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Lability of Soluble Copper(II) Complex in River Waters in the Urban Area

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Synopsis. Hourly variation of the lability of soluble copper(II) complex in water samples from the Kiryu River in Gunma prefecture was investigated. By considering the relationship between the lability of soluble copper(II) complexes and the copper(II) complexing capacity, the lability was found to reflect the presence of weak $\mathrm{Cu^{II}}$ complexes.

Since the toxicity of a metal towards aquatic organisms depends on the chemical form of the metal, the speciation of trace metal species in natural water may elucidate its environmental significance.[1] In some cases, kinetics rather than thermodynamics is more suitable to investigate the behavior of biologically-active chemical species.[2] In the previous paper, the authors have developed a method for the determination of lability of soluble copper(II) complex in natural water sample by chelex column technique,[3] in which the lability is defined as the adsorption rate of $\mathrm{Cu^{2+}}$ on the chelex column. In the present work, the proposed method was applied to analysis of water samples from the Kiryu River, and the lability of soluble copper(II) complex was discussed in relation to the copper(II) complexing capacity.

Experimental

A Shimadzu Model AA-670 atomic absorption/flame emission spectrophotometer equipped with a copper hollow cathode lamp (Hamamatsu Photonics) was used. A Hitachi Model F-3010 fluorescence spectrophotometer was used for the determination of amino acids, and a Horiba Model F-16 pH meter was used for pH measurements. Total organic carbon (TOC) in sample solutions was determined with a Shimadzu Model TOC-500 total organic carbon analyzer, and analytical results were expressed by $\mu\mathrm{mol\,dm^{-3}}$ unit for the sake of comparison.

Reagents. All the chemicals used were of guaranteed grade. Deionized water was used throughout. Analytical grade Chelex-100, 100—200 mesh, was obtained from Bio-rad Laboratories, Dow Chemical Co. (lot no. 35095).

Sampling Location. Water samples were collected on 6th February, 1992 from the Kiryu River of Gunma prefecture, and the sampling point was situated below Kiryu Town.

Determination of Amino Acids. The determination of amino acids was carried out by the ninhydrin method.[4]

Determination of Copper(II) Complexing Capacity (CuCC). The CuCC was determined by the previously proposed method,[5] in which CuCC was defined as the amount of copper(II) back-extracted into a water sample from the organic phase containing bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)copper(II), $\mathrm{Cu(bfa)_2}$.

Chelex Column Parameters. Na-Chelex (1.0 g), direct from bottles, was slurried into a 0.7 cm i.d. polyethylene columns, and converted to Ca-form by the method reported in the literature.[6] Each flow rate was adjusted by using an aspirator equipped with the column. Column operations were carried at room temperature (ca. 293 K).

Speciation Procedure.[3] Solution containing $1.00\times10^{-5}\ \mathrm{mol\,dm^{-3}}$ ($=C_0$) copper(II) was passed through the column at a controlled flow rate. The copper(II) content (C) in the eluate was measured by flame atomic absorption spectrometry and a contact time (t) which was defined as a time from the beginning of flow-out to the end, was also measured. The rate constant (k_{obsd}) for the adsorption of $\mathrm{Cu^{2+}}$ on the chelex column was obtained from the equation:

$$t=\frac{2.30}{k_{\mathrm{obsd}}}\log\frac{1}{1-X}\,, \tag{1}$$

where $X=(C_0-C)C_0^{-1}$. In case of no ligand present, the k_{obsd} was $1.3\times10^{-1}\ \mathrm{s^{-1}}$ which was defined as k_0. The $\log k_{\mathrm{obsd}}k_0^{-1}$ value can be considered as a measure of relative lability of copper(II) complex on the basis of k_0 value.

Results and Discussion

At first, the $-\log k_{\mathrm{obsd}}k_0^{-1}$ value was measured by taking nitrilotriacetate (nta=L) as a model ligand. The results are shown in Fig. 1 as a function of $\log\beta'[L]$, which is a measure of complexing ability of nta. Here, β' denotes a conditional stability constant for CuL. Plots fall on a straight line, suggesting that the value of $-\log k_{\mathrm{obsd}}k_0^{-1}$ can be used as a quantitative measure of the relative stability of a copper(II) complex.

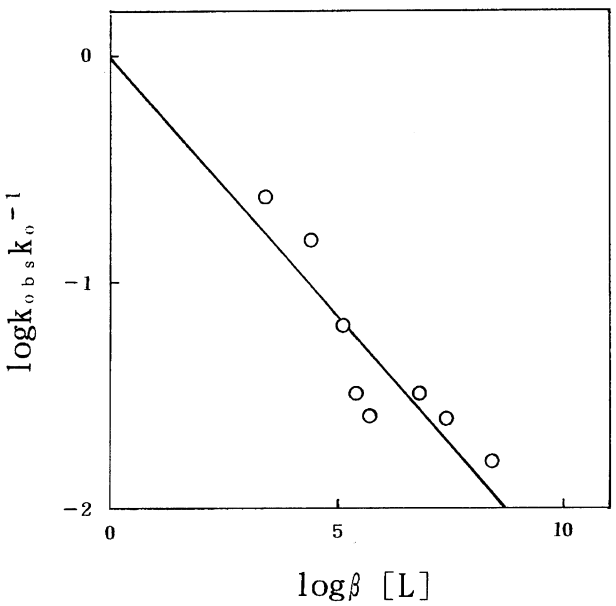

Fig. 1. $\log k_{\mathrm{obsd}}k_0^{-1}$ vs. $\log\beta'[L]$.

Table 1. Analytical Results of Kiryu River Water Samples

Sampling time	pH	$-\log k_{\mathrm{obsd}} k_0^{-1}$	TOC	Amino acid	CuCC
o'clock			µmol dm^{-3}		
6	7.21	0.69	146	0.22	0.97
7	7.19	0.43	106	0.46	0.91
8	7.29	0.61	132	0.35	0.84
9	7.36	0.63	61	0.57	0.84
10	7.49	0.51	82	0.32	1.08
12	7.67	0.78	304	0.17	1.78
14	8.33	0.82	326	0.14	1.51
16	8.65	0.99	500	0.14	1.96
18	7.65	0.71	782	0.19	1.62
19	7.57	0.88	540	0.06	1.51
20	7.48	0.57	484	0	1.43
21	7.35	0.60	509	0.07	1.63
22	7.34	0.73	390	0.17	1.72
24	7.30	0.70	208	0.04	1.53

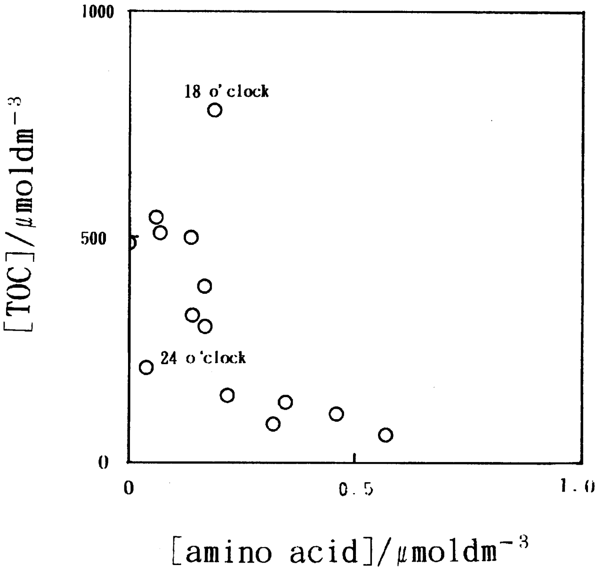

Fig. 2. Relationship between TOC and amino acid.

Since the straight line given in Fig. 1 passes through the origin, one can estimate the relative stability for weak complexes by $-\log k_{\mathrm{obsd}} k_0^{-1}$. It should be noted that the relative stability of very stable complexes like metal-edta can not be expressed by the lability. On the other hand, the back-extraction technique can not be applicable to the measurements of the complexing abilities of weak ligands.[5] Analytical results of the water samples are given in Table 1. As is seen in Fig. 2, an increase in amino acid concentration tends to decrease in TOC value, although some deviations are seen in water samples taken at 18 and 24 o'clock. The above trend strongly suggests that the origin of amino acids differs from that of TOC. Judging from sampling time, major part of TOC may depend upon human activities whereas amino acids may be derived from naturally-occurring matter, and both of these may act as ligands in the complexation of copper(II). Figure 3 shows a plot of $-\log k_{\mathrm{obsd}} k_0^{-1}$ (lability) against CuCC, in which plots may be divided into two groups A and B. A straight line belonging to A group is expressed by $-\log k_{\mathrm{obsd}} k_0^{-1} = 0.33\mathrm{CuCC} + 0.36$, and that belonging to B group is given by $-\log k_{\mathrm{obsd}} k_0^{-1} = 0.36\mathrm{CuCC} + 0.11$. As mentioned above, the CuCC obtained by back-extraction technique can only represent the concentration of ligands which are stronger than bfa$^-$ and no information is obtained on weaker ligands. On the other hand, weak complexes may contribute to the value of $-\log k_{\mathrm{obsd}} k_0^{-1}$. For this reason, the $-\log k_{\mathrm{obsd}} k_0^{-1}$ may have a positive value at CuCC=0, and higher value of intercept obtained from water samples belonging to A group may be attributable to the presence of a large amount of weak ligands. In contrast, water samples belonging to B group have smaller value of intercept, indicating the presence of a small amount of weak ligands. Although we tried to speciate those ligands in relation to the TOC and amino acid concentrations, no explicit relation has been obtained at present.

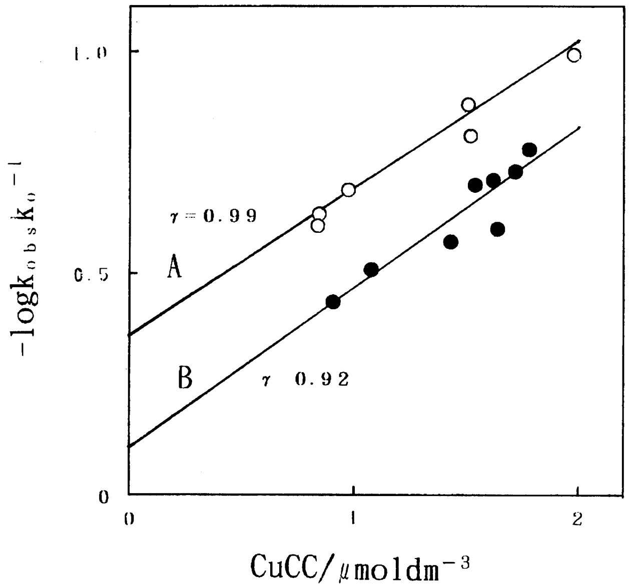

Fig. 3. $-\log k_{\mathrm{obsd}} k_0^{-1}$ vs. CuCC.

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