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## METAL-ORGANIC INTERACTIONS IN NATURAL AQUATIC SYSTEMS

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This paper presents a mechanistic approach to interpret titration curves of cupric ion complexation by physically and chemically heterogeneous organic moieties (i.e. M-humic acids) extracted from the sediments of River Mahaweli, Sri Lanka. The affinity spectrum function, N(k), of the M-humic- $Cu^{++}$  system differentiated the total number of sites into three types. The discrete ligand based calculations fit the Cu-humic binding data reasonably well.

KEYWORDS: Humic acid, copper, complexation, Sri Lanka.

#### INTRODUCTION

The importance of organic matter in complexing trace elements in aquatic environment is now being increasingly recognized. Organic compounds constitute only two to three percent of the river sediment and their concentrations rarely exceeds a maximum of 20 mg/L. They are known to play an important role in various geochemical processes such as the solubility, mobility, concentration and accumulation of metals.<sup>1</sup> In the organic matter associated with soils, sedimentary deposits, sediments and natural waters, humic compounds comprise the major part. Rashid and Leonard.<sup>2</sup> clearly indicate the role of humic acids in retarding the precipitation processes of metals as sulphides, carbonates or hydroxides.It is noted that when metals are complexed with humic acid, the solutions are thought to behave as though other ions are present in the reaction media and the ion becomes unavailable to sulphide, hydroxides, carbonates etc., to form insoluble salts, thereby keeping the cations in solution.<sup>3</sup>

Fulvic acids play an extremely important role in transport of trace elements in sediment water-interface due to their low molecular masses, larger number of functional groups and greater solubility than that of the humic fraction. On the other hand, the humic acid fraction is more important in trace element transport and retention by sediments.<sup>4</sup> Hence, it is important to investigate the interaction of metals with humic and fulvic acids found in various environmental compartments. The objective of this work is to quantify the copper-humic acid complexation interactions in the sediment collected from the Mahaweli River, Sri Lanka.

#### MATERIALS AND METHODS

#### 1. Materials

The bottom sediments were collected from the Mahaweli River where the Mid-canal confluences with the main river before it intercepts the city of Kandy. A detailed account

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of the geological and hydrological features of this location is given in Dissanayake and Weerasooriya.<sup>5</sup> The sediments collected were air dried for 48 h. A sample of 200g, was used to extract humid acids following the technique adopted by The International Humic Substances Society Procedures (IHSS).<sup>6</sup> A stock solution of M-humic acids was prepared by dissolving 5g of the freeze dried material in one liter of deionized water. Only analytical grade chemicals from MERCS were used in this study.

#### 2. Complexometric Titrations

M-humic acid (0.10 ml) plus 10 ml of 0.1M NaNO<sub>3</sub> (0.01M ionic strength) was placed in a 100 ml beaker at pH 5.00 using 0.005M NaOH as a titrant. While passing liquid nitrogen through the solution, proper mixing was achieved by bubbling the gas and stirring with a Teflon coated magnetic bar. Free Cu<sup>++</sup> was added and the sample was kept for a certain period until equilibration and the unbound Cu<sup>++</sup> measured. For each Cu<sup>++</sup> addition, the total copper concentration [Cu]<sub>total</sub> was calculated. A correction was made for the volume changes due to the Cu<sup>++</sup> and NaOH additions. The range of Cu<sup>++</sup> additions was from  $1.0 \times 10^{-6}$  M to  $7.00 \times 10^{-4}$  M.

#### 3. Analytical Computational Methods

The pH of the titration mixture was monitored by an automated titration system. The activity of the free copper ion was determined potentiometrically, using ion analyzer (Orion model EA920), Cu selective ion electrode (Orion model 94–29) and a double junction reference electrode (Orion model 90–20). The numerical calculations were performed computationally using standard mathematical subprograms.<sup>7</sup>

#### **RESULTS AND DISCUSSION**

Since the chemical structure and composition, of humic acid is not known, the stoichiometry of the metal coordinating groups is also unknown. As a result, a complexing site can only be defined operationally as consisting of all functional groups involved in the complexation reaction under the condition existing at the titration point of interest.<sup>8</sup> This definition of "site" does not make any reference to the chemical nature of the coordinating group, and the corresponding stoichiometry therefore becomes irrelevant. All binding site reactions are then treated on a 1:1 basis with no implication being made concerning the actual nature of the coordinating group. Humic acids derived from the bottom sediment of the Mahaweli River was titrated with cupric ion at pH 5.00. As shown in Figure 1, the experimental data are plotted as complexed Cu<sup>++</sup> vs-log Cu<sub>total</sub> for which complexed Cu<sup>++</sup> was calculated from

$$[CuL]_{complex} = [Cu^{++}]_{total} - [Cu^{++}]_{free} - [Cu^{++}]_{ppt}$$
(1)

Where [CuL] is the concentration of all bound copper species,  $[Cu^{++}]$  total is the total concentration of  $[Cu^{++}]$  added to the system,  $[Cu^{++}]_{free}$  is unbound metal concentration and  $[Cu^{++}]_{ppt}$  is the precipitated concentration of  $Cu^{++}$ . (Solubility product determinations confirmed that the precipitation of  $Cu^{++}$  as  $Cu(OH)_2$  is negligible at pH=5.00. It is reasonable to assume that the term  $[Cu^{++}]_{ppt}$  as zero).

The total site concentration in M-humic acids,  $L_{Total}$ , was estimated as 12  $\mu$ M from Figure 1 (e.g. AB region). Since it was difficult to saturate all available sites in human acids with a metal ion of interest, an exact value for  $L_{Total}$  cannot be measured



FIGURE 1 Variation of complexed Cu concentration with total Cu for experimental data.

unambiguously. However  $L_{Total}$  is an important variable in the calculation of trace element speciation in humic acid mediated aquatic systems.

Recently, Dzomback *et al.*<sup>9</sup> argued against the normalization of binding data to  $L_{Total}$  (i.e. the use of formation functions). Furthermore, humic acids are considered as cross linked polymeric molecule-bearing ligands that in total exhibit a wide range of affinities for protons and metal ions.<sup>10</sup>

Humic acid shows a large preference for Cu<sup>++</sup>. This may be due to the Jahn Teller distortion of cupric aquoligand, where the bond length can stretch along the z axis, and can remove COO<sup>-</sup> groups.<sup>11</sup> The ligand field stabilization energy is less significant in this case due to the comparable energy of H<sub>2</sub>O and COO<sup>-</sup> ligands.

The binding of Cu(II) to a particular site in M-humic acid at a given pH can be given by

$$K_i^{Cu} = [CuL_i] / \{ [Cu^{++}] \}_{\text{free}} \{ [L_i^F] \}$$
(2)

From equations [1] and [2] the titration of a mixture of ligands with Cu(II) can be expressed at each point as

$$\overline{v} = \Sigma\{(n_i K_i [Cu^{++}])/(1 + K_i [Cu^{++}])\}$$
(3)

where v is the formation function, and  $n_i$  is fraction of the ligands in ith class ( $n_i = L_i/L_T$ ). In this approach, adjacent site interaction (if any) effect was neglected. The Cu<sup>++</sup> binding onto M-Humic acids were calculated for its formation function  $\bar{v}$  using equation [3]. Figure 2 shows the variation of formation function with pCu at a pH value of 5.00.

Both discrete and continuous ligand modelling techniques have been used to calculate the experimentally derived metal-humic acid data.<sup>12</sup> In discrete ligand models, only a few sites have been selected as binding sites for metals. Since humic acid can be considered



FIGURE 2 The variation of formation function with  $pCu^{2+}_{free}$  for experimental data (solid line depicts calculated values).

as an array of binding sites of varying affinities, the continuous ligand modelling approach was suggested recently. However, none of these methods provide a direct insight into the chemical nature of the metal-humic bonds. In this approach we have used both modelling techniques to fit the experimental data. The number of dominant binding sites in M-humic acids for Cu<sup>++</sup> binding were calculated using the affinity spectrum modelling method.<sup>13</sup> Here it has been assumed that the log K varies continuously and that the ligand frequency distribution can be integrated over this variable. The probability that any given binding site has a binding constant log K between a and b is

$$P(a,b) = \int_{b}^{a} N(k) d(\log K)$$
(4)

and the formation function is defined from equations [3] and [4] as

$$v = \int_{0}^{\infty} \left\{ \left( N(k)[M]K \right) / \left( 1 + [M]K \right) d(\log K) \right\}$$
(5)

where N(k) is the distribution function of logK. By making some approximations<sup>14</sup> it is also possible to solve eq. (5) analytically for f(logK). In the present study, we have smoothed the Cu<sup>++</sup>—humate titration data given in Figure 2 using the cubic spline technique to obtain a solution for the integral equation. As shown in Figure 3, the affinity spectrum, N(k), thus obtained for Cu-humate binding data exhibits three very clearly defined peaks at log K 8.98, 6.38 and 3.75 which corresponds to the occurrence of three types of binding sites (three operationally defined ligands) in M-humic acids. The Cu-humate titration data was modelled using the information and the resulting calculations are shown in Figure 1.

All calculations were made using discrete ligand modelling method assuming three dominant binding sites as identified with numerically determined N(k) function for M-humic acids. As illustrated in Figure 2, the model calculation predicts well up to pCu  $\sim$  5.00. It therefore underestimates the experimentally defined values. This may be due to the appearance of a less dominant binding site in M-humic acids at low Cu<sup>++</sup> conditions.

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