

Potentiometric Investigation on Heavy Metal-Humic Acid Interaction : Determination of Formation Constants of Cu(II), Pb(II), Zn(II), Co(II), Ni(II) and Cd(II) Humic Acid Complexes at pH 4.0

B. CHAKRAVARTI, S. K. SAHA and S. K. CHAKRAVARTI

Department of Chemistry, University of North Bengal, Darjeeling-734 430

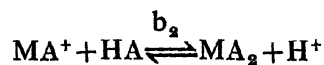
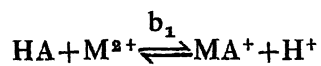
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Heavy metal-humic acid interactions at different pH and ionic strength have been studied by modified potentiometric technique. Logarithms of overall formation constants for different heavy metal complexes at pH 4.0 ranged from 5.98 to 8.80 in 0.05 M KNO₃ and 5.10 to 8.14 in 0.1 M KNO₃ and follow the order Cu(II) > Pb(II) > Ni(II) > Cd(II) > Co(II) > Zn(II). At high pH, extra protons are released either through dissociation of hydration water or from very weak acidic functions not titrable within the apparent neutralisation of humic acid. An attempt has been made to interpret the results.

THE importance of the study on the interactions of heavy metal cations with humic acid has been discussed^{1,2,6,7}. Determination of the formation constants forms an essential part of such a quantitative study⁸. In addition, stepwise formation constants of the bivalent metal complexes of such naturally occurring polyelectrolytes are of considerable interest, specially in view of the inadequate knowledge of the existence of actual species of metal complexes in soil and aquatic environment^{9,10}. Potentiometric measurement has been claimed to be a convenient way to study such metal-humic acid interaction^{5,9,11}. In the present communication the results of the investigation on the interaction of heavy metals e.g., Cu(II), Pb(II), Zn(II), Cd(II), Co(II) and Ni(II) with humic acid isolated from soil and peat have been reported.

Theoretical considerations :

Considering the competition of H⁺ with the metal ions for the acidic sites of humic acids, the successive equilibria of bivalent metals and the acidic sites of humic acids may be depicted as



$$\text{where } b_1 = \frac{[MA^+][H^+]}{[HA][M^{2+}]}$$

$$\text{and } b_2 = \frac{[MA_2][H^+]}{[MA^+][HA]}$$

The formation function \bar{n} for the polymeric acid may be defined as the average number of "complexing sites" bound per metal ion

$$\text{Thus, } \bar{n} = \frac{A_t - (HA) - (A^-)}{(M_t)} = \frac{[MA^+] + 2[MA_2]}{[M^{2+}] + [MA^+] + [MA_2]}$$

where M_t and A_t are the total concentration of metal and the complexing sites, respectively. Introducing the respective formation constant b₁ and b₂, \bar{n} takes

$$\text{the form } \bar{n} = \frac{b_1(HA/H^+) + 2B_2(HA/H^+)^2}{1 + b_1(HA/H^+) + B_2(HA/H^+)^2}$$

where B₂ (= b₁.b₂) is the overall formation constant. On rearrangement it gives,

$$\frac{\bar{n}}{(1-\bar{n})(HA/H^+)} = \frac{(2-\bar{n})(HA/H^+)}{(1-\bar{n})} B_2 + b_1$$

Graphical solution of the above equation gives the value of B₂, b₁ and b₂ provided, of course, \bar{n} and (HA/H⁺) are determined experimentally.

In determining \bar{n} , the concentration of complexing sites i.e. the quantity [MA⁺] + 2[MA₂] must be known in equilibrium condition of metals and the substrate. Amount of liberated H⁺ is an indirect measure of this quantity. In other words, [MA⁺] + 2[MA₂] may be measured by the amount of base required for the neutralisation of the released H⁺. Also, in such equilibrium condition total undissociated free complexing sites (A_t) is equal to the quantity A_T - (KOH) - H⁺ + OH⁻, where A_T is the overall sites in humic acid. Quantity (KOH) is the amount of base required to raise the pH of the solution to appropriate experimental value from the initial pH of the humic acid.

The value of B₂, as obtained from the above, may then be transformed into more commonly expressed constant K₂ where, $K_2 = \frac{(MA_2)}{(A^-)^2(M^{2+})}$, and the two constants are related to each other by the relation,

$K_2 = b_1/k_1$ where b₁ and k₁ are the corresponding successive formation constants.

Experimental

Humic acid was extracted from the surface forest soil of Darjeeling by the standard alkali extraction procedure using 0.3 N NaOH at room temp. Peat humic acid was from the sample supplied by Fluka A.G. Purification and fractionation were performed by the procedure reported earlier⁷. The analytical data of the humic acids are given in Table 1.

pH measurements were made in nitrogen atmosphere with Radelkis pH meter, (type OP-205) having an accuracy of 0.005 pH unit coupled with a Radelkis combined glass electrode (OP 8071-1/A) at 27.2°. The metals were taken as their nitrate salts because of their high solubility and almost null power of the nitrates to coordinate to metals. Ionic strength was adjusted with standard KNO₃ solution.

Results and Discussion

Tables 2 and 3 show the drop in pH when different amounts of metal ions are added to the humic acids whose pH were initially raised by dilute

alkali to 4.0, 5.0, and 6.0 in presence of 0.05 and 0.1 N KNO₃. It is seen from the Tables that the pH of the solution shows a gradual decrease with the increase in the concentration of a bivalent heavy metal ion. However, at the higher concentration of the metal ions, the pH attains almost a steady value. This decrease in pH is due to the release of protons by the metal ions from the acidic functional groups of the humic substances. It appears, therefore, that the interaction of these metals [e.g. Pb(II), Cu(II), Ni(II), Co(II), Zn(II) and Cd(II)] with humic acids involves the acidic sites of the latter. Tables 2 and 3 also show that the depression of pH (Δ pH) following the addition of Cu(II) and Pb(II) are considerably higher than the same with Co(II), Ni(II), Zn(II) or Cd(II). This may be related to much stronger affinity of Cu(II) and Pb(II) for the organic matter ligand than the other four metals of the series.

Consumption of base by the acid released :

Figs. 1 and 2 show the amount of alkali required to raise the pH of the system to the initial value i.e.

TABLE-1

Sample	Abbreviation	Analysis %				Total acidity (meq/100 g) in presence of KNO ₃			K _a in presence of KNO ₃	
		C	H	N	Ash	0.05 M	0.1 M	1.0 M	0.05 N	0.01 M
Soil humic acid	SHA	48.74	3.61	3.97	2.30	408	418	446	5.13	4.88
Peat humic acid	PHA	56.78	4.00	1.03	1.1	417	426	461	5.21	4.94

TABLE 2—DROP IN THE pH VALUES ON THE ADDITION OF METAL IONS TO THE HUMIC ACID (SHA) IN PRESENCE OF 0.05 N AND 0.1 N KNO₃

Total titrable acids in presence of 0.05 N KNO₃ = 2.78 × 10⁻³ M ; and the same in presence of 0.1 M KNO₃ = 2.85 × 10⁻³ M

Metal	M _t × 10 ⁴ moles/lit	Decrease in pH (Δ pH) following the addition of metal ions					
		at pH 4.0		at pH 5.0		at pH 6.0	
		i=0.05	i=0.10	i=0.05	i=0.10	i=0.50	i=0.10
Cu(II)	3.96	0.46	0.40	0.82	0.75	—	—
	7.81	0.58	0.51	1.00	0.92	—	—
	11.56	0.63	0.56	1.04	1.00	—	—
	15.24	0.64	0.60	1.07	1.03	—	—
Pb(II)	3.96	0.44	0.38	0.62	0.59	—	—
	7.81	0.57	0.52	0.92	0.83	—	—
	11.56	0.65	0.61	0.99	0.93	—	—
	15.24	0.66	0.64	1.03	0.78	—	—
Ni(II)	4.84	0.22	0.16	0.48	0.42	0.63	0.62
	9.56	0.26	0.21	0.54	0.49	0.70	0.62
	14.19	0.28	0.23	0.57	0.53	0.75	0.75
	18.73	0.30	0.25	0.59	0.55	0.78	0.78
Cd(II)	5.25	0.24	0.15	0.46	0.89	0.70	0.66
	10.38	0.29	0.19	0.53	0.47	0.83	0.73
	15.41	0.32	0.22	0.56	0.50	0.89	0.83
	20.33	0.34	0.25	0.58	0.52	0.92	0.85
Co(II)	5.00	0.19	0.16	0.42	0.36	0.58	0.56
	9.88	0.24	0.22	0.48	0.45	0.65	0.64
	14.66	0.27	0.25	0.52	0.48	0.70	0.68
	19.35	0.29	0.27	0.55	0.50	0.72	0.70
Zn(II)	5.60	0.20	0.16	0.53	0.46	0.81	0.74
	11.07	0.23	0.22	0.60	0.54	0.88	0.83
	16.42	0.26	0.25	0.67	0.58	0.92	0.86
	21.67	0.28	0.27	0.66	0.60	0.94	0.83

TABLE 3—DROP IN pH VALUE ON THE ADDITION OF METAL IONS TO THE HUMIC ACID (PHA) IN PRESENCE OF 0.05 N AND 0.1 N KNO₃

 Total titrable acids in presence of 0.05 N KNO₃ = 2.39×10^{-3} N ; and the same in presence of 0.1 N KNO₃ = 2.44×10^{-3} N

Metal	M _i × 10 ⁴ moles/lit	Decrease in pH (ΔpH) following the addition of metal ions					
		at pH 4.0		at pH 5.0		at pH 6.0	
		i=0.05	i=0.1	i=0.05	i=0.1	i=0.05	i=0.1
Cu(II)	3.96	0.53	0.42	0.84	0.75	—	—
	7.81	0.64	0.51	0.98	0.90	—	—
	11.56	0.69	0.55	1.00	0.95	—	—
	15.24	0.71	0.58	1.02	0.98	—	—
Pb(II)	3.96	0.48	0.38	0.74	0.69	—	—
	7.81	0.61	0.49	0.95	0.91	—	—
	11.56	0.66	0.53	0.98	0.99	—	—
	15.24	0.68	0.56	1.00	1.00	—	—
Ni(II)	4.48	0.21	0.18	0.39	0.32	0.57	0.54
	9.56	0.25	0.27	0.46	0.38	0.62	0.60
	14.19	0.27	0.25	0.49	0.41	0.66	0.64
	18.73	0.28	0.23	0.51	0.43	0.68	0.66
Cd(II)	5.25	0.23	0.16	0.45	0.39	0.74	0.70
	10.38	0.27	0.20	0.51	0.47	0.86	0.82
	15.41	0.29	0.23	0.54	0.51	0.90	0.86
	20.33	0.31	0.24	0.56	0.54	0.92	0.88
Co(II)	5.00	0.21	0.15	0.37	0.30	0.59	0.50
	9.88	0.24	0.20	0.42	0.37	0.60	0.59
	14.16	0.27	0.23	0.44	0.40	0.63	0.61
	19.35	0.29	0.25	0.46	0.42	0.65	0.63
Zn(II)	5.60	0.25	0.20	0.46	0.38	0.68	0.62
	11.07	0.29	0.24	0.52	0.45	0.80	0.73
	16.42	0.31	0.26	0.54	0.49	0.82	0.76
	21.67	0.33	0.28	0.56	0.51	0.84	0.78

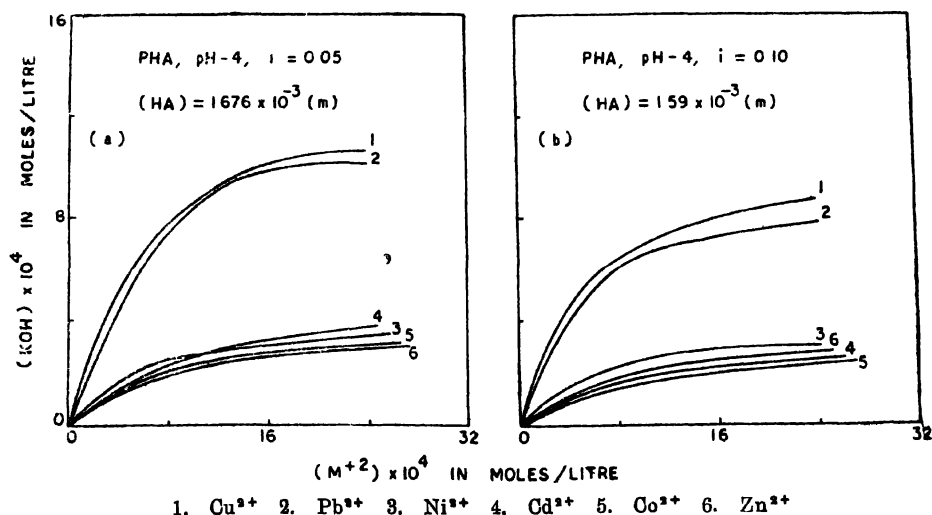


Fig. 1. Amount of alkali required to raise the pH to 4 after addition of metal vs amount of metal ions added (HA) is the content of undissociated acidic groups at the pH mentioned.

4.0 (the pH at which metals are added) plotted against the corresponding amount of added metals in presence of 0.05 and 0.1 N KNO₃. In general, it is observed that with the initial sharp rise in the amount of base consumed on increasing the concentration of the metal ions followed by gradual diminution in the extent of such rise, the curves appear to resemble a Langmuir type isotherm. Thus, in consonance with the earlier observations we may reasonably assume that the metal ions displace H⁺ from the acidic groups of the humic acid to form complexes and the complexing tendency diminishes

as the stronger sites available for metal binding get relatively few with the increasing addition of metal ions.

For Cu(II) and Pb(II), it is also found that at pH ≥ 5.0 the amount of alkali consumed by the released acid exceeds the total quantity of undissociated acids. This indicates the existence of some apparently unaccountable H⁺ in the system. Similar observation has also been made by other workers^{8,10}. This observation may conveniently be related to the following factors :

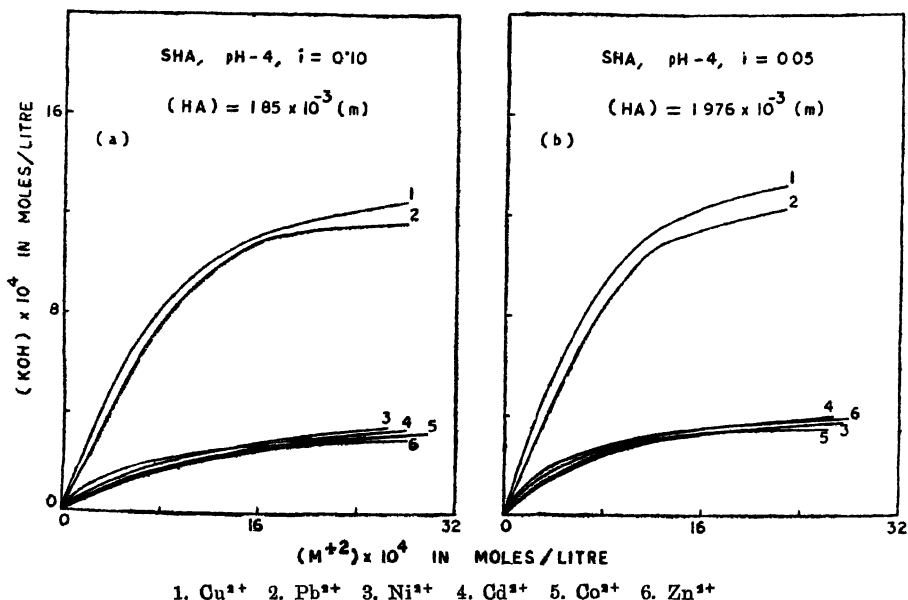


Fig. 2. Amount of alkali required to raise the pH to 4 after addition of metal vs amount of metal ions added (HA) is the content of undissociated acidic groups at the pH mentioned.

(i) The existence of very weak acidic sites, not titratable at the apparent neutralisation point (pH ~7.0) of humic acid samples. These very weak acidic groups may be available for strong complexing heavy metals such as Cu(II) and Pb(II) releasing an excess, apparently hidden, H⁺.

(ii) Possible ionisation of hydration water of the metals. At pH ≥ 5.0 heavy metals having high tendency to get hydrolysed may release extra protons to form negatively charged hydroxo metal complexes. This phenomenon occurs increasingly with the increase in pH of the solution.

Recent study¹¹ reveals that trivalent cations [Coen₃]³⁺ having very high tendency to get complexed with humic substances always release extra protons at high cation concentration although the possibility of hydrolysis of [Coen₃]³⁺ at experimental condition (pH upto 7.0) is unlikely. It is believed, therefore, that of the above two factors, the first one may occur. If not, or when does not at least, the second factor comes into play. On the other hand, at pH 5.0, the other four metals do not release extra protons even at sufficiently high concentration because neither have they such strong complexing capacities nor do they form hydroxo metal complexes releasing protons from hydration water. All the metals show similar behaviour at lower pH (4.0) in this respect.

Formation constants of the complex :

The constant B_a and K_a have been calculated using the method of least square. It is evident from Table 4 that at a particular ionic strength and pH, the formation constant values follow the order Cu(II) > Pb(II) > Ni(II) > Cd(II) > Co(II) > Zn(II). The order is in general agreement with the Irving-William series for chelate stability constants, suggest-

TABLE 4—FORMATION CONSTANTS FOR THE METAL COMPLEXES AT pH 4.0

Metal	log B _a		log K _a	
	i=0.05	i=0.10	i=0.05	i=0.1
SHA				
Cu(II)	-1.64	-1.81	8.62	7.95
Pb(II)	-1.74	-1.97	8.52	7.79
Ni(II)	-4.25	-4.51	6.01	5.24
Cd(II)	-4.23	-4.52	6.03	5.23
Co(II)	-4.27	-4.54	5.99	5.22
Zn(II)	-4.28	-4.54	5.98	5.21
PHA				
Cu(II)	-1.62	-1.74	8.80	8.14
Pb(II)	-1.70	-1.95	8.72	7.98
Ni(II)	-4.20	-4.50	6.22	5.38
Cd(II)	-4.21	-4.57	6.21	5.31
Co(II)	-4.35	-4.70	6.07	5.18
Zn(II)	-4.21	-4.71	6.21	5.17

ing that probably chelates are formed in the present systems. Many other workers² have also indicated the formation of chelates for humic and fulvic acids with different heavy metals.

The formation constant values for humic acids obtained in the present investigation are almost of the same order as obtained by Takamatsu *et al*¹², who made the use of a comparatively direct approach of potentiometry and ion-selective electrode together. Results (log B_a and log K_a) of the present study also agree with those of Stevenson⁹. Determination of formation constants at pH 5.0 and above has been avoided due to the possible participation of unaccountable H⁺ in the system from the dissociation of hydration water.

Fig. 3 enables one to get an idea of the variation of log B_a and log K_a with ionic strength. As the present study was performed only at two different

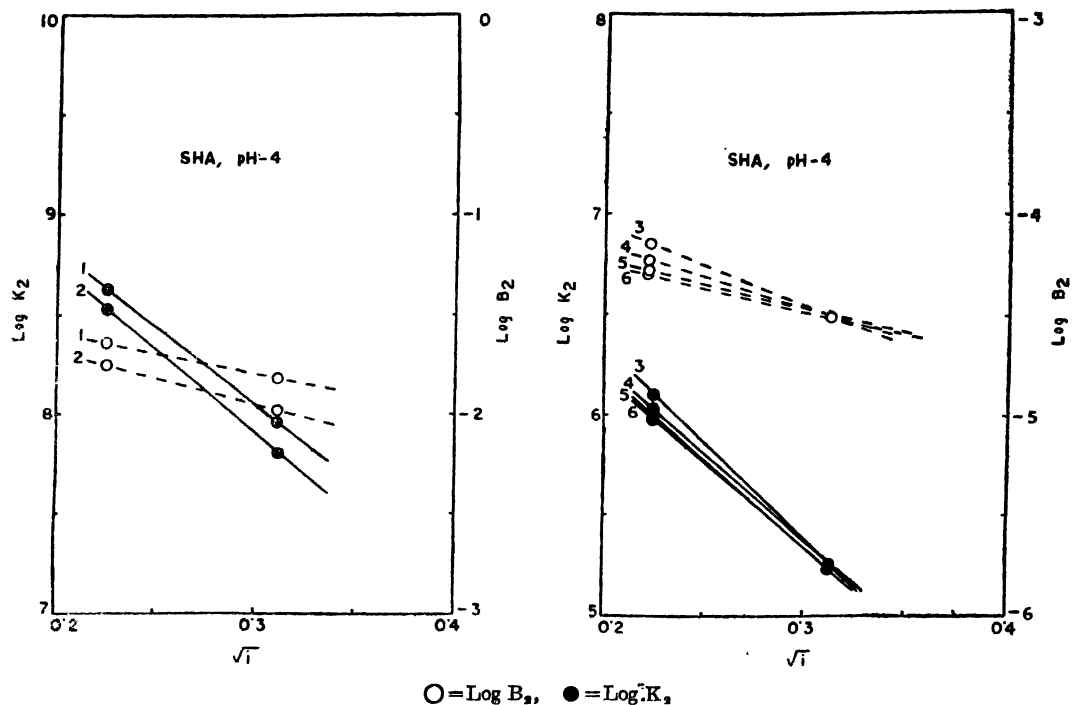


Fig. 3. Effect of ionic strength (i) on log B₂ and log K₂.
 1. Cu²⁺ 2. Pb²⁺ 3. Ni²⁺ 4. Cd²⁺ 5. Co²⁺ 6. Zn²⁺

ionic strengths, the straight line drawn in the figure may not represent the actual mode of the variation. However, it has been observed that with increasing ionic strength both B₂ and K₂ decreased; the decrease is more prominent for K₂. This is not unlikely because evaluation of K₂ from experimental data involves the dissociation constant K₂ of the organic acid which is also increased with decreasing concentration of ionic strength adjuster KNO₃.

References

1. J. L. MORTENSEN, *Soil Sci. Soc. Amer. Proc.*, 1963, 27, 179.
2. D. S. GANBLE, M. SCHNITZER and I. HOFFMAN, *Canad. J. Chem.*, 1970, 48, 3197.
3. H. VAN DIJK, *Geoderma*, 1971, 5, 53.
4. F. J. STEVENSON, S. A. KRASTANOV and M. S. ARDAKARI, *Geoderma*, 1973, 9, 129.
5. M. SCHNITZER and S. I. M. SKINNER, *Soil Sci.*, 1965a, 99, 278.
6. M. SCHNITZER and S. I. M. SKINNER, *Soil Sci.*, 1966a, 102, 361.
7. S. K. SAHA, Ph.D. Thesis, N. B. Univ., Darjeeling, 1979.
8. S. S. KHANNA and F. J. STEVENSON, *Soil Sci.*, 1962, 93, 298.
9. F. J. STEVENSON, *Soil Sci.*, 1977, 123, 10.
10. F. J. STEVENSON, "Environmental Bio-Geochemistry", Ann Arbor Publishers, Michigan, 1976, Vol. 2, pp. 519-540.
11. U. K. PAUL, Ph.D. Thesis, N. B. Univ., Darjeeling, 1981.
12. T. TAKAMATSU and T. YOSHIDA, *Soil Sci.*, 1978, 125, 377.