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Response of a Copper(II) Ion-selective Electrode in Cupric Buffers Based on Macrocyclic Polyamines

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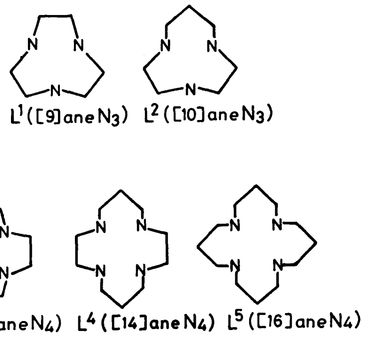
The behavior of a copper(II) ion-selective electrode at extremely low activity levels of free copper(II) was examined in copper(II) buffers based on macrocyclic triamines ([9]aneN_3 and [10]aneN_3) and macrocyclic tetramines ([12]aneN_4, [14]aneN_4, and [16]aneN_4). Although the electrode showed the ideal behavior in the buffers based on [12]aneN_4 and [16]aneN_4, non-ideal behavior was observed for the macrocyclic triamines and [14]aneN_4. Thus, the macrocyclic polyamines did not always give the ideal copper(II) buffers for the electrode, in contrast to the case of acyclic polyamines. Stability constants, which were in good agreement with the reported values, could be determined only for [12]aneN_4 and [16]aneN_4. An application of the cyclic tetramines to complexiometry is also presented.

Recently, much attention is being paid to metal complexes of macrocyclic polyamines. Particular attention has been paid for copper(II) complexes of the amines, since some of them can be regarded as simplified models for naturally occurring structures in proteins.[1)] The solution chemistry of the copper(II) complexes has produced a number of stability constants. Although several techniques have been used in determination of stability constants of copper(II)–macrocyclic polyamine complexes,[2,3)] no use of a copper(II) ion-selective electrode in determination of their stability constants has been reported.

An ion-selective electrode provides a simple method for determination of a stability constant if the electrode behaves ideally in buffered solutions of the objective ion of the electrode. However, the copper(II) ion-selective electrode does not always respond to its objective ion at extremely low activity levels. In this connection, Nakagawa *et al.* and Heijne *et al.* have found the ideal behavior of the electrode down to 10^{-22}—10^{-23} M (M=mol dm^{-3}) of free copper(II) activity in copper(II) buffers based on acyclic polyamines.[4—6)] This led us to investigate the behavior of the electrode in copper(II) buffers based on the macrocyclic polyamines, since the complexing behavior of copper(II) with the macrocyclic polyamines is considerably different from that with the acyclic polyamines.[2,3)] This paper describes the behavior of the electrode in the copper(II) buffers based on the following macrocyclic polyamines (L^1—L^5).



Scheme 1.

Experimental

Materials. The macrocyclic triamines, L^1 and L^2 (as 3HBr salts), were prepared by the method of Koyama *et al.*[7)] The macrocyclic tetramines, L^3—L^5 (L^3 and L^5 as 4HCl salts, L^4 as $2H_2SO_4$ salt) were prepared by the method of Richman *et al.*[8)] Their purities were checked by CHN analysis, ^1H NMR, melting point or potentiometric titration. A copper(II) standard was prepared from a reagent grade copper(II) sulfate and standardized against an EDTA solution by the use of a copper(II) ion-selective electrode as an indicator. Other reagents were of reagent grade and were used as received.

Apparatus. A Denki Kagaku Keiki (DKK) digital mV meter IOC 10 was used in potential and pH measurements. The following cell was arranged by using an Orion 94-29A copper(II) ion-selective electrode and a DKK reference electrode (silver/silver chloride electrode of a double junction type): Ag/AgCl/stand. KCl//10% KNO_3//test solution/copper(II) ion-selective electrode.

The ionic strength of the test solution was adjusted with potassium nitrate. During potential measurements, the test solution was stirred. At first, preliminary measurements were made under ambient conditions, and then almost the same measurements were repeated at 25±0.1 °C.

Testing of Electrode Response in the Copper(II) Buffers. The behavior of the electrode was examined in the presence of a given macrocyclic polyamine in excess. Here, the total concentration of copper(II) was varied, while that of the amine, pH, and ionic strength were maintained at appropriate values. In the case of the triamines, the electrode response was examined in the pH range 5.5—6.8, because of the relatively small stability constants of the copper(II)–triamine complexes.[2,3)] For the tetramines, the electrode response was tested in the pH range of 10.4—11.1 since the tetramines form extremely stable copper(II) complexes.[2,3)]

Determination of Stability Constants. Two kinds of solutions containing copper(II) and a given polyamine were prepared. Both had the same compositions except for pH. In each solution, the total concentration of the amine is greater than that of copper(II) by about ten times. One solution had a high pH and the other a low pH; the pH of each was adjusted with sodium hydroxide or nitric acid. The solution with a high pH was titrated with the solution with a low pH. Potentials of the electrode and pH were measured during the titration.

Results and Discussion

Electrode Response in the Copper(II) Buffers. In the case of the triamines, ideal behavior of the electrode was

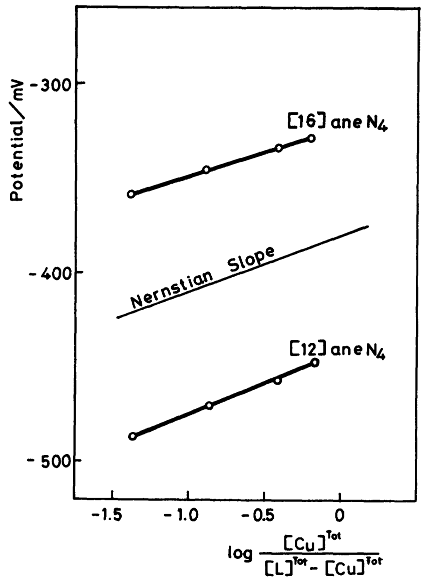


Fig. 1. Electrode response in cupric buffers at 25 °C. $[\mathrm{L}]^{\mathrm{Tot}}$: $8.9_2\times10^{-3}$ M, $[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}$: $3.5_8\times10^{-4}$—$3.5_8\times10^{-3}$ M, pH: 10.85±0.05 for [12]aneN$_4$ and 10.55±0.15 for [16]aneN$_4$, ionic strength: 0.14.

not observed. Potentials were not so stable and prolonged response time longer than 10 min was frequently observed. In addition, electrode potentials themselves were not highly reproducible. In the case of the tetramines, on the other hand, the response was rapid and the potentials were stable. However, [14]aneN$_4$ gave rather strange results; the response was rapid and potentials were stable, but the potential values changed from run to run. Accordingly, only [12]aneN$_4$ and [16]aneN$_4$ gave satisfactory results.

As described later, [12]aneN$_4$ and [16]aneN$_4$ form the 1 : 1 complexes with copper(II) and their stability constants are extremely large. Thus, one can get the relation at a given pH:

$$[\mathrm{Cu}^{2+}] \propto [\mathrm{Cu}^{2+}]^{\mathrm{Tot}}/([\mathrm{L}]^{\mathrm{Tot}}-[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}), \quad (1)$$

where $[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}$ and $[\mathrm{L}]^{\mathrm{Tot}}$ are respective total concentrations of copper(II) and the ligand, and $[\mathrm{Cu}^{2+}]$ represents the concentration of free copper(II). Then, if the electrode shows a Nernstian response even in the copper(II) buffers, one can expect that the plot of the electrode potential against log $([\mathrm{Cu}^{2+}]^{\mathrm{Tot}}/([\mathrm{L}]^{\mathrm{Tot}}-[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}))$ will give a straight line having a slope of $2.303RT/2F$. This expectation is satisfied for the copper(II) buffers based on [12]aneN$_4$ and [16]aneN$_4$, as is shown in Fig. 1.

Determination of Stability Constants. As mentioned in the previous section, one can expect that the stability constants of the copper(II) complexes with [12]aneN$_4$ and [16]aneN$_4$ can be determined by the copper(II) ion-selective electrode. The results for potentiometric titrations are shown in Fig. 2. From the definition, and from the mass balance, one can get the relations:

$$\mathrm{pCu} = \log\beta_n - n\mathrm{pL} - \log[\mathrm{CuL}_n], \quad (2)$$

$$[\mathrm{CuL}_n] = [\mathrm{Cu}^{2+}]^{\mathrm{Tot}} - [\mathrm{Cu}^{2+}], \quad (3)$$

$$[\mathrm{L}] = ([\mathrm{L}]^{\mathrm{Tot}} - n[\mathrm{CuL}_n])/\alpha_{\mathrm{L(H)}}. \quad (4)$$

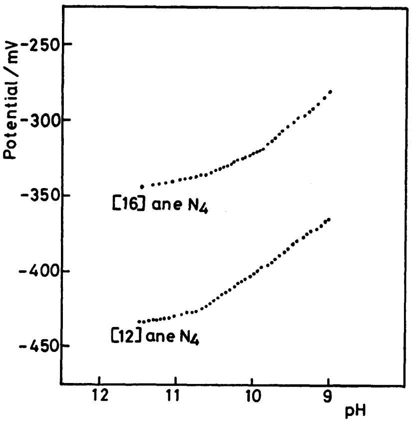


Fig. 2. Response potentials *vs.* pH at 25 °C. [12]aneN$_4$: $[\mathrm{L}]^{\mathrm{Tot}}=5.0_0\times10^{-3}$ M, $[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}=5.0_0\times10^{-4}$ M, ionic strength=0.10. [16]aneN$_4$: $[\mathrm{L}]^{\mathrm{Tot}}=1.0_0\times10^{-2}$ M, $[\mathrm{Cu}^{2+}]^{\mathrm{Tot}}=1.0_0\times10^{-3}$ M, ionic strength =0.10.

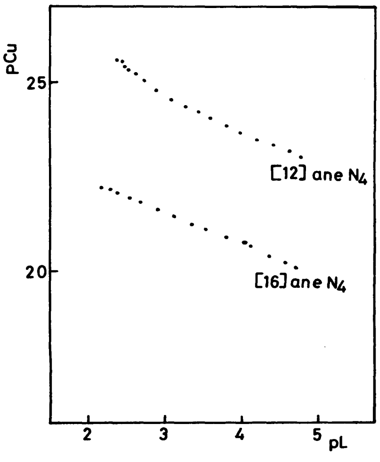


Fig. 3. Plots of pCu *vs.* pL. Conditions are given in Fig. 2.

Here, $\alpha_{\mathrm{L(H)}}$ is a side reaction coefficient of the ligand and other symbols have their usual meanings. As pCu can be estimated from the electrode potential, β_n can be calculated from Eqs. 2, 3, and 4. The relations between pCu and pL are shown in Fig. 3. Figure 3 shows that the coordination number, *n*, is unity for both ligands. The stability constants determined are given in Table 1. Although our experimental conditions are somewhat different from the reported ones, the determined stability constants are in fair agreement with the reported values.

In conclusion, the macrocyclic polyamines do not always give the copper(II) buffers in which the electrode responds to free copper(II) ideally. This is in contrast to the case of acyclic polyamines; most of them give the ideal copper(II) buffers for the electrode.[4-6,9] In this work, we could show that the electrode responds to free copper(II) down to 10^{-25}—10^{-26} M in the copper(II) buffer based on [12]aneN$_4$.

Application of the Macrocyclic Tetramines to Complexiometry. Although fundamental works on macro-

Table 1. Stability constants of Cu(II) complexes at 25 °C

Ligand	$\log \beta_1$	
	Determined[a)]	Reported
[12]aneN_4	24.4	24.8[b)]
[16]aneN_4	21.6	20.9[c)]

a) Ionic strength: 0.10 (KNO_3). b) Taken from Ref. 2a. Determined by polarography, ionic strength: 0.20 (KNO_3). c) Taken from Ref. 3g. Determined by potentiometric titration with a glass electrode, ionic strength: 0.50 (KNO_3).

cyclic polyamines have been reported, practical studies are rare. In this work, the solutions of the tetramines were standardized against a copper(II) sulfate solution by the use of the electrode as an indicator. Some examples of titration curves are shown in Fig. 4. The ligands, [12]aneN_4 and [16]aneN_4, give greater breaks than EDTA. This means that both amines are preferable to EDTA as the reagent for complexation titration of copper(II) as long as the end point is detected with the electrode. Although the stability constants predict that [14]aneN_4 will give a greater break than [12]aneN_4 does, the reversed results are observed. This may be ascribable to the anomalous response of the electrode in the presence of [14]aneN_4.

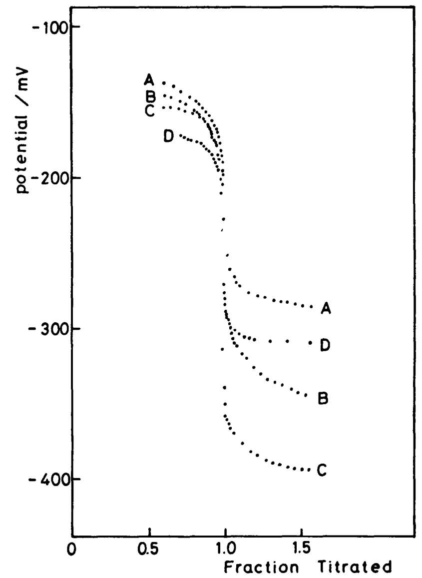


Fig. 4. Titration curves of copper(II) with macrocyclic tetramines and EDTA.
Sample: 10.0 ml of $1.01_0 \times 10^{-2}$ M $CuSO_4$ (pH 10.0, NH_3–NH_4Cl buffer). Titrant: *ca.* 10^{-2} M of each ligand, A: [16]aneN_4, B: [14]aneN_4, C: [12]aneN_4, D: EDTA.

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