

AN ION-FLOTATION METHOD FOR EVALUATING THE INTERACTION  
OF ZINC ION WITH HUMIC ACID

Masao SUGAWARA, Shigeru SAITO,<sup>†</sup> and Tomihito KAMBARA\*

Department of Chemistry, Faculty of Science, Hokkaido University,

<sup>†</sup>Division of Environmental Conservation, Graduate School of

Environmental Science, Hokkaido University,

Kita-ku, Sapporo 060

An ion-flotation technique by using a surface-active cetylpyridinium chloride (CPC) in conjunction with spectrophotometry was found to be a useful method for evaluating the degree of interaction of zinc(II) with soil-derived humic acid.

The complexation of metal ions with humic substances will affect the speciation of metal ions in soils and natural waters. The so-called humic acid (HA) is the mixture of organic compounds with different molecular weight and regarded as polyelectrolytes, whose acidic property is principally due to carboxylic and phenolic hydroxyl groups. Interaction of metal ions with HA is investigated by dialysis, gel-filtration chromatography, potentiometry with ion-selective electrodes, voltammetry and so on,<sup>1)</sup> although these methods have more or less methodological disadvantage to distinguish free metal ions from the complexed species.<sup>2)</sup>

In the present paper, an ion-flotation method is developed for evaluating the degree of complexation between zinc(II) and soil-derived HA. The HA and zinc(II)-HA complex anions bound to the CPC cation are floated to the solution surface by a streaming of tiny nitrogen bubbles, the separation of the complexed species from the free zinc(II), thus, being attained.

The sample of HA was extracted with a mixture of  $0.1 \text{ mol dm}^{-3}$  sodium pyrophosphate and  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide from soils collected at the north

part of the university campus in July 1981. The HA was purified by centrifugation, redissolution, reprecipitation and cation exchange. The flotation procedure is as follows. At first nitrogen gas is passed through a sintered-glass filter (LG4) attached at the bottom of a flotation cell (20 cm in height, 2.7 cm in diameter). In the cell is taken a 30.0-cm<sup>3</sup> portion of HA solution adjusted at pH 6.0 (phosphate buffer) and  $\mu = 0.1$  (Na<sub>2</sub>SO<sub>4</sub>). A 10 to 170-mm<sup>3</sup> portion of zinc(II) solution is added with micropipettes and mixed well by bubbling nitrogen for 10 min. After adding 5.0-cm<sup>3</sup> portion of 0.01 mol dm<sup>-3</sup> CPC solution, the flotation is performed for about 2 h until foaming is almost completely finished, meanwhile foams being separated from the top of cell. A 5.0-cm<sup>3</sup> portion of the solution remained in the cell is taken in a 10-cm<sup>3</sup> volumetric flask, adjusted at pH 11 with sodium hydroxide solution and diluted to the volume with deionized water. The concentration of HA is determined by measuring the absorbance at 400 nm against water. Another 5.0-cm<sup>3</sup> portion of the solution is used for determining the concentration of zinc(II) by Zincon method.<sup>3)</sup>

The flotation of HA is quantitative in the pH range from 3.3 to 7.9 and only about 5% of the initial amount of HA remains in the solution. On the other hand, the fraction of floated zinc(II) increases with increasing pH value between 5.0

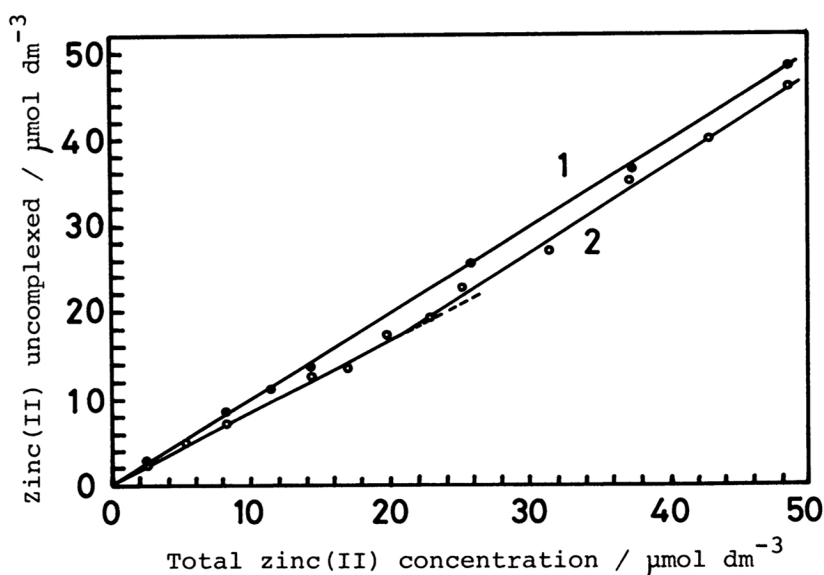


Fig. 1. Titration of (1) 0 and (2) 56.5 mg dm<sup>-3</sup> HA with zinc(II) at pH 6.0 (phosphate buffer) and  $\mu = 0.1$  (Na<sub>2</sub>SO<sub>4</sub>) by means of flotation. [CPC] = 1.4 mmol dm<sup>-3</sup>.

and 7.9. At pH below 5, almost all of zinc(II) added remains in the solution. The pH value coincides with the results of Rainville and Weber<sup>4)</sup> who have found that at pH 5 the complexing capacity  $C_L$  of soil fulvic acid for zinc(II) was  $0 \text{ mol dm}^{-3}$ . At pH above 7, a significant fraction of zinc(II) is adsorbed on the glass wall of cell.<sup>5)</sup> Therefore, the subsequent experiments were carried out at pH 6. The complexometric titration curve of HA with zinc(II) by means of flotation is shown in Fig. 1. The results of titration in the absence of HA (curve 1) indicate that the free zinc(II) ion is not floated unless the HA is present, which is one of the essential requirements of the present method. The titration curve of HA underlies the curve 1 and beyond the breaking point, it parallels the curve 1. The difference of amounts of free zinc(II) between the two titrations when the total concentration of zinc(II) is constant may correspond to the amount of zinc(II) bound to HA. Under assuming that the 1:1 zinc(II)-HA complex is predominantly formed, the titration data up to  $23 \text{ } \mu\text{mol dm}^{-3}$  zinc(II) were fitted to the equation of Buffle et al.<sup>6)</sup> according to

$$\frac{[L]_t \alpha}{C_{Zn} (\alpha - 1)} = M_w + \frac{M_w [H^+]^x \alpha}{\beta_1 C_{Zn}} \quad (1)$$

where  $[L]_t$  is the total HA concentration expressed in  $\text{g dm}^{-3}$ ,  $C_{Zn}$  is the total concentration of zinc(II),  $M_w$  is the molecular weight of HA,  $\beta_1$  is the formation constant of zinc(II)-HA complex,  $x$  is the order of the hydrogen ion concentration and  $\alpha$  is the complexation coefficient defined by

$$\alpha = \frac{C_{Zn}}{[Zn(II)]} \quad (2)$$

A plot of the left-hand term of the eqn. (1) against  $\alpha / C_{Zn}$  gave a straight line with a slope of  $0.291 \text{ g dm}^{-3}$  and an intercept of  $2262 \text{ g mol}^{-1}$ , as shown in Fig. 2. From the results, the value  $\beta_1 / [H^+]^x$  is found to be  $10^{3.9}$  at pH 6.0. Buffle et al.<sup>6)</sup> found the values  $\beta_1 / [H^+]^x$  and  $M_w$  for the copper(II) complex of humic substances dissolved in a pond water to be  $10^{5.0}$  at pH 6.0 and 1700, respectively. The values  $\beta_1 / [H^+]^x = 10^{6.0}$  at pH 6.7 and  $M_w = 2060$  for the lead(II) complex is also reported.<sup>6)</sup> Since the stabilities of metal humic

acid complexes are known to follow the familiar Irving-Williams order of the stabilities of chelates,<sup>7)</sup> it seems that the values for zinc(II)-HA complex obtained in the present work are concordant with the results of Buffle et al.,<sup>6)</sup> although the origin of HA is different.

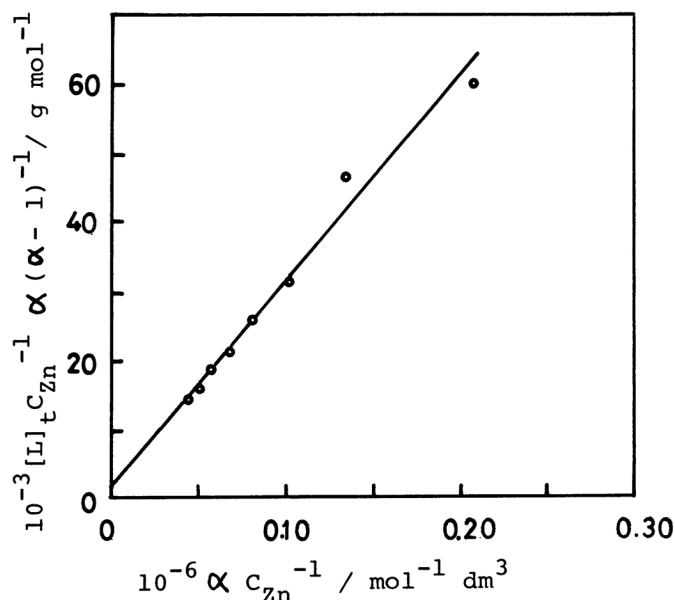


Fig. 2. A plot evaluating  $\beta_1 / [H^+]^x$  and  $M_w$  by using the titration data in Fig. 1.

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