Bull. Chem. Soc. Jpn., ***53****, 2548—2551 (1980)* [Vol. 53, No. 9

Use of the Copper(II) Ion-selective Electrode for the Determination of the Stability Constant of Binuclear Copper(II) Complex with 3,6-Dioxaoctane-1,8-diamine-*N*,*N*,*N'*,*N'*-tetraacetric Acid

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(Received March 18, 1980)

The stability constant of binuclear copper(II) complex with 3,6-dioxaoctane-1,8-diamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (ethylene glycol bis[2-[bis(carboxymethyl)amino] ethyl] ether, customarily abbreviated to EGTA of Y) was determined on the basis of potentiometric titration by means of a copper(II) ion-selective electrode. In acetate buffer solution of pH 5.8 titration curves of copper(II) with EGTA show two distinct end points corresponding to Cu_2Y and CuY complexes. The formation constant of the binuclear copper(II) complex was determined from the potential response in the titration fraction between first and second end points. The logarithmic value was found to be $\log K_{Cu_2Y}=6.40$ at ionic strength of 0.2 M (KNO_3–acetate buffer solution) at 25± 0.5 °C.

The response of copper(II) ion-selective electrode in the aqueous solution of complexing agent has been studied. Nakagawa *et al.*1) found that the stability constants of copper(II) complexes with several ligands such as acetate, ammonia, ethylenediamine, *etc.* agreed very well with those given in the literature, except EDTA and NTA complexes. Similar behavior has recently been observed by Heijine and Linden.2)

In the present paper a successful application of copper(II) ion-selective electrode to the determination of binuclear copper(II)–EGTA complex is described.

Theoretical

When copper(II) is titrated with EGTA forming only two complexes CuY and Cu_2Y, the total concentration of copper(II) and EGTA in the titration vessel can be written as:

$$C_{Cu} = [CuY] + 2[Cu_2Y] + [Cu]\alpha_{Cu} \tag{1}$$

and

$$C_Y = [CuY] + [Cu_2Y] + [Y]\alpha_Y, \tag{2}$$

where α_{Cu} denotes the side reaction coefficient of copper(II) with component of buffer system, and α_Y indicates that of titrant with hydrogen ion. The stability constants of CuY and Cu_2Y are given

$$K_{CuY} = \frac{[CuY]}{[Cu][Y]} \tag{3}$$

and

$$K_{Cu_2Y} = \frac{[Cu_2Y]}{[Cu][CuY]}. \tag{4}$$

Introducing Eqs. 3 and 4 into Eqs. 1 and 2 and eliminating [Y], one obtains

$$\frac{C_Y}{C_{Cu}} = \frac{K_{CuY}[Cu]+K_{CuY}K_{Cu_2Y}[Cu]^2+\alpha_Y}{K_{CuY}[Cu]+2K_{CuY}K_{Cu_2Y}[Cu]^2}\left(1-\frac{[Cu]\alpha_{Cu}}{C_{Cu}}\right). \tag{5}$$

Between the first and second end points, Eq. 5 can be simply written as:

$$\frac{C_Y}{C_{Cu}} = \frac{1+K_{Cu_2Y}[Cu]}{1+2K_{Cu_2Y}[Cu]}. \tag{6}$$

When *a* ml of copper(II) solution in the initial concentration of C_{Cu}° is diluted in the titration vessel to *V* ml, and then titrated with ΔV ml of titrant of the concentration of C_Y°, the titration fraction is given by

$$\frac{C_Y}{C_{Cu}} = \frac{\Delta V C_Y^\circ}{aC_{Cu}^\circ}. \tag{7}$$

Combination of Eqs. 6 and 7 yields

$$K_{Cu_2Y}[Cu] = \frac{aC_{Cu}^\circ - \Delta V C_Y^\circ}{2\Delta V C_Y^\circ - aC_{Cu}^\circ}. \tag{8}$$

When the titration is carried out in acetate or ammonia buffer solution, the formation of the mixed ligand complex such as $Cu_2Y(NH_3)$ should be considered. In this case, K_{Cu_2Y} in Eq. 8 is replaced by

$$K'_{Cu_2Y} = K_{Cu_2Y}(1+K_{Cu_2YL}[L]+K_{Cu_2YL}K_{Cu_2YL_2}[L]^2), \tag{9}$$

where K'_{Cu_2Y} is the apparent formation constant, K_{Cu_2YL} and $K_{Cu_2YL_2}$ are the formation constants of the mixed ligand complexes, and L denotes the acetate or ammonia. In the logarithmic expression of the resulting equation, one derives

$$pCu = \log K'_{Cu_2Y} - \log\frac{aC_{Cu}^\circ - \Delta V C_Y^\circ}{2\Delta V C_Y^\circ - aC_{Cu}^\circ}. \tag{10}$$

A plot of pCu against the logarithmic term in the right-hand side will show a straight line with a negative slope of unity and K'_{Cu_2Y} value is estimated from the intercept of the line.

Experimental

Reagents. A Dotite reagent EGTA (Dojindo Lab.) was used as received. Other chemicals used were all of analytical reagent grade. A 10^{-2} M (1 M=1 mol dm^{-3}) copper(II) stock solution was prepared from copper(II) sulfate pentahydrate. A 10^{-2} M EGTA solution (pH=4.8) was prepared by dissolving the acid with appropriate amount of potassium hydroxide, the ionic strength being adjusted to 0.2 M with potassium nitrate. The EGTA solution was standardized against the copper(II) solution. A solution containing 0.1 M acetate buffer solution (pH=6.0) and 0.1 M potassium nitrate was used for conditioning the copper(II) ion-selective electrode.

Apparatus. The copper(II) ion activities were measured with an Orion copper(II) ion-selective electrode, Model 94-29. A Horiba double junction SCE with the outer compartment filled with 0.2 M potassium nitrate was used as the reference electrode. The potential measurements were made by the aid of a Hiranuma recording auto titrator, Type RAT-11. A Hitachi-Horiba pH meter, F-5, was used for pH measurements.

Procedure. All experiments were carried out in a thermostat kept at 25±0.5 °C. The electrode potential was recorded while the solution was gently stirred.

Conditioning: The surface of copper(II) ion-selective electrode was polished gently with a tooth paste and then soaked in the conditioning solution until a constant potential value was attained.

Calibration: A series of standard copper(II) solution from 10^{-3} to 10^{-7} M was prepared by diluting the stock solution immediately before the measurements, the ionic strength being adjusted to 0.2 M with potassium nitrate. The pH of final solution was in the range of 5.0—5.4. The potenital was recorded for 30 s with a Hiranuma recording auto titrator without titrant supply.

Titration: Titrations of copper(II) with EGTA were performed in acetate or ammonia buffer solution. The ionic strength of test solutions was adjusted to 0.2 M with potassium nitrate. The EGTA solution was automatically supplied to a 50-ml portion of the test solution containing copper(II) in the analytical concentration range from 2×10^{-4} to 10^{-3} M. A 30-μl portion of the titrant was delivered to a titration vessel within 0.5 s and the electrode potential was measured after 9.5 s, and the procedure was repeated. Titration curves with stepwise potential decreases were recorded automatically.

Results and Discussion

Calibration Curve. The electrode potential drifted slightly in the 10^{-7} M copper(II) solution, while above 10^{-6} M a stable potential was observed during 30 s. The Nernstian response was found to hold from 10^{-3} to 10^{-6} M of copper(II), obeying the equation:

$$E = E' + S \log a_{\mathrm{Cu}^{2+}}$$
$$= E'' + S \log [\mathrm{Cu}]$$
$$= 260 + 29.9 \log [\mathrm{Cu}].$$

In the equations, E' and E'' are constants, S the Nernstian coefficient, and the figures in the last equation are expressed in mV.

Titration in Acetate Buffer Solution. Titrations were made with varying acetate buffer concentrations, namely, 0.06, 0.10, 0.14, and 0.20 M. The pH values of test solutions were in the range 5.76—5.80. These values decreased slightly as titration proceeded. A typical titration curve was shown in Fig. 1. Two distinct end points were found. The ratio of amount of titrant at the second end point to that at the first end point was found to be 2.00 (number of determinations $n=6$). The first end point is due to the formation of binuclear copper(II) complex $\mathrm{Cu_2Y}$. The results of log-log plot according to Eq. 10 were shown in Fig. 2. Each plot gave a straight line with a negative slope of unity as expected theoretically. The apparent formation constant is evaluated from the intercept of each line at the abscissa zero line, where the titration fraction is two-thirds. A constant $K'_{\mathrm{Cu_2Y}}$ value was obtained irrespective of the initial copper(II) concentration ranging from 2×10^{-4} to 10^{-3} M. However, the value increased with increasing concentration of buffer solution as shown in Fig. 2, which suggests the formation of mixed ligand binuclear copper(II) complex such as $\mathrm{Cu_2Y(CH_3COO)}$. When the forma-

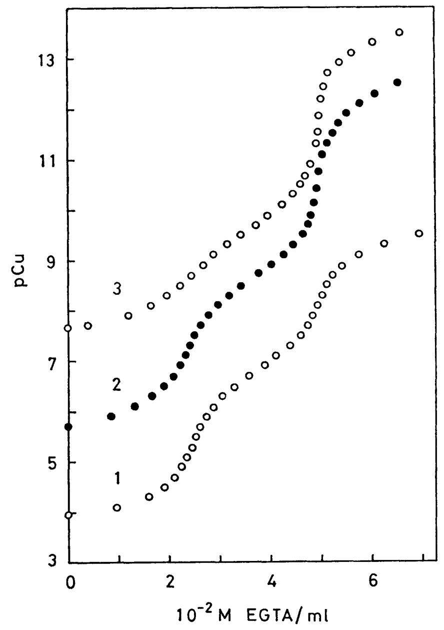

Fig. 1. Titration of a 50-ml portion of 10^{-3} M (f=0.995) copper(II) with 10^{-2} M (f=1.000) EGTA performed in: 1; 0.10 M ($\mathrm{CH_3COOH\text{-}CH_3COONa}$), pH 5.8, 2; 0.06 M ($\mathrm{NH_3\text{-}NH_4Cl}$), pH 8.0, 3; 0.20 M ($\mathrm{NH_3\text{-}NH_4Cl}$), pH 8.4.

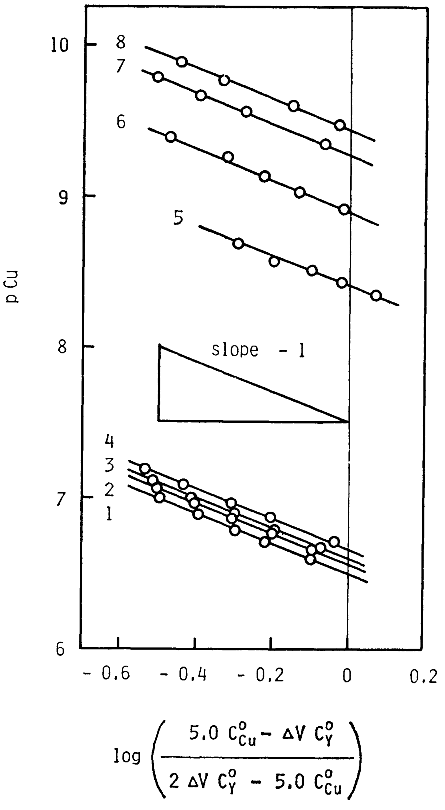

Fig. 2. Plots according to Eq. 10. Titrations were made in: 1; 0.06, 2; 0.10, 3; 0.14, 4; 0.20 M acetate buffer solution (nominal pH=5.8) and 5; 0.06, 6; 0.10, 7; 0.16, 8; 0.20 M ammonia buffer solution (nominal pH=8.5).

tion of $Cu_2Y(CH_3COO)_2$ is negligible, Eq. 9 is expressed as:

$$K'_{Cu_2Y} = K_{Cu_2Y} + K_{Cu_2Y}K_{Cu_2Y(CH_3COO)}[CH_3COO^-] \qquad (12)$$

and a plot of the apparent formation constant K'_{Cu_2Y} against the concentration of acetate ion at the titration fraction of two-thirds will show a straight line. The result given in Fig. 3 supports the above assumption. The values of intercept and slope of the regression equation of Eq. 12 were determined with 95% confidence limits as $(2.50 \pm 0.19) \times 10^6$ and $(1.29 \pm 0.16) \times 10^7$, respectively. The logarithms of the constants were 6.40 for K_{Cu_2Y} and 0.71 for $K_{Cu_2Y(CH_3COO)}$. The value of log K_{Cu_2Y} is much greater than the value 4.31 determined by a pH-potentiometric method.[3]

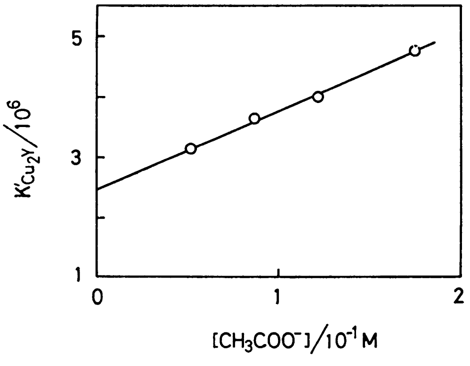

Fig. 3. Determination of K_{Cu_2Y} and $K_{Cu_2Y(CH_3COO)}$ according to Eq. 12.

Titration in Ammonia Buffer Solution. Titrations were performed with varying ammonia buffer concentrations, namely, 0.06, 0.10, 0.16, and 0.20 M. The pH values of test solutions were in the range 8.04—8.35. The values increased slightly as titration proceeded. Typical titration curves were shown in Fig. 1. Two end points were found while the potential change at the first end point decreased with increasing amount of ammonia. On the whole, the titration curves were shifted to lower potential values than those in acetate buffer solution. The formation of fairly stable mixed ligand complexes such as $Cu_2Y(NH_3)$ and $Cu_2Y(NH_3)_2$ are postulated. Equation 9 is transformed into:

$$\left(\frac{K'_{Cu_2Y}}{K_{Cu_2Y}} - 1\right)[NH_3]^{-1} = K_{Cu_2Y(NH_3)}(1 + K_{Cu_2Y(NH_3)_2}[NH_3]) . \qquad (13)$$

From the plot of left-hand side of Eq. 13 against the concentration of ammonia, the formation constants were evaluated. The values for K'_{Cu_2Y} were obtained from the plots shown in Fig. 2. The concentration of ammonia was calculated from the solution pH and the total concentration of ammonia at the titration fraction of 2/3, where average mole ratio of copper(II) to ammonia was assumed to be unity. The result was shown in Fig. 4. The values of intercept and slope of the regression equation were determined with 95% confidence limits as $(2.99 \pm 0.40) \times 10^4$ and $(2.55 \pm 0.36) \times 10^6$, respectively. The logarithms of the constants were 4.48 for $K_{Cu_2Y(NH_3)}$ and 1.88 for $K_{Cu_2Y(NH_3)_2}$.

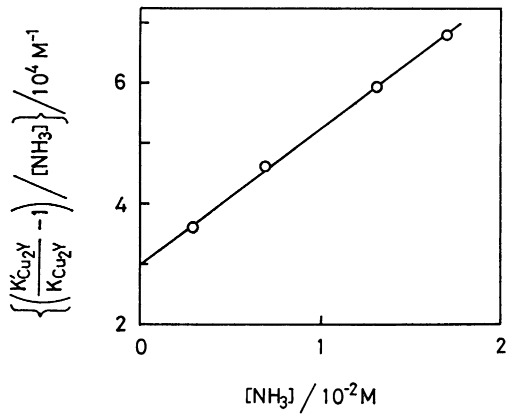

Fig. 4. Determination of $K_{Cu_2Y(NH_3)}$ and $K_{Cu_2Y(NH_3)_2}$ according to Eq. 13.

Theoretical Titration Curves. When 10^{-3} M (f= 0.995) copper(II) in a 50-ml portion of acetate or ammonia buffer solution is titrated with ΔV ml of 10^{-2} M (f=1.000) EGTA, the following equation holds:

$$\Delta V = \frac{0.995 \times 10^{-3} - \alpha_{Cu}[Cu]}{\frac{10^{-2}}{50}\left(\frac{K_{CuY}[Cu] + 2K_{CuY}K'_{Cu_2Y}[Cu]^2}{K_{CuY}[Cu] + K_{CuY}K'_{Cu_2Y}[Cu]^2 + \alpha_Y}\right) + \frac{\alpha_{Cu}[Cu]}{50}} . \qquad (14)$$

The values of K'_{Cu_2Y}, α_{Cu}, and α_Y were calculated from the concentration of ammonia or acetate ion and pH at the titration fraction of 2/3; namely, $K'_{Cu_2Y(CH_2COO)} = 3.61 \times 10^6$, $\alpha_{Cu(CH_3COO)} = 6.23$, and $\alpha_{Y(H)} = 1.17 \times 10^7$ for titration in acetate buffer solution and $K'_{Cu_2Y(NH_3)} = 2.64 \times 10^6$, $\alpha_{Cu(NH_3)} = 9.23 \times 10^2$, and $\alpha_{Y(H)} = 1.81 \times 10^2$ for titration in ammonia buffer solution, respectively. These values were assumed to be con-

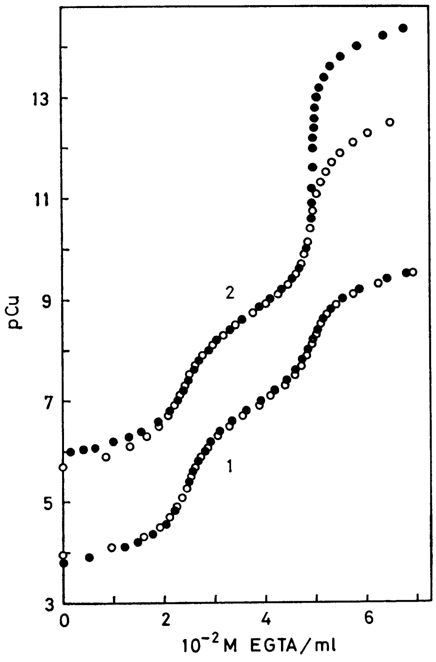

Fig. 5. Comparison of the experimental titration curves (○) with the theoretically obtained curves (●). Curves 1 (○) and 2 (○) are the same as curves 1 and 2 in Fig. 1, respectively.

stant during titration. The formation constant[4] K_{CuY} is reported to be 10^{17}. Introducing these values and copper(II) concentration into Eq. 14, one can illustrate theoretical titration curves as shown in Fig. 4. In the case of acetate buffer solution, a fairly good agreement was observed between the theoretically obtained titration curve and the experimental one. On the other hand, in ammonia buffer solution, the potential change at the second end point is much less than the theoretically expected value. Since the membrane of the Orion copper(II) electrode is made up of mixed sulfides of copper(II) and silver, the formation of silver–EGTA complex at the electrode surface may be responsible for the depression of response for copper (II).[1]

It should be noted from Eq. 14 that when titration is carried out in the acetate buffer solution of pH lower than 5, where the value of $\alpha_{\mathrm{Y(H)}}$ is approximately equal to 10^{10}, the second end point disappears, only the first end point corresponding to the formation of $\mathrm{Cu_2Y}$ being obtained. On the contrary, in concentrated ammonia buffer solution where $\alpha_{\mathrm{Cu(NH_3)}}$ is around 10^6, the first end point disappears and only the second end point is observed.

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