Use of the Copper(II)-Selective Electrode for the Determination of the Stability Constants of Copper(II) Complexes

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In the determination of stability constants of metal complexes, usually the measurements of the activities of free metal ions at very low levels are required. The electrode response of an Orion Model 94—29 copper(II) ion selective electrode at very low activity levels was studied in the various metal buffers composed of copper(II) ions and an excess of ligand. Usually the linear calibration range of the copper(II) ion selective electrode was extended to very low activity levels in the presence of a strong complexing agent. The stability constants of copper(II) complexes with acetate, ammonia, ethylenediamine, glycine, iminodiacetic acid, 1,10-phenanthroline, *etc.* were determined successfully. In the cases of EDTA and NTA, however, the lower limit of the linear calibration range was abnormally high and the stability constant of copper-EDTA or -NTA chelate could not be obtained. Some experimental results on the potentiometric titration of copper(II) ion with EDTA were also presented.

In recent years many types of ion-selective electrodes have been developed which are very useful for direct determination of various ions in solutions.[1-6] These electrodes have been also used in the study of solution equilibria[7,8] as well as for the detection of the end-point in titrations.[9-11] In these cases the measurements of activities of free ions at very low levels are usually required. However, less attention has been paid on the detection limit of the electrode.

In the present paper the potential response of an Orion solid-state copper(II) ion selective electrode Model 94—29 at very low activity levels of copper(II) ions is studied by the use of various metal buffers, and the stability constants of some copper(II) complexes are determined successfully.

Experimental

Reagents. *Stock solution of copper*: A 10^{-1} M copper(II) nitrate solution was prepared from metallic copper (99.99%). A series of standard solutions of copper(II) from 10^{-2} to 10^{-6} M was prepared by dilution of the stock solution immediately before measurements.

Complexing Agents: Reagent grade EDTA·2Na and NTA were recrystallized from water. Ammonia and ethylenediamine were purified by distillation. Other chemicals were of reagent grade and used without further purification. Deionized and redistilled water was used.

Apparatus. For the measurements of copper(II) ion activities, an Orion copper(II) ion selective electrode Model 94-29 and a Horiba SCE reference electrode were used with a Hitachi-Horiba F-5 expanded scale pH meter. The pH measurements were made with a Hitachi-Horiba M-5 pH meter equipped with Horiba glass and calomel electrodes.

Three Orion copper(II) ion selective electrodes were examined, and these showed the same characteristics of potential response.

The surface of a sulfide membrane of the electrodes was occasionally polished lightly with tooth paste to keep the electrodes at the best condition. During the potential measurement magnetic stirring with a Teflon bar was applied.

All experiments were carried out in air thermostated at 25±1 °C.

Results and Discussion

The potential response of the electrode. The experimental cell can be represented as follows.

copper(II) ion selective electrode	test solution $\mu=0.1(KNO_3)$	0.1 M KNO_3	SCE

The measurements being carried out at a constant ionic strength of 0.1, the junction potential was kept constant and the cell emf is given:

$$E = \text{const.} + 2.303\frac{RT}{2F}\log a_{Cu^{2+}} \qquad (1)$$

The potential response of the copper(II) ion selective electrode at various copper(II) ion activity levels was examined in a pH range between 2 and 10. As shown in Fig. 1 the Nernstian response held down to 10^{-6} M of copper(II) ions in a pH range of 4—6. Below 10^{-6} M the calibration curve reached to a pla-

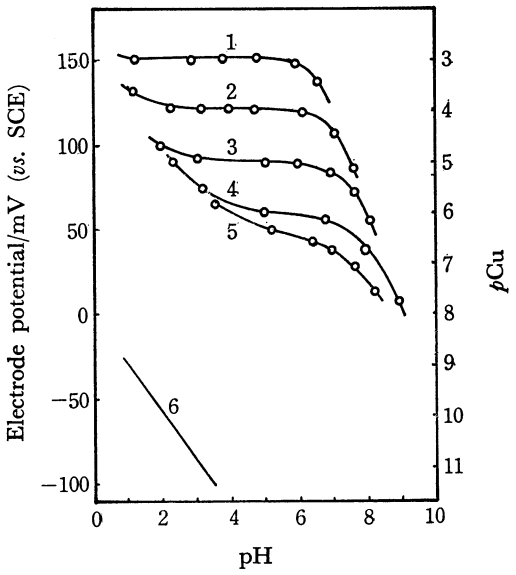

Fig. 1. Potential response of an Orion 94-29 copper(II) ion-selective.
$Cu(NO_3)_2$ 1: 10^{-3} M, 2: 10^{-4} M, 3: 10^{-5} M, 4: 10^{-6} M, 5: 0 (lower detection limit in 0.1 M MES buffer), 6: theoretical solubility of CuS.

teau, and the electrode no longer responded to change in copper(II) ion activity. This detection limit rose markedly in highly acidic solutions. At pH higher than 6 copper precipitates as a hydroxide.

The potential response of the copper(II) ion selective electrode was fast and the electrode attained a constant value within a few seconds at 10^{-2}—10^{-3} M and within a few minutes at 10^{-6} M copper(II) ion. In spite of very low activities of copper(II) ion, usually 2—5 minutes were sufficient in metal buffer solutions. The reproducibility of the electrode potential was within ±0.5 mV for 24 hours. However, since the drift of the potential during several months ranged to a few tens mV, it is advisable to calibrate the electrode with the standard copper(II) solution of 10^{-3} M before the measurements.

The Detection Limit of the Electrode. The membrane of the Orion copper(II) ion selective electrode consisting of mixed sulfides of copper(II) and silver is a source of copper(II) ions in test solutions, the lower activity limit of detection is governed by the solubility of the sulfide membrane. As seen from curves 5 and 6 in Fig. 1, however, the actual limit of detection was much higher than that calculated from the solubility of copper(II) sulfide. This disagreement may be partly attributed to copper(II) ion contamination of the test solution and partly to high activity of copper(II) ion at the surface of the sulfide membrane caused by the adsorption.

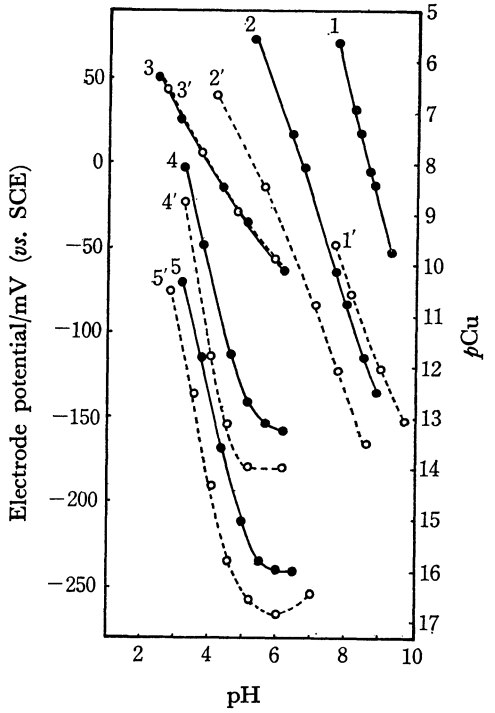

Fig. 2. The potentials of the copper(II) ion selective electrode in various copper(II) ion buffers.
Broken line shows the detection limit of the electrode in the solution containing the same ligand only.

system	C_{Cu} (M)	C_L (M)
1: NH_3	1.22×10^{-3}	0.99×10^{-1}
2: Glycine	1.99×10^{-3}	2.01×10^{-2}
3: EDTA	4.98×10^{-4}	1.02×10^{-3}
4: 1,10-Phenanthroline	0.99×10^{-4}	1.00×10^{-3}
5: 1,10-Phenanthroline	0.99×10^{-4}	5.01×10^{-3}

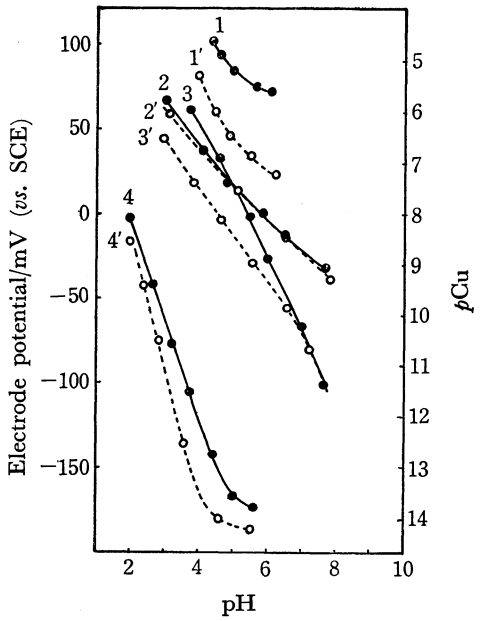

Fig. 3. The potentials of the copper(II) ion selective electrode in various copper(II) ion buffers.
Broken line shows the detection limit of the electrode in the solution containing the same ligand only.

System	C_{Cu} (M)	C_L (M)
1: OAc⁻	0.99×10^{-3}	1.03
2: NTA	4.95×10^{-3}	0.95×10^{-3}
3: IDA	2.43×10^{-3}	4.01×10^{-2}
4: Bipyridine	0.99×10^{-4}	4.98×10^{-3}

Many complexing agents forming stable complexes with copper(II) ions may reduce the activity of copper(II) ion in solutions or at the electrode surface. The detection limit of the electrode was measured in various ligand solutions containing no copper ion. As shown in Figs. 2 and 3, the detection limit was affected markedly by the type of complexing agent in the test solutions, its concentration and pH. Strong complexing agents lowered the detection limit to a large extent. For example, the lower activity limit of detection was around 10^{-6} M at pH 4 in the buffer solution composed of MES[12] which forms copper complex only negligibly, while in the presence of 0.001 M 1,10-phenanthroline the detection limit became to the order of 10^{-14} M at a pH higher than 5.

However, in spite of a high stability of copper(II)-EDTA chelate the detection limit in EDTA solutions was abnormally high. Since the stability of silver-EDTA chelate is relatively small, the activity of silver ion at the electrode surface may be much higher than that of copper. The Orion copper(II) ion selective electrode also responds to silver ion, thus the detection limit in this case may be determined by the activity of silver ion at the electrode surface. On the other hand, ligands which form fairly stable complexes with both silver and copper(II) ions, *i.e.* NH_3, ethylenediamine, 1,10-phenanthroline *etc.*, may shift the detection limit of the electrode to very low copper(II) ion levels.

Determination of the Stability Constants of Copper(II) Complexes. The stability constants of various cop-

per(II) complexes were determined by measuring the activities of free copper(II) ion in the metal buffer solutions which consist of copper complex CuL_n and the excess of the ligand L.

From the over-all stability constant of the complex CuL_n, the activities of free copper(II) ion in a metal buffer solution are given:

$$pCu = \log \beta_n + n \log[L] - \log[CuL_n] \quad (2)$$

When the solution contains a large excess of ligand and the formation of CuL_n is practically complete, $[CuL_n]=C_{Cu}$, and [L] can be represented by Eq. (3).

$$[L] = \frac{C_L}{\alpha_{L(H)}} \quad (3)$$

where C_L is the total concentration of the ligand, and $\alpha_{L(H)}$ is the side reaction coefficient taking into account the protonation of ligand and calculated from the concentration of hydrogen ion in the solution and the acid dissociation constants of the ligand. As pCu is obtained from the measured cell potential, β_n can be calculated by Eq. (2).

Figures 2 and 3 show the cell potential measured in various copper(II) buffer solutions. The relation between pCu and pL are plotted in Fig. 4. These plots yielded the straight lines of slope n. In the case of bipyridine the slope was 2 at pL>5 and 3 at pL<4, and β_2 and β_3 could be evaluated.

The stability constants determined are summarized in Table 1. Those values are in good agreement with the values reported in the literature.[13]

For the EDTA or NTA chelate, however, good results could not be obtained, because in these cases the activities of copper(II) ion in the solutions were much lower than the detection limit of the electrode, so the true activities of copper(II) ion were not obtained. Also this was the case for IDA at pH>7.

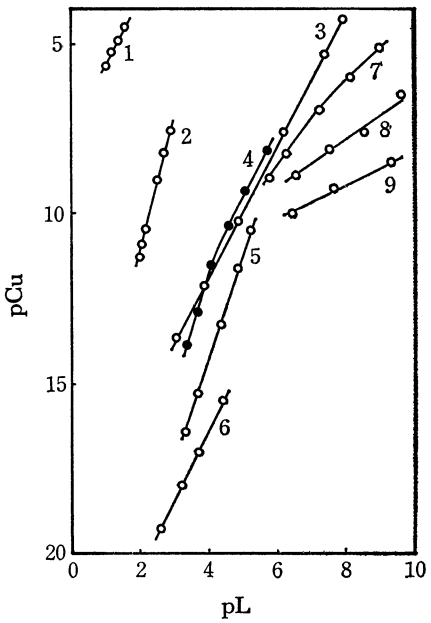

Fig. 4. Relations between pCu and pL.
1: OAc^-, 2: NH_3, 3: glycine, 4: bipyridine, 5: 1,10-phenanthroline, 6: ethylenediamine, 7: iminodiacetic acid, 8: NTA, 9: EDTA.

Table 1. Stability constants of copper(II) complexes (μ=0.1, 25 °C)

Ligand		Logarithmic values of β_n (measured)	(literature)
OAc^-	β_2	2.58 (μ=1.0)	2.7
NH_3	β_4	12.49	12.59
Ethylenediamine	β_2	19.40	19.60
Glycine	β_2	15.28	15.1
Iminodiacetic acid	β_1	10.54	10.5
Bipyridine	β_2	13.65	13.57
	β_3	16.75	17.0
1,10-Phenanthroline	β_3	19.10	21.0

These values were omitted for the calculation of the stability constant.

The use of the ion selective electrode provides the simple and reliable method for studying the stability of metal complexes. However, the lower limits of detection of the ion selective electrode should be checked under the same experimental conditions.

Application to EDTA Titration. The potentiometric titration curves of copper(II) ion with EDTA using the copper(II) ion selective electrode are shown in Fig. 5A. The titration curves after the equivalence point were leveled at the detection limit of the electrode and deviated from the typical sigmoid shape. Addition of a small amount of 1,10-phenanthroline *i.e.* 10^{-5} M improved titration curves markedly. As seen from Fig. 5B this is of special advantage when the metals stabilities of EDTA chelates of which are lower than that of copper, are to be determined by back titration of the

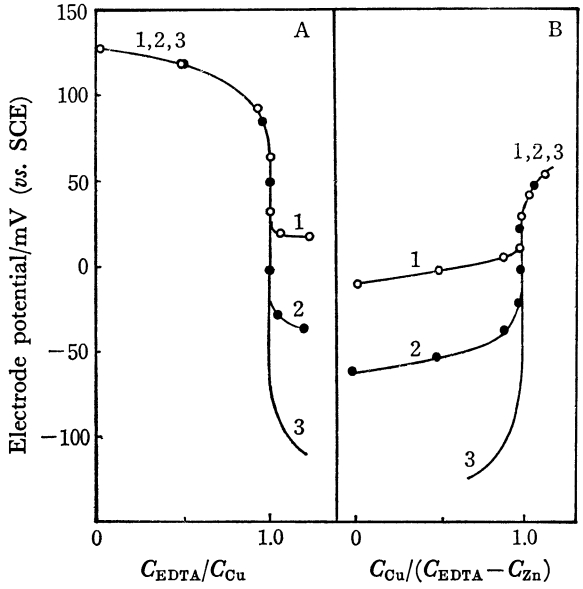

Fig. 5. Titration of copper with EDTA (A) and determination of zinc by back titration of excess EDTA with copper (B).
(A) 1: Cu 2×10^{-3}M, pH 5.8 (0.1M HOAc-OAc^-), 2: the same as 1 but 10^{-5}M 1,10-phenanthroline added, 3: theoretical curve.
(B) 1: Zn 2×10^{-3}M, EDTA 4×10^{-3}M, 2: the same as 1 but 10^{-5}M 1,10-phenanthroline added, 3: theoretical curve.

excess of EDTA with copper(II) ion standard solution. In these cases the potential jump at the equivalence point is depressed by the following exchange reaction:

$$ZnY^{2-} + Cu^{2+} \rightleftharpoons CuY^{2-} + Zn^{2+}$$

Thus the electrode response in the low copper(II) ion levels becomes increasingly important to obtain a sharp end point.

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