

Complex Formation Equilibria of Methioninehydroxamic Acid with Proton and Iron(III) in Aqueous Organic Solvents

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In continuation of our earlier work¹, the present work reports the determination of protonation constants of methioninehydroxamic acid (MetHA) [2-amino-*N*-hydroxy-4-(methylthio)butanamide] and formation constants of its complex with Fe^{III} in aqueous, methanol-water and isopropanol-water mixtures at constant mole fraction (0.24) of organic solvent in aqueous organic mixtures at ionic strength of 0.2 M (NaCl).

Results and Discussion

Potentiometric titration curves of pH versus volume of NaOH added in different solvent media were drawn (figures not shown). The protonation constants ($\log K_1^H$ and $\log K_2^H$) and metal-ligand stability constants were calculated by computational methods² (Table 1). It is evident that the presence of α -amino group MetHA increases the acidic character of NHOH moiety ($\log K_2^H$ 6.78 in aqueous medium) compared to *n*-butyrohydroxamic acid³ ($\log K_1^H$ 9.50). A comparison of present value of $\log K_1^H$ ($^+NH_3$) 9.00 for MetHA in aqueous medium with corresponding amino acid methionine⁴ ($\log K_1^H$ ($^+NH_3$) 9.15) shows that the substitution of an NHOH group for OH group of carboxyl moiety slightly lowers the protonation constant (increase the acidic character of $^+NH_3$ group) in accordance with the electron-withdrawing character of NHOH group. The present $\log K_1^H$ and $\log K_2^H$ values for MetHA are in close agreement with the reported values⁵ in aqueous medium. The values of $\log K_1^H$ and $\log K_2^H$ increase with the decrease in dielectric constant of the medium.

TABLE 1-PROTONATION CONSTANTS* OF METHIONINEHYDROXAMIC ACID AND FORMATION CONSTANTS OF Fe^{III}-METHIONINEHYDROXAMIC ACID COMPLEXES IN AQUEOUS ORGANIC MEDIA

Temp. = 30°, *I* = 0.2 M (NaCl)

Solvent composition (%, v/v)	H ⁺		Fe ^{III}			1/ <i>E</i>
	$\log K_1^H$	$\log K_2^H$	$\log K_1$	$\log K_2$	$\log \beta_2$	
Aqueous	9.00	6.78	11.42	7.46	18.88	0.013
Methanol-water (42.5 : 57.5)	9.21	6.83	11.62	8.54	20.16	0.0167
Isopropanol-water (58.6 : 41.4)	9.68	6.94	12.40	8.74	21.14	0.0254

*Standard deviation of values are ± 0.02 log units.

Complexation between Fe^{III} and MetHA initiates at about pH 3.3 and \bar{n} values between 1 and 2. A comparison of formation constants (Table 1) with Fe^{III}-methionine system⁴ ($\log K_1$ 9.1) shows that MetHA formed complexes of greater stability than methionine. This may be attributed to the strong binding of Fe^{III} by CONHOH group due to its greater basic nature as compared to COOH group binding with Fe^{III} in methionine. The trend in variation of $\log \beta_2$ versus reciprocal of dielectric constant ($1/E$) shows that these values increase with increase in $1/E$. In other words, $\log \beta_2$ values decrease in various solvents in the order : isopropanol-water > methanol-water > water. This sequence is parallel to the order of dielectric constant of the media : isopropanol-water < methanol-water < water.

Experimental

DL-Methioninehydroxamate (Sigma) was used. All other chemicals were of AnalaR grade. pH-metric titration technique of Irving and Rossotti² was used to determine protonation constants and formation constants. The following solutions (20 ml) : (A), 5×10^{-3} M HC; (B) (A) + 1×10^{-3} M MetHA; (C), (B) + 1.7×10^{-4} M Fe^{III} solution, were separately titrated against 0.1 N NaOH in water, methanol-water (42.5 : 57.5) and isopropanol-water (59.6 : 41.4, %v/v) mixtures keeping ionic strength at 0.2 M (NaCl) as well as at constant mole fraction (0.24) of organic solvent in aqueous organic media.

An ECIL 5652 pH-meter with combined glass and calomel electrode assembly was used and pH values in aqueous organic mixtures were corrected⁶. The values of dielectric constant (*E*) for the solvent composition were either obtained or calculated from the reported data⁷.

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