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# Performances of Lead and Copper(II) Ion-selective Electrodes in Metal Buffer Solutions and the Determination of the Stability Constants of Lead and Copper(II) Complexes

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The behaviour of lead and copper(II) ion-selective electrodes (Denki Kagaku Keiki Co., Japan) at very low activity levels was examined in metal buffer solutions. In the absence of complexing agents, the Nernstian responses were obtained down to $10^{-6}$ mol dm$^{-3}$ ($\mu=0.1$) $Pb^{2+}$ in the pH range from 4 to 7, and down to $10^{-7}$ mol dm$^{-3}$ ($\mu=0.1$) $Cu^{2+}$ in the pH range from 4 to 6. The complexing agents which form stable complexes with Pb or Cu(II) were very effective in lowering the detection limits. The stability constants of the Pb and Cu(II) complexes with several ligands[$CH_3COO^-$, 1,10-phenanthroline(Phen), glycine(Hgly), iminodiacetic acid($H_2$ida), nitrilotriacetic acid($H_3$nta), *etc.*] were determined by measuring the activities of the free Pb or Cu(II) ion in metal buffer solutions. However, in spite of the high stability of the Pb– or Cu(II)–edta complex, the lower limit of the electrode response was abnormally high and the stability constant of Pb– or Cu(II)–edta complex could not be obtained. Some reasons for the abnormalities with EDTA were discussed.

The response of ion-selective electrodes at very low activity levels has been studied in metal buffer solutions.[1–4] Some authors have used ion-selective electrodes for the determination of the stability constants of metal complexes.[5,7] In these cases, measurements of the activitites of free metal ions at a very low level, *i.e.*, $<10^{-5}$ mol dm$^{-3}$, are usually required. On the other hand, in the potentiometric titrations of copper (II) or lead(II) with EDTA by the use of copper(II) or lead ion-selective electrodes, the electrode potentials after the equivalence point were found to be higher than the theoretical values.[6] This deviation implies that the determination of the stability constants of copper(II)- or lead-edta complex with copper(II) or lead ion-selective electrodes is impossible.

In our previous work,[7] the potential response of the Orion copper(II) ion-selective electrode Model 94-29 was examined in various copper(II) buffer solutions containing copper complexes and an excess of the ligand; the stability constants of copper(II) complexes were thus determined successfully. In the cases of the edta$^{4-}$ and nta$^{3-}$ complexes, however, good results could not be obtained, while in the case of 1,10-phenanthroline the electrode responded to $10^{-16}$ mol dm$^{-3}$ of the copper ion. Therefore, we suggested that, for the determination of the stability constants, the lower limits of the electrode response should be checked in a solution containing the same ligand in the same pH range. The use of the ion-selective electrode provides a simple and reliable method for determining the stability constants of metal complexes.

In the present work, the performance of the lead ion-selective electrode from the Denki Kagaku Keiki Co. (DKK), Japan, has been examined, and the stability constants of several lead complexes have been determined. The potential response of the copper(II) ion-selective electrode from the Denki Kagaku Keiki Co. has also been examined, and compared with that of the Orion copper(II) ion-selective electrode Model 94-29.

## Experimental

*Reagents.* A lead(II) standard solution was prepared from analytical-grade lead nitrate and standardized against an EDTA solution by the use of Xylenol Orange as an indicator. A copper(II) standard solution was prepared from metallic copper (99.99% purity).

*Ligands*: Analytical-grade $Na_2H_2edta\cdot 2H_2O$ and $H_3$nta were recrystallized. The other ligands were of an analytical-grade and were used without further purification.

The potassium nitrate was recrystallized from distilled water.

*Apparatus.* Two Hitachi-Horiba F-5 Type pH Meters were used. One was equipped with a lead or copper(II) ion-selective electrode and a Horiba calomel electrode. Before the lead or copper(II) ion-selective electrode was used, the surface of the active membrane was polished with electrode polishing paper from the DKK Co.; then it was soaked in a *ca.* 0.2% $CH_3COONa$–$CH_3COOH$ buffer (pH 6) containing 0.1% $KNO_3$ until the electrode potentials dropped down to −150—−170 mV for the lead ion-selective electrode and to 80—50 mV for the copper(II) ion-selective electrode. The electrodes were kept in distilled water. The calomel electrodes were connected to the test solution *via* a salt bridge of 0.1 mol dm$^{-3}$ $KNO_3$ in agar-agar.

The following cell arrangement was used for measuring the lead or copper(II) ion activities:

| | | | |
|---|---|---|---|
| Pb or Cu(II) ion-selective electrode | test solution | 0.1 mol dm$^{-3}$ $KNO_3$ | calomel electrode (3.33 mol dm$^{-3}$) |

The ionic strength of the test solutions was maintained at 0.1 with $KNO_3$ except in the case of acetate, and measurements were made at 25 °C. During the potential measurements, magnetic stirring was done with a Teflon bar.

The equilibrium potential of this cell is expressed as Eq. 1 from the Nernst equation:

$$E = E' + \frac{RT}{2F}\ln[M^{2+}] \qquad (1)$$

where $E'$ is a constant consisting of the standard potential of the electrode, the junction potential and $(RT/2F)\ln\gamma_{M^{2+}}$, and where $[M^{2+}]$ is the concentration of the lead or copper(II) ion.

*Response Time of Ion-selective Electrode.* The constant potential reading were usually obtained within one minute for $10^{-2}$—$10^{-3}$ mol dm$^{-3}$ metal ion solutions, within 5 minutes in $10^{-6}$ mol dm$^{-3}$ solutions, and within 10 minutes in metal buffer solutions containing less than $10^{-10}$ mol dm$^{-3}$ free metal ions.

## Results

*Potential Response of Pb and Cu(II) Ion-selective Electrodes.* The potential response of a DKK lead ion-selective electrode was examined over the pH range between 3 and 9. The test solutions were prepared by stepwise dilution of a $10^{-2}$ mol dm$^{-3}$ lead standard solution, and the pH was adjusted by adding a dilute $HNO_3$ or NaOH solution. As is shown in Fig. 1, the Nernstian response with a 29.0 mV slope was observed down to $10^{-6}$ mol dm$^{-3}$ lead ion in the pH region of 4—7. The lowest line (D.L.) in Fig. 1 shows the detection limit of the electrode, which was obtained with the solution containing no lead ion. Below these potentials, the electrode no longer responded to the lead ion activity.

In the case of the copper(II) ion-selective electrode, the Nernstian response with a 29.2 mV solpe was obtained down to $10^{-7}$ mol dm$^{-3}$ copper(II) ion in the pH range between 4 and 6 (Fig. 2). The detection limit of the DKK copper(II) ion-selective electrode used in this study was lower by one order than that of the Orion copper(II) ion-selective electrode employed in the previous work.

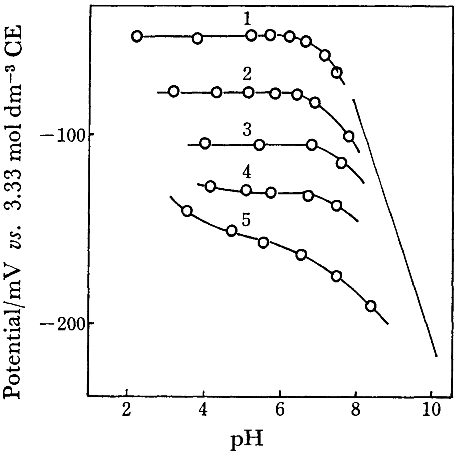

Fig. 1. Potential response of DKK Pb ion-selective electrode at $\mu=0.1$, at 25 °C.
$Pb^{2+}$/mol dm$^{-3}$: 1: $10^{-3}$, 2: $10^{-4}$, 3: $10^{-5}$, 4: $10^{-6}$ 5: detection limit.

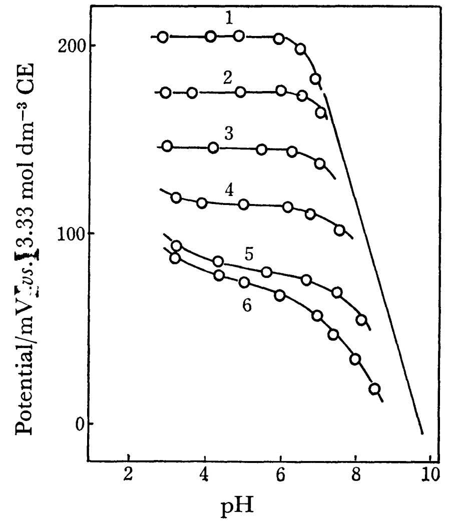

Fig. 2. Potential response of DKK Cu(II) ion-selective electrode at $\mu=0.1$, at 25 °C.
$Cu^{2+}$/mol dm$^{-3}$: 1: $10^{-3}$, 2: $10^{-4}$, 3: $10^{-5}$, 4: $10^{-6}$ 5: $10^{-7}$, 6: detection limit.

*Effects of Complexing Agents on the Detection Limit.* The electrode response was examined in a metal buffer solution containing an excess of complexing agents. The broken lines in Figs. 3 and 4 show the detection limits of the lead and copper(II) ion-selective electrodes in the solutions containing a complexing agent and no metal ion. Complexing agents which form stable complexes with the lead or copper(II) ion were very effective in lowering the detection limit, as was observed in the previous work with the Orion copper(II) ion-selective electrode.[7] With the DKK lead ion-selective electrode, the detection limit was

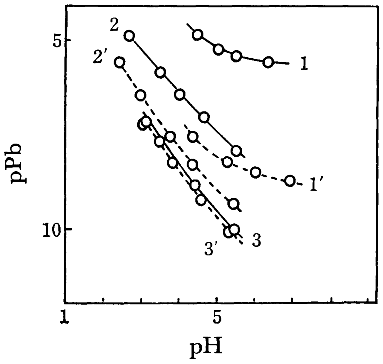

Fig. 3. Electrode response in lead buffer solutions. Broken lines show the detection limits in the solutions containing only complexing agents.
1: $CH_3COO^-$, $C_{Pb}$: $1.03\times10^{-3}$ mol dm$^{-3}$, $C_L$: $5.93\times10^{-2}$ mol dm$^{-3}$, 2: $H_2$nta $C_{Pb}$: $1.01\times10^{-3}$ mol dm$^{-3}$, $C_L$: $5.04\times10^{-3}$ mol dm$^{-3}$, 3: $H_4$edta $C_{Pb}$: $1.01\times10^{-3}$ mol dm$^{-3}$, $C_L$: $5.19\times10^{-3}$ mol dm$^{-3}$.

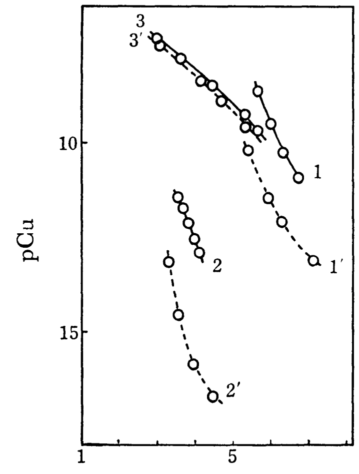

Fig. 4. Electrode response in copper(II) buffer solutions. Broken lines show the detection limits in the solutions containing only complexing agents.
1: $NH_3$, $C_{Cu}$: $1.08\times10^{-3}$ mol dm$^{-3}$, $C_L$: $1.03\times10^{-1}$ mol dm$^{-3}$. 2: phen, $C_{Cu}$: $1.08\times10^{-4}$ mol dm$^{-3}$, $C_L$: $4.74\times10^{-3}$ mol dm$^{-3}$. 3: $H_4$edta $C_{Cu}$: $1.08\times10^{-3}$ mol dm$^{-3}$, $C_L$: $2.06\times10^{-3}$ mol dm$^{-3}$.

around $10^{-6}$ mol dm$^{-3}$ at pH 5 in the absence of complexing agents, while in the presence of 0.01 mol dm$^{-3}$ $H_2$ida the detection limit was around $10^{-10}$ mol dm$^{-3}$ at pH 7. Although $H_4$edta forms stable complexes with lead and copper(II) ions, the detection limits of both the DKK lead and copper(II) ion-selective electrode in $H_4$edta solutions were abnormally high, as with the Orion copper(II) ion-selective electrode.

The solid lines in Figs. 3 and 4 show the electrode potentials observed in lead and copper(II) buffer solutions respectively. The activities of the lead ion in the lead buffer solutions were much higher than the lower response limits of the lead ion-selective electrode except in the case of $H_4$edta. In $H_4$edta solutions the two curves almost coincided with each other; this means that the electrode potential does not give the correct activities of the lead ion in the solution. Again, the DKK copper(II) ion-selective electrode did not respond normally to the activities of the copper(II) ion in the $H_4$edta solution, as may be seen in Fig. 4.

*Determination of Stability Constants of Lead Complexes.* If the electrode potentials represent the true pPb values ($-\log[\mathrm{Pb}^{2+}]$) in the lead-ion buffer solutions, the stability constants of the lead complexes in the buffer solutions can be determined from the electrode potential measured in the presence of the complexes and a large excess of the ligand, L, at different pH values (Fig. 3). The overall stability constants are defined as (charges are omitted for the sake of generality):

$$\beta_n = \frac{[\mathrm{PbL}_n]}{[\mathrm{Pb}][\mathrm{L}]^n}. \tag{2}$$

Thus, the concentration of the free lead ion in a lead-ion buffer solution is given by:

$$\mathrm{pPb} = \log\beta_n + n\log[\mathrm{L}] - \log[\mathrm{PbL}_n]. \tag{3}$$

$[\mathrm{PbL}_n]$ and [L] are calculated by means of Eqs. 4 and 5 respectively;

$$[\mathrm{PbL}_n] = C_{\mathrm{Pb}} - [\mathrm{Pb}], \tag{4}$$

$$[\mathrm{L}] = [C_{\mathrm{L}} - n(C_{\mathrm{Pb}} - [\mathrm{Pb}])]/\alpha_{\mathrm{L(H)}}, \tag{5}$$

where $C_{\mathrm{L}}$ and $C_{\mathrm{Pb}}$ are the total concentrations of the ligand and the lead ion respectively, and where

$$\alpha_{\mathrm{L(H)}} = 1 + \sum_{m=1}^{m}([\mathrm{H}]^m K_1 K_2 \cdots K_m), \tag{6}$$

the successive protonation constants of the ligand being represented as $K_1$, $k_2, \cdots K_m$. From the cell potential measured, pPb was obtained by means of Eq. 1; then $\beta_n$ could be calculated. In Fig. 5 the pPb values are plotted against pL($-\log$[L]); straight lines with the slopes of 1 and 2 with $CH_3COO^-$ and Hgly, of 1, 2, and 3 with phen, and of 1 with 8-hydroxy-5-quinolinesulfonic acid($H_2$oxs), $H_2$ida, and $H_3$nta were obtained, while with $H_4$edta the slope was 0.4 instead of 1. Except for $H_4$edta, the values of the stability constants of the lead complexes obtained all agreed with the values reported in the literature.

*Determination of the Stability Constants of Copper(II) Complexes.* The relations between pCu and pL are plotted in Fig. 6. These plots yielded straight lines with slopes of 4 with $NH_3$, of 1 and 2 with $H_2$ida, of 2 and 3 with phen, and of 1 with $H_3$nta, while it was 0.5 with $H_4$edta. Although the Orion copper(II) ion-selective electrode employed in the previous work did not give reliable results for the copper(II)–edta or nta complex, with the DKK copper(II) ion-selective electrode a good result was obtained for the $H_3$nta complex.

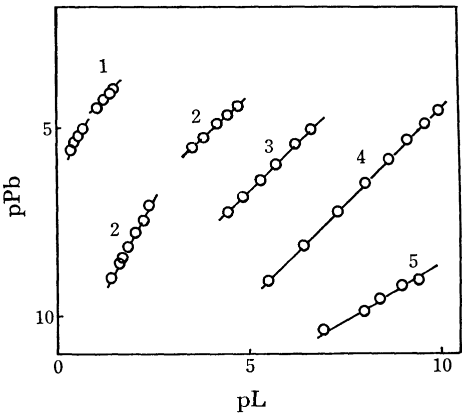

Fig. 5. Plots of pPb *vs.* pL.
1: $CH_3COO^-$, 2: Hgly, 3: $H_2$ida, 4: $H_3$nta, 5: $H_4$edta.

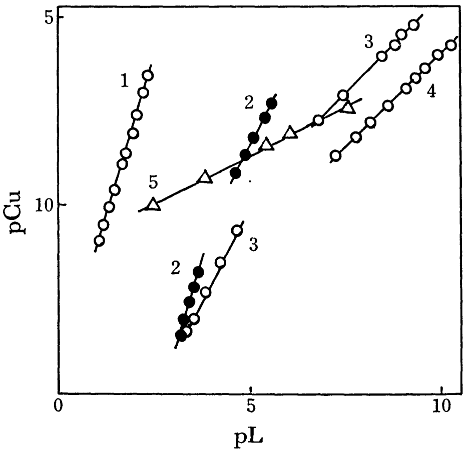

Fig. 6. Plots of pCu *vs.* pL.
1: $NH_3$, 2: phen, 3: $H_2$ida, 4: $H_3$nta, 5: $H_4$edta.

The stability constants of the lead and copper(II) complexes determined in this study are summarized in Table 1, along with the values in the literature.[8,9]

*Application to EDTA Titrations.* The potentiometric titration of lead with EDTA was carried out by means of the lead ion-selective electrode. The results are shown in Fig. 7. The electrode potentials after the equivalence point leveled out at the detection limit of the electrode and deviated from the theoretical titration curves in a way similar to that is the case with the Orion copper(II) ion-selective electrode.

## Discussion

The active membranes of the DKK copper or lead ion-selective electrodes consist of mixed sulfides of copper(II) or lead and silver(I), as is the case of the Orion electrodes. Recently several papers have been published concerning the electrode potential of the mixed-sulfide membrane electrodes; however, the mechanism

Table 1. Stability constants of Pb or Cu(II) complexes (25 °C, $\mu=0.1$)

| Ligand | log $\beta$ | | | |
|---|---|---|---|---|
| | Pb(II) Complexes | | Cu(II) Complexes | |
| | (Determined) | (Literature) | (Determined) | (Literature) |
| $CH_3COO^-$ | $\beta_1$ 2.09 | 2.1 | $\beta_2$ 2.58 | 2.7 |
| | $\beta_2$ 3.29 | 3.3 | ($\mu=1.0$) | |
| $NH_3$ | | | $\beta_4$ 12.49[a] | 12.59 |
| | | | 12.53 | |
| en | | | $\beta_2$ 19.40 | 19.60 |
| bpy | | | $\beta_2$ 13.65 | 13.57 |
| | | | $\beta_3$ 16.75 | 17.0 |
| phen | $\beta_1$ 4.8 | 4.65 | $\beta_2$ 15.8 | 15.4 |
| | $\beta_2$ 7.8 | 7.5 | $\beta_3$ 19.8 | 20.4 |
| | $\beta_3$ 10.3 | ~9 | | |
| Hgly | $\beta_1$ 5.00 | 5.1 | $\beta_2$ 15.28 | 15.1 |
| | $\beta_2$ 7.73 | 7.7 | | |
| $H_2$ida | $\beta_1$ 7.67 | 7.45 | $\beta$ 10.54[a] | 10.5 |
| | | | 10.48 | |
| | | | $\beta_2$ 16.35 | 16.5 |
| $H_3$nta | $\beta_1$ 11.56 | 11.39 | $\beta_1$ 12.97 | 12.96 |
| $H_2$oxs | $\beta_1$ 7.77 | 7.7 | | |

a) Orion 94-29 Cu(II) electrode.

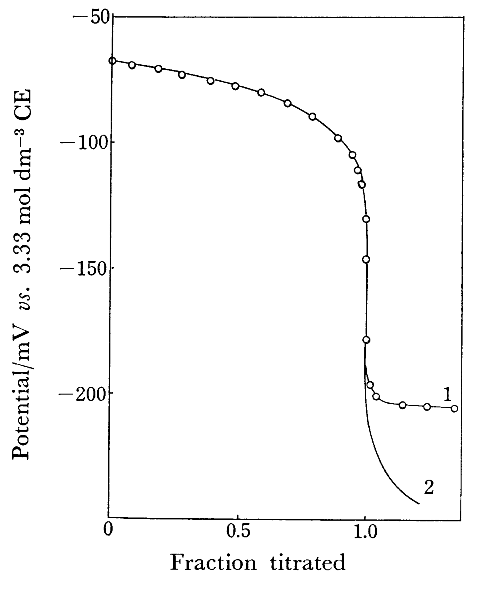

Fig. 7. Titration curve of Pb with EDTA.
1: Experimental, 2: theoretical, $C_{Pb}$: $1.01\times10^{-3}$ mol dm$^{-3}$, $C_{EDTA}$: $1.04\times10^{-2}$ mol dm$^{-3}$, pH 4.3 ($CH_3COOH$–$CH_3COONa$ buffer).

of potential response of these electrodes are not yet fully clarified. As an approximation, the potential response of these electrodes can be understood by considering these materials as the third class of electrodes for the silver(I) ion;

$$Ag_2S + M^{2+} \rightleftharpoons MS + 2Ag^+. \qquad (7)$$

Thus, the electrode potentials are given by

$$E = {}^\circ E_{Ag^+/Ag} + \frac{RT}{2F}\ln\frac{K_{s(Ag_2S)}}{K_{s(MS)}} + \frac{RT}{2F}\ln a_{M^{2+}}. \qquad (8)$$

The difference in the detection limits between the DKK copper(II) electrode and the Orion copper(II) electrode may be attributed to the differences in the methods of preparing the mixed sulfides and the membranes. Although the detection limits of ion-selective electrodes were determined by the solubility of the active materials of the electrode, the observed detection limits of the lead and copper(II) electrodes were much higher than the values calculated from solubility of PbS or CuS; for example, at pH 4 the solubilities of PbS and CuS are calculated to be around $10^{-9}$ mol dm$^{-3}$ and $10^{-14}$ mol dm$^{-3}$ respectively. This may be caused by the high activities of lead or copper (II) at the membrane surface resulting from the adsorption of these ions. The strong complexing agent reduces the activities of the copper(II) or lead ion at the membrane surface and shifts the detection limits to lower levels

In $H_4$edta solutions the detection limits of the lead and copper(II) ions were abnormally high compared with those in the solutions containing the other complexing agents. This fact is explained as follows. Since the stability of the silver complex with edta$^{4-}$ is very small in comparison with the stability of the lead- or copper(II)-edta complex, the decrease in the activity of the silver ion at the membrane surface is not so marked as the decrease in the lead or copper(II) ion activity. Therefore, the equilibrium represented by Eq. 7 is shifted to the left, and finally the surface of the active membrane is converted to $Ag_2S$. Thus, the electrode would lose its selectivity toward the lead or copper(II) ion, and the detection limits may be determined by the activity of the silver ion at the membrane surface. On the other hand, complexing agents which form fairly stable complexes with both silver and lead or copper(II) ions, such as phen, may shift the detection limits of these electrodes to a very low level. If the electrode potential measured in the metal buffer solution is sufficiently higher than the detection limits measured in the solution containing the same ligand, reliable stability constants of the metal complexes can be determined.

Recently, it was found that a mixed sulfide of copper(I) and silver(I) such as $Ag_{1.55}Cu_{0.45}S$ was formed in the active material of the copper(II) ion-selective electrode.[10,11] Since $H_4$edta forms weaker complex with the Cu(I) ion than with the Cu(II) ion, the high activities of the copper(I) ion at the membrane surface may also interfere with the measurement of the activities of copper(II) at very low levels.

Although some authors[1,12] have recommended the use of a metal buffer system which consists of copper(II)–edta or lead–edta for the calibration of the copper(II) or lead ion-selective electrode at low activitity levels, other metal buffer systems rather than $H_4$edta are to be preferred.

Part of this study was presented at the 26th International Congress of Pure and Applied Chemistry, Tokyo (1977).

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