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Author(s)	MATSUNAGA, Katsuhiko; NEGISHI, Masami; FUKASE, Sigeru
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## Stability Constant of Copper with Fulvic Acid

Katsuhiko MATSUNAGA\*, Masami NEGISHI\* and Sigeru FUKASE\*

### Abstract

Fulvic acid, which is extracted from bottom sediments in both the Kunebetsu River and Shukunohe River, was titrated by the addition of copper ion and the uncomplexed copper ion was measured with a copper ion-selective electrode. From equation (4), the stability constant of copper with fulvic acid was calculated and then the value of  $\log \beta=5.3$  was obtained.

### Introduction

Though the chemical species of heavy metals which were utilized or taken up by phytoplankton are not clearly known, we found that a fulvic acid-Fe complex in Ohnuma Lake was utilized by phytoplankton<sup>1)</sup>. Thus, it is very important to study the chemical species of heavy metals in natural waters.

Zirino and Yamamoto<sup>2)</sup>, and Long and Angino<sup>3)</sup> estimated thermodynamically the chemical species of several metals by using several inorganic anions as ligand. However, natural waters contain not only the inorganic ligands but also organic ligands. Thus, it is insufficient to take into account only the inorganic anions as ligands. In recent, Mantoura et al.<sup>4)</sup> calculated the chemical species of heavy metal ions on the assumption of the presence of organic ligands such as humic material. However, the stability constant of copper with humic material which they used for the calculation was higher than already reported values.<sup>5,6)</sup>

The purpose of this paper is to measure the stability constant of copper with fulvic acid, which is the main humic materials in river.<sup>7,8)</sup> By measuring the stability constant, the chemical species of copper in rivers or lakes in a suburb of Hakodate would be thermodynamically calculated and then chemical species which are utilized by phytoplankton would be known.

### Experiment

#### Reagents

1 M NaClO<sub>4</sub>: 12.2 g of NaClO<sub>4</sub> was dissolved in 100 ml of distilled water. Cu<sup>2+</sup> standard solution (10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup>, 10<sup>-4</sup> M): 2.49 g of CuSO<sub>4</sub>·5H<sub>2</sub>O was dissolved in 100 ml of distilled water and 10<sup>-2</sup>, 10<sup>-3</sup>, and 10<sup>-4</sup> M standard solutions were prepared by diluting the 10<sup>-1</sup> M Cu<sup>2+</sup> solution.

All chemical reagents used were of analytical grade.

\* Laboratory of Marine Chemistry, Faculty of Fisheries, Hokkaido University  
(北海道大学水産学部海洋化学講座)

*Apparatus*

The potentials were measured with a Toa Denpa HM-15A digital pH meter by using an Orion copper ion-selective electrode (ISE). pH was measured with a Hitachi-Horiba F-5 pH meter.

*Sample used*

Bottom sediments both in the Kunebetsu River in October 1977 and in the Shukunohe River which flows in Ohnuma Lake in June 1978 were taken.

Extraction of fulvic acid from the bottom sediments: 200 ml of 1 N NaOH was added to 50 g of the sediment and the mixed solution was shaken for 2 hr. The undissolved solid was separated by a centrifuge and then the upper layer was adjusted to pH to 1 with the addition of HCl. The solution was again centrifugalized to remove a precipitation which was humic acid. The upper layer was filtered through an HA type Millipore filter with a 0.45  $\mu\text{m}$  pore size. The filtrate obtained was used as a sample of fulvic acid.

*Procedures*

A solution, which was adjusted ion intensity to 0.6 with  $\text{NaClO}_4$  and the concentration of fulvic acid to about  $10^{-3}$  M, was adjusted pH to 6.0 with NaOH at 25°C. After an aliquot of a standard  $\text{Cu}^{2+}$  solution was added to the solution, the solution was mixed with a stirrer. The uncomplexed concentration of  $\text{Cu}^{2+}$  was measured by ISE.

*Calculations*

The response of ISE is given by

$$E = E_0 + \frac{RT}{2F} \ln[\text{Cu}] = E_0 + \rho \log [\text{Cu}] \quad (1)$$

where  $[\text{Cu}]$  is the concentration of the hydrated ion  $\text{Cu}^{2+}$  in the solution,  $E$  and  $E_0$  are the potentials of  $\text{Cu}^{2+}$  and the standard potential of  $\text{Cu}^{2+}$  respectively.  $R$ ,  $T$ ,  $F$  and  $\rho$  are gas constant, absolute temperature, Farady constant and  $2.3 RT/2F$  respectively.

The degree of complexation of  $\text{Cu}^{2+}$ ,  $\alpha$ , is defined as

$$\alpha = [\text{Cu}]_T / [\text{Cu}] \quad (2)$$

where  $[\text{Cu}]_T$  and  $[\text{Cu}]$  are the total concentration of  $\text{Cu}^{2+}$  and the hydrated  $\text{Cu}^{2+}$  respectively.

By combining equations (1) and (2)

$$\alpha = [\text{Cu}]_T \times 10^{(E_0 - E)/\rho} \quad (3)$$

It is assumed that fulvic acid is approximately dissociated at pH 6.0 because of the dissociation constant of  $pK_a=4.2$ .<sup>9)</sup> Thus, the calculation of the stability constant of  $\text{Cu}^{2+}$  with fulvic acid was slightly modified by the Buffle method.<sup>6)</sup>

$$Y = \left( \frac{[\text{L}]_T}{[\text{Cu}]_T} \right) \left( \frac{\alpha}{\alpha - 1} \right) = M_W + \left( \frac{M_W}{\beta} \right) \left( \frac{\alpha}{[\text{Cu}]_T} \right) \quad (4)$$

where  $[L]_T$ ,  $M_w$  and  $\beta$  are the total concentration of fulvic acid, the molecular weight of fulvic acid and the stability constant of  $\text{Cu}^{2+}$  with fulvic acid respectively.

A plot of the left hand term of equation (4) vs.  $\alpha/[\text{Cu}]_T$  should give a straight line and from the slope and the intercept on the ordinate,  $M_w$  and  $\beta$  can be evaluated.

### Results and discussion

Plots of  $E$  vs.  $[\text{Cu}]_T$  for the titration of fulvic acid with  $\text{Cu}^{2+}$  at pH 6.0 in the Kunebetsu River are shown in Fig. 1. Solid and dotted lines represent the plots in the absence of fulvic acid and in the presence of fulvic acid respectively. The difference of both lines shows the formation of a fulvic acid-Cu complex. From equation (4), plots of  $Y$  vs.  $\alpha/[\text{Cu}]_T$  are shown in Fig. 2. The straight line was calculated by the method of least squares and the equation,  $Y=515+2.6 \times 10^{-3} \times \alpha/[\text{Cu}]_T$  was obtained. From the slope and intercept,  $M_w=515$  and  $\log \beta=5.3$  were obtained. From the results,  $\text{Cu}^{2+}$  forms 1:1 complex with fulvic acid.

The stability constant of  $\text{Cu}^{2+}$  with fulvic acid which was extracted from bottom sediment in the Shukunohe River was also the same results as that in the Kunebetsu River. The value obtained  $\log \beta=5.3$  is assumed to be reasonable one because already reported values are  $\log \beta=5.67-5.95^5)$ ,  $4.8-5.0^6)$ . By using the value, chemical species of copper in river or lake waters in a suburb of Hakodate were thermodynamically calculated.<sup>10)</sup>

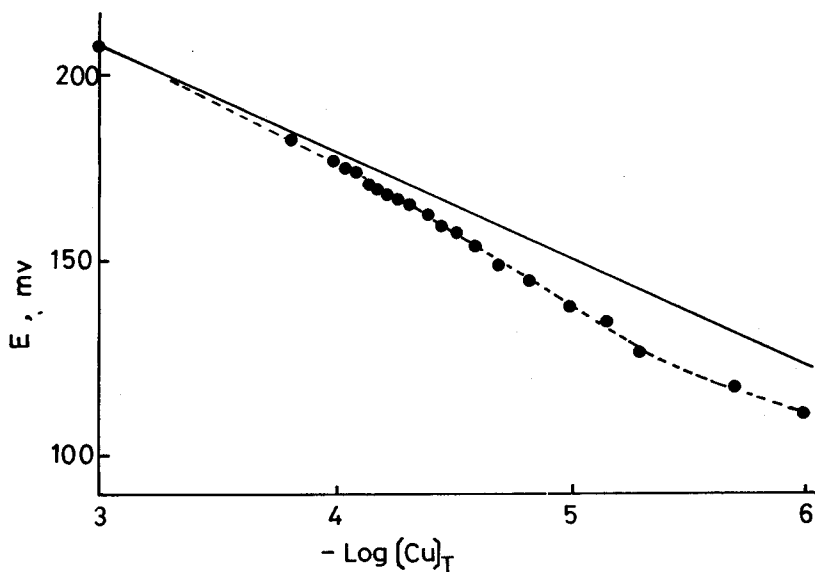


Fig. 1. Variation of potential titrated with copper.  
Solid line: in absence of fulvic acid; ●: in presence of fulvic acid

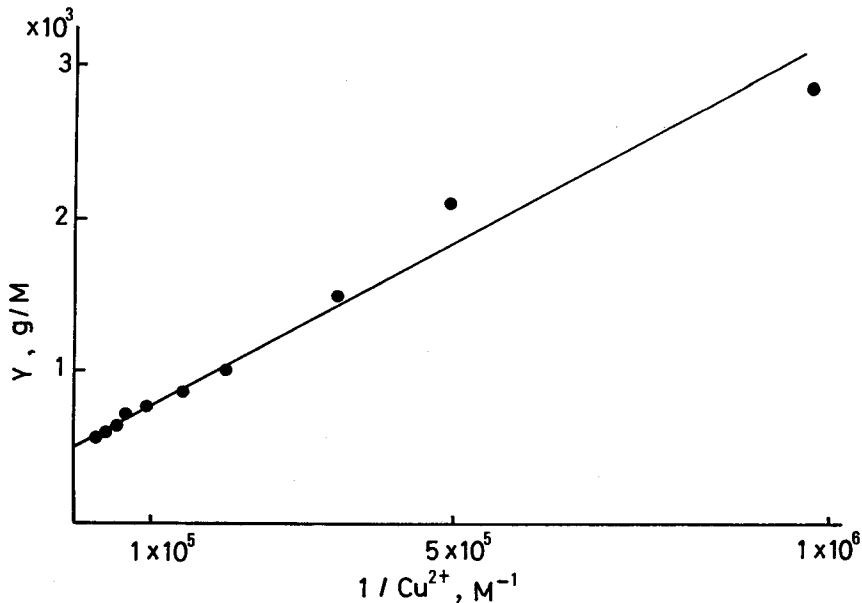


Fig. 2. Relation between Y and  $1/[\text{Cu}]$  according to eq. (4).

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