ $\times 10^{-3}$	$Y = 1/[L]$ $\times 10^{-4}$	$f_1 = \bar{e}/[L]$ $\times 10^{-6}$	$f_2 = \frac{f_1 - a_1}{[L]}$ $\times 10^{-7}$	$f_3 = \frac{f_2 - a_2}{[L]}$ $\times 10^{-9}$	$f_4 = \frac{f_3 - a_3}{[L]}$ $\times 10^{-11}$	$g_1 = \frac{\bar{e} - b_1}{1/[L]}$ $\times 10^2$	$g_2 = \frac{g_1 - b_2}{1/[L]}$ $\times 10^6$	$g_3 = \frac{g_2 - b_3}{1[L]}$ $\times 10^{10}$
0.282	2.4167	1.1414	0.2917	0.8760	0.2555	–3.2767	—	—	-7.2542	—	—
0.333	2.9000	1.3942	0.3445	0.7172	0.2470	–3.2872	—	—	–8.1242	—	—
0.365	3.1900	1.5395	0.3775	0.6496	0.2453	—	—	—	–8.4607	—	—
0.374	3.2867	1.5955	0.3869	0.6268	0.2425	–3.1589	—	—	–8.6195	4.5158	–2.4772
0.384	3.3833	1.6469	0.3972	0.6072	0.2412	–3.1392	—	—	–8.7281	4.4827	–2.6117
0.404	3.5767	1.7494	0.4179	0.5715	0.2388	–3.0918	2.1077	–6.379	–8.9110	—	—
0.429	3.8666	1.9267	0.4488	0.5190	0.2303	—	—	—	–9.3135	—	—
0.509	4.6400	2.3383	0.5265	0.4276	0.2252	—	—	—	–9.3702	4.8639	–2.8171
0.522	4.8330	2.4730	0.5399	0.4044	0.2182	–3.0206	1.7792	–5.8419	–9.5764	—	—
0.562	5.3167	2.7753	0.5814	0.3603	0.2095	–3.0051	1.6413	–5.7024	–9.5967	5.1438	—

TABLE 2
V(V)-FHA COMPLEX YSTSIMIRSKII'S METHOD

[Metal] = [Ligand] = 0.005 M
Metal taken = 2.0 ml of 0.005 M
Temperature 30 ± 0.1°C

Solvent = 30% Ethanol – Water
Final volume = 30 ml

Buffer 5 ml of pH 2
Wave length for measurement = 470 nm
$\varepsilon_{max.}$ = 0.2.0034 × 10^3 $dm^3/mol^{-1}cm^{-1}$

Absorbance	Total ligand conc. (Mole/dm^3)	Equilibrium ligand Conc. (Mole/dm^3)	Molar extinction coefficient $\bar{e} = A/C_M$	$Y = 1/[L]$	$f_1 = \bar{e}/[L]$	$f_2 = \frac{f_1 - a_1}{[L]}$	$f_3 = \frac{f_2 - a_2}{[L]}$	$f_4 = \frac{f_3 - a_3}{[L]}$	$g_1 = \frac{\bar{e} - b_1}{1/[L]}$	$g_2 = \frac{g_1 - b_2}{1/[L]}$	$g_3 = \frac{g_2 - b_3}{1[L]}$
	$C_L \times 10^3$	$[L] \times 10^4$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-7}$	$\times 10^{-10}$	$\times 10^{-13}$	$\times 10^{17}$	$\times 10^2$	$\times 10^6$	$\times 10^{10}$
0.417	0.91667	0.84084	1.251	1.1893	1.4878	—	—	—	–6.143	3.4239	–0.9302
0.427	0.96670	1.1412	1.281	0.8763	1.1225	–4.6083	7.2573	–5.3870	—	—	—
0.457	1.0500	1.3755	1.371	0.7270	0.9967	–4.7378	—	—	—	—	—
0.473	1.0833	1.3894	1.419	0.7197	1.0213	–4.5135	6.6432	—	–7.8167	3.3322	–1.6645
0.489	1.1333	1.5699	1.467	0.6369	0.9344	–4.5478	5.6609	–4.9329	–8.0798	3.3525	–1.8491
0.500	1.1667	1.6836	1.500	0.5939	0.8909	–4.4991	5.5678	–4.6550	–8.1091	3.5459	—
0.523	1.2167	1.7244	1.569	0.5799	0.9098	–4.2828	—	—	—	—	—
0.596	1.5833	3.9330	1.788	0.2542	0.4545	–3.0355	—	—	—	—	—
0.618	1.6333	3.9943	1.854	0.2503	0.4641	–2.9648	—	—	—	—	—

to zero values of [L]. An exponential curve and linear regression analyses were employed to calculate the intercepts a_1, a_2, a_3 and a_4. The various intercept values are

V(V)–FHA system	V(V)–FAHA system
$a_1 = 2.9290 \times 10^5$	$a_1 = 1.6484 \times 10^7$
$a_2 = -3.4606 \times 10^7$	$a_2 = -5.4365 \times 10^{10}$
$a_3 = 3.2239 \times 10^9$	$a_3 = 1.3050 \times 10^{14}$
$a_4 = -7.5488 \times 10^{11}$	$a_4 = -6.8516 \times 10^{17}$

Similarly, the functions $\bar{e}$, g_1, g_2 and g_3 have been plotted against the reciprocal of free ligand concentration and extrapolated to zero value of [1/L]. An exponential curve and linear regression analyses were employed to calculate the intercepts b_1, b_2, b_3 and b_4. the various intercept values are

V(V)–FHA system	V(V)–FAHA system
$b_1 = 9.2719 \times 10^2$	$b_1 = 1.9848 \times 10^3$
$b_2 = -0.1145$	$b_2 = -0.1012$
$b_3 = 6.0685 \times 10^{-6}$	$b_3 = 4.5302 \times 10^{-6}$
$b_4 = -3.4566 \times 10^{-10}$	$b_4 = -2.8640 \times 10^{-10}$

The relationship between the stability constants and the intercepts are as fellows:

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

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

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

$$\lim_{[L] \to 0} f_4 = a_4 = e_4\beta_4 - e_1\beta_1^4 \tag{4}$$

and introducing $[1/L] = Y$

$$\lim_{Y \to 0} \bar{e} = b_1 = e_4 \tag{5}$$

$$\lim_{Y \to 0} g_1 = b_2 = (e_3 - e_4)\beta_3/\beta_4 \tag{6}$$

$$\lim_{Y \to 0} g_2 = b_3 = (e_2 - e_4)\beta_2/\beta_4 - (e_3 - e_4)(\beta_3/\beta_4)^2 \tag{7}$$

$$\lim_{Y \to 0} g_3 = b_4 = (e_1 - e_4)\beta_1/\beta_4 - (e_2 + e_3 - 2e_4)\,\beta_2\beta_3/\beta_4^2 + (e_3 - e_4)(\beta_3/\beta_4)^3 \tag{8}$$

By solving the above equations a third degree equation in β_1 is obtained.

$$[2a_1b_2b_3/b_1 - a_1b_2^3/b_1^2 - a_1b_4]\beta_1^3 + [a_1b_2^2/b_1 - a_1b_3]\beta_1^2 - [b_1^2 + a_1b_2]\beta_1 + [a_1b_1 - a_2b_2 - a_3b_3 - a_4b_4 + a_3b_2^2/b_1 - b_2^3a_4/b_1^2 + 2b_2b_3a_4/b_1] = 0$$

and from this Newton-Raphson's method[16] was used to calculate the value of β_1.

From the degree of complex formation (ϕ), we are able to calculate only two series of subsidiary functions ψ_1 and ψ_2. These values are reported in Tables 3 and 4. These functions have been plotted against equilibrium ligand concentration. The overall stability constants can be directly obtained as the intercepts on the ordinate from these plots (Leden's method). The intercepts were calculated from extrapolation plots using exponential curve and linear regression analyses for both the systems.

TABLE 3

V(V)-FHA COMPLEX LEDEN'S METHOD

[Metal] = [Ligand] = 0.0145 M Solvent = 30% Ethanol – water Buffer 5 ml of pH 2

Metal taken = 2.0 ml of 0.0145 M Final volume = 30 ml

Wave length for measurement = 460 nm $\varepsilon_{max.} = 0.8846 \times 10^3\ dm^3 mol^{-1} cm^{-1}$

Temperature 30 ± 0.1°C

Absorbance	Total ligand conc. (Mole/dm^3) $C_L \times 10^3$	Equilibrium ligand conc. (Mole/dm^3) $[L] \times 10^3$	Equilibrium metal conc. (Mole/dm^3) $[M] \times 10^4$	Degree of complex formation $\phi = \frac{C_M}{[M]}$	$\psi_1 = \frac{\phi - 1}{[L]}$ $\times 10^{-3}$	$\psi_2 = \frac{\psi_1 - \beta_1}{[L]}$ $\times 10^{-5}$
0.333	2.9000	1.3942	5.9025	1.6378	0.4574	1.1907
0.365	3.1900	1.5395	5.5407	1.7447	0.4837	–
0.374	3.2867	1.5955	5.4390	1.7770	0.4872	1.2270
0.384	3.3833	1.6469	5.3259	1.8150	0.4949	1.2354
0.404	3.5767	1.7498	5.0990	1.8955	0.5118	1.2593
0.429	3.8660	1.9267	4.8170	2.0007	0.5225	—

TABLE 4

V(V)-FAHA COMPLEX LEDEN'S METHOD

[Metal] = [Ligand] = 0.005 M Solvent = 30% Ethanol – water Buffer 5 ml of pH 2

Metal taken = 2.0 ml of 0.005 M Final volume = 30 ml

Wave length for measurement = 470 nm $\varepsilon_{max.} = 2.0034 \times 10^3\ dm^3 mol^{-1} cm^{-1}$

Temperature 30 ± 0.1°C

Absorbance	Total ligand conc. (Mole/dm^3) $C_L \times 10^3$	Equilibrium ligand conc. (Mole/dm^3) $[L] \times 10^4$	Equilibrium metal conc. (Mole/dm^3) $[M] \times 10^4$	Degree of complex formation $\phi = \frac{C_M}{[M]}$	$\psi_1 = \frac{\phi - 1}{[L]}$ $\times 10^{-4}$	$\psi_2 = \frac{\psi_1 - \beta_1}{[L]}$ $\times 10^{-7}$
0.427	0.9667	1.1412	1.2016	2.7737	1.5543	—
0.457	1.0500	1.3755	1.0521	3.1686	1.5766	4.9861
0.473	1.0333	1.3894	0.9720	3.4290	1.7482	—
0.500	1.1667	1.6836	0.8372	3.9809	1.7705	5.2254
0.618	1.6333	3.9943	0.2482	13.4260	3.1110	5.5585

TABLE 5
COMPARATIVE ACCOUNT OF V(V)-FHA AND FAHA COMPLEXES AT 30 ± 0.1°C

Method/System	Wave length (λ_{max}) nm	Molar extinction coefficient $\varepsilon \times 10^{-3}$ dm^3 mol^{-1}cm^{-1}	log K_1	log K_2	log K_3	log K_4	log β_4
Yatsimirskii's							
V–FHA	460	0.8846	2.51	2.33	2.74	2.42	10.00
V–FAHA	470	2.0034	4.22	4.17	4.25	3.95	16.59
Leden's							
V–FHA	460	0.8846	2.46	2.50	—	—	—
V–FAHA	470	2.0034	3.95	3.73	—	—	—

Table-5 reports the comparative account of stabilities of V(V)-FHA and V(V)-FAHA systems by Yatsimirskii's and Leden's methods. From Table-5 it is inferred that log $K_2 <$ log K_1 and this is in accordance with that of the statistical factors. However, log K_3 is found to be slightly greater than that of log K_4 though one can expect a steady descending progression in the values of χ in any particular system. Generally hydroxamic acids behave as a uninegative bidentate ligand and this kind of behaviour may be noted up to the second stage of the complexation. Higher value of log K_3 indicates that the ligand behaves somewhat in a different manner in the third and fourth steps. This may be due to the association of the two of the ligand molecules from outer sphere of the coordination zone. The probable structure of the complex may be $[VO(OH)R_2]RH$ RH, where RH stands for the ligand. This kind of different association behaviour is already noted by Bag and Khastagir[12] during the fourth stage complexation of Ti (IV) with N–benzoylphenyl hydroxylamine. The other possibility is the ligand may act as uninegative unidentate ligand during the third and fourth stage of complexation *i.e.*, the probable structure may be depicted as $[V(OH)(R)_2RR]$. Whatever may be the order of the step-wise stability constants, it is definite that the introduction of double bond increases the step-wise stability constants and overall stability constants. Comparison also reveals that the introduction of double bond increases the molar absorptivity and wave length of the systems.

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