Measurement of Stability Constant of Hymatomelanic Acid Metal Complexes

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Log k values of Hymatomelanic acid metal complexes are evaluated at pH 4.0 and 5.5.

Log k values for Ferric Hy.A. complex changes from 3.97 to 4.93 with change in pH from 4.0 to 5.5, same values for Al-Hy.A. complex are 3.81 at pH 4.0 and 3.88 at pH 5.5 which indicate that stabilities of Al-Hy.A. complex are not affected by change in pH. The Log k values for Cu-Hy.A., Ni-Hy.A. and Zn-Hy.A. compleaes are 3.43, 2.75, 3.59 at pH 4.0 and 5.86, 5.42 and 4.82 at pH 5.5 an appreciable change in stabilities on change in pH. The result of this investigation indicate the following sequences $Ni^{2+} < Cu^{2+} < Zn^{2+} < Al^{3+} < Fe^{3+}$ at pH 4.0 and $Al^{3+} < Zn^{2+} < Fe^{3+} < Ni^{2+} < Cu^{2+}$ at pH 5.5.

CHELATES can function as metal buffers[1]. Hence metal ions capable to form stable water soluble chelates may' be used to control the concentration and also the behaviour of these ions in aqueous media. A knowledge of stability constants of different soil humus fraction metal complexes, therefore, will be helpful to understand the fate of nutrients to plant roots or to biological systems.

A number of studies have been made on the determination of nature and relative stability of the products formed by reaction of metals with different soil organic matters[2-6]. The object of this paper is to evaluate stability constant values of hymatomelanic acid (alcohol soluble humic acid fraction) metal complexes at different pH ion exchange technique.

Theory : Based on Martell and Calvin's[7] idea on equilibrium for chelation reaction the formation constant (K) may be written as

$$\log \left(\frac{\lambda_0}{\lambda}-1\right) = \log K + n \log (Ke) \qquad \ldots \ (1)$$

where, $\lambda_0 =$ distribution constant in absence of chelating agent and λ is the distribution constant in presence of chelating agent, n is the number of moles of complexing agent that combine with one mole of metal and Ke is the concentration of complexing agent. λ_0 and λ can be obtained from the relation

$$\lambda_0 = \frac{\alpha_0 V}{(100-\alpha_0)g} \qquad \ldots \ (2)$$

where $\alpha_0 =$ % of total metal used which is bound to exchanger.

$(100-\alpha_0) =$ % of total metal used which remained in solution.

$V =$ Volume of solution.

$g =$ Weight of cation exchanger.

For measurement of λ_0 and λ, solutions were maintained at constant ionic strength, temperature, pH, volume and weight of absorbent. The exchanger was previously saturated with NaCl solution.

$\log K$ and n may be obtained directly from, the intercept and slope of the plot of

$$\log \left(\frac{\lambda_0}{\lambda}-1\right) \text{ vs } \log (Ke).$$

In the present study, however, $\log K$ has been calculated from the following statistical equation—

$$\log K = \frac{\Sigma X^2 \, \Sigma Y - \Sigma X \, \Sigma X Y}{b \, \Sigma X^2 - (\Sigma X)^2}$$

where $X = \log (Ke)$

$Y = \log \left(\frac{\lambda_0}{\lambda}-1\right)$

$b =$ number of observations.

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Hymatomelanic acid (Hy.A.) was extracted, fractionated and purified from Chinsura soil, West Bengal (0–15 cm depth) by the standard procedure[8][9]. Complex forming capabilities of this was shown earlier[13].

0 to 2·5 ml solutions of hymatomelanic acid were taken in 25 ml volumetric-flasks in which 5 ml of (N) NaCl solutions and 5 ml of different solutions of Fe^{3+}, Al^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} salts were added. The solutions were diluted, pH of these solutions were adjusted to 4·0 and the volumes were made upto the mark. In a separate set, pH of different solutions were adjusted to 5·5. Known weights of Na-saturated Amberlite IR-120 resin were taken in 100 ml ground glass stoppered Erlenmeyer flasks. Solutions from the volumetric flasks were transferred to these flasks and the contents shaken for 6 hr and

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allowed to equilibrate for 24 hr. Solutions from flasks were transferred to 50 ml volumetric flasks quantitatively and volumes made to the mark. 10 ml of these solutions were titrated with E.D.T.A. solution in presence of solochrome black indicator after decomposing the organic matters with H_2O_2 in alkaline medium. The titrations were carried out at pH 10 using NH_4Cl and NH_4OH buffer. Since there was no appreciable change in pH, like the previous workers[2-6], the final pH of the equilibrated solutions were not noted.

comparison of stability constants amongst various fractions of humic acids and also to understand the fate of a particular metal ion in soils, this method has been used in the present study. For calculation of log K values least-square-method has been used
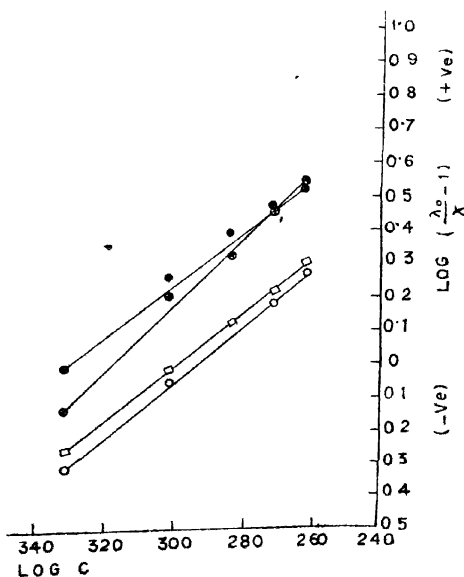

Fig 1

$$pH = 4.0 \left\{ \begin{array}{lll} \text{Fe—Hy.A Complex} & \bigcirc \\ \text{Al} & ,, & ,, & \square \end{array} \right.$$

$$pH \quad 5.5 \left\{ \begin{array}{lll} \text{Fe—Hy.A Complex} & \otimes \\ \text{Al} & ,, & ,, & \bullet \end{array} \right.$$

Fig. 2

$$pH \quad 4.0 \left\{ \begin{array}{ll} \square & \text{Cu—Hy.A.} \\ \triangle & \text{Zn—} \quad ,, \\ \bullet & \text{Ni—} \quad ,, \end{array} \right.$$

$$pH = 5.5 \left\{ \begin{array}{ll} \bullet & \text{Cu} \quad ,, \\ \bigcirc & \text{Zn—} \quad ,, \\ \ominus & \text{Ni—} \quad ,, \end{array} \right.$$
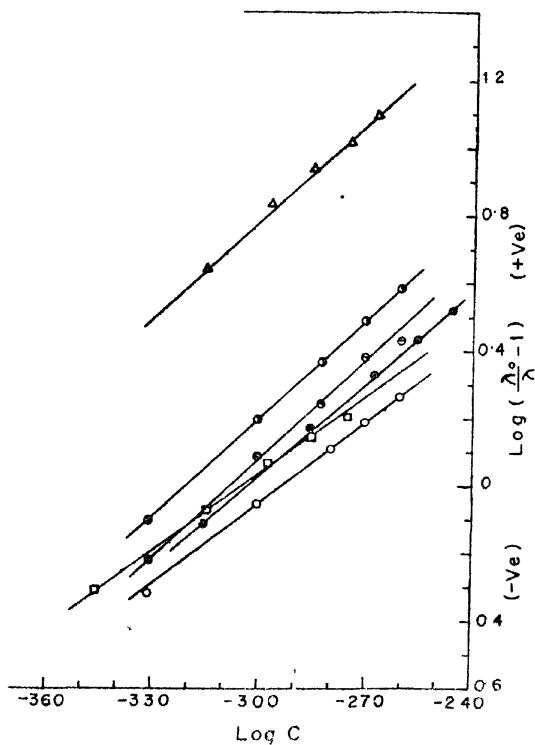
Results and Discussion

The average molecular weight of electrodialysed Hy.A. as determined by electrometric method[8] is found to be 1020. Results are given in Tables 1 and 2. As variation in ionic strength affects the stability of organic matter metal combinations considerably, ionic strength in all the cases are kept constant to 0.2. The ionic exchange method as mentioned by earlier workers[2-6'12] is not free from criticism, on the ground that there is possibility of more than one reactions due to presence of acidic carboxyl, phenolic hydroxyl and amino groups, besides formation of polynuclear complexes with metals. However, the method has been employed by many[4-6] to get log K values of different fractions of soil organic matter metal combinations. For

The log K value for the Fe^{3+} hymatomelanic acid complex changes from 3.97 at pH 4.0 to 4.93 at pH 5.5 indicating lower stability of the complex in acidic solution. The values for the Al-complex, however, remain practically unaltered with change in pH (i.e., from 3.81 at pH 4.0 to 3.88 at pH 5.5) indicating that the stabilities of such complexes are least affected due to pH change. Stability constant values for Fe^{3+} and Al^{3+} complexes with humic acid as determined by this method[11] are of the same order as reported by other workers[8] but no published data are available to compare the values for allied complexes with hymatomelanic acid.

The log K value for Cu-Hy.A. complex changes from 3.43 at pH 4.0 to 5.86 at pH 5.5. The same for Zn-Hy.A. is 3.59 at pH 4.0 and 4.82 at pH 5.5 and for Ni-Hy.A. complex the value changes from

TABLE 1. pH 4.0

Fe-HyA Complex

Wt. of Resin = 0 1 g.   Total Volume = 50 ml   Temp. = 30°

Concentration of HyA $0 \times 10^{-4} M$	Log C	α_0	λ_0	λ	$\log \left(\frac{\lambda_0}{\lambda} - 1\right)$	X	$\log K$
4.8510	−3.3142	75.25	1520.3				
		87.30		1029.0	−0.3215		
9.7020	−3.0131	61.85		810.8	−0.0580		
14.5530	−2.8372	57.20		668.3	0.1402	0.83	3.97
19.4040	−2.7122	54.70		603.9	0.1821		
24.2550	−2.6151	51.45		530.1	0.2711		

Al-HyA Complex

Wt of Resin = 0.1 g.   Total Volume = 50 ml.   Temp. = 30°

Concentration of HyA $0 \times 10^{-4} M$	Log C	α_0	λ_0	λ	$\log \left(\frac{\lambda_0}{\lambda} - 1\right)$	X	$\log K$
		77.84	1756.0				
4.8510	−3.3142	69.35		1132.0	−0.2588		
9.7020	−3.0131	64.35		893.5	−0.0155		
14.5530	−2.8372	60.08		752.6	0.1249	0 80	3.81
19.4040	−2.7122	56.88		659.5	0.2209		
24.2550	−2.6151	53.48		574.6	0.3131		

TABLE 2. pH 5.5

Fe-HyA Complex

Wt. of Resin = 0 1 g.   Total Volume = 50 ml.   Temp. = 30°

Concentration of HyA $0 \times 10^{-4} M$	log C	α_0	λ_0	λ	$\log \left(\frac{\lambda_0}{\lambda} - 1\right)$	X	$\log K$
		83.30	2494.0				
4.8510	−3.3142	74.35		1449.5	−0.1427		
9.7020	−3.0131	65.84		963.8	0.2009		
14.5530	−2.8372	61.55		800.4	0.3255	0 98	4.93
19.4040	−2.7122	56.30		644.2	0.4581		
24.2550	−2.6151	52.45		551.6	0.5468		

Al-HyA Complex

Wt. of Resin = 0 1 g.   Total Volume = 50 ml.   Temp. = 30°

Concentration of HyA $0 \times 10^{-4} M$	log C	α_0	λ_0	λ	$\log \left(\frac{\lambda_0}{\lambda} - 1\right)$	X	$\log K$
		90.83	4952.0				
4.8510	−3.3142	83.48		2527.0	−0.0171		
9.7020	−3.0131	78.22		1796.0	0.2450		
14.5530	−2.8372	74.13		1433.0	0.3903	.078	3.88
19.4040	−2.7122	71.78		1272.0	0.4614		
24.2550	−2.6151	69.64		1117.0	0.5208		

TABLE 3. pH 4.0

Zn-HyA Complex

Wt. of Resin = 0.03 g. Total Volume = 10 ml. Temp. = 30°

Concentration of HyA $0 \times 10^{-4} M$	log C	α_0	λ_0	λ	$\log \left(\dfrac{\lambda_0}{\lambda}-1\right)$	X	$\log K$
		97.93	1576.9				
6.862	−3.1636	89.73		2912.0	0.6447		
10.290	−2.9876	85.66		1992.0	0.8400		
13.720	−2.8628	82.95		1622.0	0.9406	1.0	3.59
17.150	−2.7657	80.40		1367.0	1.0224		
20.580	−2.6864	77.97		1179.0	1.0923		

Ni–HyA Complex

Wt. of Resin = 0.03 g. Total Volume = 10 ml. Temp. = 30°

		85.75	2005.0				
6.862	−3.1636	77.05		1135.0	−0.1155		
13.730	−2.8626	70.55		798.5	0.1793		
20.595	−2.6864	65.60		635.6	0.3334	0.92	2.75
27.460	−2.5613	61.78		538.8	0.4349		
34.320	−2.4644	58.42		468.3	0.5162		

Cu-HyA Complex

Wt. of Resin = 0.1 g. Total Volume = 50 ml. Temp. = 30°

		75.15	1496.0				
3.432	−3.4644	75.15		1008.0	−0.3150		
6.865	−3.1636	70.99		815.4	−0.0785		
10.297	−2.9872	67.22		683.6	0.0737	0.78	3.43
13.730	−2.8626	63.97		591.8	0.1440		
17.160	−2.7655	61.17		576.6	0.2028		

TABLE 4. pH 5.5

Zn-HyA Complex

Wt. of Resin = 0.1 g Total Voulme = 45 ml. Temp. = 30°

Concentration at HyA $0 \times 10^{-4} M$	log C	α_0	λ_0	λ	$\log \left(\dfrac{\lambda_0}{\lambda}-1\right)$	X	$\log K$
		78.12	1606.0			0.81	4.82
4.8515	−3.4142	70.87		1097.0	−0.3314		
9.7030	−3.0131	65.42		851.4	−0.0531		
14.5545	−2.8372	61.37		714.3	0.1004		
19.4060	−2.7120	58.21		626.3	0.1945		
24.2500	−2.6151	55.71		566.1	0.2634		

Ni-HyA Complex

Wt. of Resin = 0.1 g. Total Volume = 45 ml. Temp. = 30°

		89.43	3807.0				
4.8515	−3.3142	83.95		2357.0	−0.2104		
9.7030	−3.0131	79.10		1703.0	0.0917		
14.5545	−2.8372	75.30		1372.0	0.2492	1.0	5.42
19.4060	−2.7120	72.10		1114.0	0.3824		
24.2800	−2.6151	69.60		1032.0	0.4294		

Cu-HyA Complex

Wt. of Resin = 0.1 g. Total Volume = 50 ml Temp. = 30°

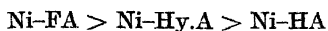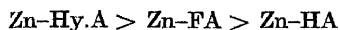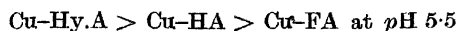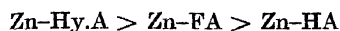|		86.17	2805.0				
4.8515	−3.3142	77.95		1592.0	−0.1152		
9.7030	−3.0131	70.12		1056.0	0.2191		
14.5545	−2.8372	64.86		830.6	0.3753	1.0	5.86
19.4060	−2.7120	60.23		681.6	0.4931		
24.2600	−2.6151	56.41		582.4	0.5810		

2·75 at pH 4·0 to 5·42 at pH 5·5. The results of this investigation indicate the following order of stabilities of complexes formed between Hy.A. and a number of bivalent and trivalent metal ions.

$Ni^{2+} < Cu^{2+} < Zn^{2+} < Al^{3+} < Fe^{3+}$ and $Al^{3+} < Zn^{2+} < Fe^{3+} < Ni^{2+} < Cu^{2+}$ at pH 4·0 and 5·5 respectively. In no case Irving Williams series[10] for stability constant of metal ligand combination are followed.

Comparison of the present results on hymatomelanic acid metal complexes with those on humic acid and fulvic acid metal complxes[8,11] reveals the following sequences in stabilities (for Fe^{3+} and Al^3 ions).

$$Fe-FA > Fe-HyA > Fe-HA.$$
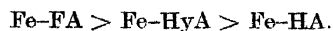
$Al-FA > Al-Hy.A > Al-HA$ at these pHs, whereas in case of bivalent metal complexes, the sequences followed are :

$$Zn-Hy.A > Zn-FA > Zn-HA$$

$$Ni-Hy.A > Ni-HA > Ni-FA$$

$$Cu-Hy.A > Cu-HA > Cu-FA \text{ at } pH\ 5\cdot5$$

$$Zn-Hy.A > Zn-FA > Zn-HA$$

$$Ni-FA > Ni-Hy.A > Ni-HA$$

$$Cu-FA > Cu-Hy.A > Cu-HA \text{ at } pH\ 4\cdot0$$

Moreover, it is evident from these results that both the bivalent and trivalent metal complexes of HyA have lower stability in acidic solution comparable to those of humic and fulvic acids at similar pH.

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