

Use of Ligand Buffers in the Determination of the Stability Constants of Metal Complexes with Ion-Selective Electrodes

Akio YUCHI, Hiroko WADA and Genkichi NAKAGAWA

Laboratory of Analytical Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466

The potential response of copper(II), lead and cadmium ion-selective electrodes was studied in ligand buffers which contain a complex ML ($M: Cu^{2+}, Pb^{2+}$ or Cd^{2+}), a ligand L and an excess of a second metal N . By measuring $[M]$ with the ion-selective electrode, the ratio of the stability constants, K_{ML}/K_{NL} was determined. The effects of pH, the second metal ion N and the ratio of $[N]/[NL]$ on the electrode response were studied in detail. The K_{ML}/K_{NL} values obtained for EDTA were in good agreement with those calculated from K_{ML} and K_{NL} in the literature. The stability constants of N -hydroxyethylenediamine- N,N',N' -triacetate complexes were determined successfully. These logarithmic values of K_{NL} were found: Pb^{2+} , 15.59; Zn^{2+} , 14.59; Co^{2+} , 14.49; Cd^{2+} , 14.24; Mn^{2+} , 11.41. These results show that the method is very useful for the determination of the stability constants of complexes with metal ions for which suitable ion-selective electrodes are not available.

Keywords Ion-selective electrode, determination of the stability constant, ligand buffer, metal exchange reaction

Ion-selective electrodes have been increasingly used in the study of solution equilibria. Previously, the performance of copper(II), lead and cadmium ion-selective electrodes consisting of mixed sulfides of silver and one of these metals was studied in various metal buffer solutions¹⁻³. In the presence of an excess of ligand, ion-selective electrodes usually extend the dynamic concentration range to a low level, and very low concentrations of the free metal ion can be measured. Then the stability constants of the metal complexes can be determined. But with aminopolycarboxylates which form rather stable complexes, such as EDTA and ethyleneglycolbis(2-aminoethylether)- N,N,N',N' -tetraacetate (EGTA) the ion-selective electrodes do not give the correct $pM(-\log[M])$ value in the solutions, and the attainment of a constant electrode potential was extremely slow. Even with these ligands, a correct response could be obtained in the low pH range as a result of a decrease in the conditional stability constants of the metal complexes due to the protonation of the ligand.

Another way to diminish the conditional stability constants is to use a "ligand buffer" system by adding an excess of a second metal ion N .⁴ Such a system is encountered also in the complexometric titration of M with a ligand L in the presence of a second metal N , and potentiometric titration of a metal N by measuring pM with an ion-selective electrode sensitive to M in the presence of an indicator ML .⁵⁻⁷ Hansen and Růžička briefly mentioned the use of an exchange reaction to

determine the stability constants of metal complexes.⁸ This paper describes the response of the copper, lead and cadmium ion-selective electrodes in ligand buffer systems involving aminopolycarboxylates and the results for the determination of the stability constants of N -hydroxyethylethylenediamine- N,N',N' -triacetate (HEDTA) complexes with various metal ions.

Experimental

Reagents

Stock solutions of metal ions (10^{-2} mol dm^{-3}) were prepared from their nitrates which had been recrystallized twice; the solutions were standardized against EDTA solution. Other reagents were the same as described previously.³

Procedure

All measurements were carried out in an air bath thermostated at 25.0 ± 0.5 °C; the ionic strength was kept at 0.10 mol dm^{-3} with potassium nitrate. Apparatus and methods for measuring the potential were the same as described previously.³ Two types of titrations were carried out.

Titration with potassium hydroxide. The solution containing a metal complex ML , the ligand L , and a second metal ion N in excess was titrated with a 0.10 mol dm^{-3} of potassium hydroxide solution. The total con-

centrations of M, L and N were kept constant during the titration. The concentration [M] of the free metal ion was monitored with an ion-selective electrode as a function of hydrogen ion concentration. When Mn^{2+} was used as a second metal ion, batch measurement was employed to avoid the air oxidation of the manganese complex during the titration.

Titration with N. The solution containing 10^{-3} mol dm^{-3} of M, 1.1×10^{-3} mol dm^{-3} of L and 0.01 mol dm^{-3} of 2-(N-morpholino)ethanesulfonic acid (MES)-sodium hydroxide buffer (pH 5.8) was titrated with a 8×10^{-2} mol dm^{-3} solution of a second metal ion N.

Results and Discussion

In the solution containing metal complexes ML, NL ($K_{ML} > K_{NL}$) and the metal ion N in excess, the concentration of free ligand [L] is buffered at a low concentration level with the excess metal ion N and/or hydrogen ion H^+ , and the following stoichiometric relations hold⁴:

$$C_M = [ML] + [M] \quad \dots\dots\dots (1)$$

$$C_N = [NL] + [N] \quad \dots\dots\dots (2)$$

$$C_L = [ML] + [NL] + [L'] \quad \dots\dots\dots (3)$$

where C_i ($i=M, N, L$) is the total concentration of M, N and L, respectively, and $[L']$ denotes the total concentration of L not combined with M or N.

The conditional stability constant, K'_{ML} , is expressed as

$$K'_{ML} = \frac{K_{ML}}{\alpha_{L(N,H)}} \quad \dots\dots\dots (4)$$

where $\alpha_{L(N,H)}$ is the side reaction coefficient of the ligand L taking into account the complexation with N as well as the protonation,

$$\alpha_{L(N,H)} = \alpha_{L(H)} + K_{NL}[N] \quad \dots\dots\dots (5)$$

where $\alpha_{L(H)}$ is that only by protonation.

$K_{NL}[N] > \alpha_{L(H)}$:

From Eqs. 1-5 the following relation holds:

$$\frac{K_{ML}}{K_{NL}} = \frac{[ML][N]}{[M][NL]} = \frac{(C_M - [M])(C_N - C_L + C_M - [M])}{[M](C_L - C_M + [M])} \quad \dots\dots\dots (6)$$

i.e. [M] is independent of $[H^+]$ and determined only by K_{ML} , K_{NL} and $[N]/[NL]$. When the potentials of the ion-selective electrode correctly reflect [M] in the solution, K_{ML} or K_{NL} can be determined if K_{NL} or K_{ML} is known.

$K_{NL}[N] < \alpha_{L(H)}$:

In this case the second metal ion N does not affect

Table 1 Determination of the stability constants of EDTA complexes

| No. | N | $10^3 C_N / \text{mol } dm^{-3}$ | pM | $\log (K_{ML} / K_{NL})$ | $\log K_{NL}$ | |
|---------------------------|-----------|----------------------------------|----------------|--------------------------|---------------|-------------------------|
| | | | | | Obtained | Literature ^a |
| M, Cu^{2+} ^b | | | | | | |
| 1 | none | | | | 18.80 | 18.87 |
| 2 | Pb^{2+} | 0.958 | 3.67 | 0.87 | 17.93 | 18.04 |
| 3 | Zn^{2+} | 1.013 | 4.21 | 2.34 | | |
| 4 | Zn^{2+} | 1.013 | 4.68 | 2.55 | 16.25 | 16.24 |
| 5 | Zn^{2+} | 2.026 | 5.69 | 2.52 | 16.28 | |
| 6 | Cd^{2+} | 0.988 | 4.73 | 2.60 | 16.20 | 16.54 |
| 7 | Mn^{2+} | 0.987 | 6.84 | 4.82 | 13.98 | 14.05 |
| 8 | Ca^{2+} | 1.852 | 8.15 | 7.75 | | |
| 9 | Ca^{2+} | 0.926 | 10.20 | 8.13 | 10.67 | 10.78 |
| 10 | Ca^{2+} | 1.852 | — ^e | | | |
| 11 | Mg^{2+} | 1.027 | — ^e | | | |
| 12 | Mg^{2+} | 9.800 | — ^e | | | |
| M, Pb^{2+} ^c | | | | | | |
| 13 | none | | | | 17.89 | 18.04 |
| 14 | Zn^{2+} | 1.013 | 4.23 | 1.75 | 16.14 | 16.24 |
| 15 | Mn^{2+} | 0.987 | 6.28 | 3.99 | 13.90 | 14.05 |
| 16 | Ca^{2+} | 0.926 | 9.60 | 7.28 | 10.61 | 10.78 |
| 17 | Mg^{2+} | 9.800 | — ^e | | | |
| M, Cd^{2+} ^d | | | | | | |
| 18 | none | | | | 16.59 | 16.54 |
| 19 | Zn^{2+} | 1.013 | 3.43 | 0.23 | 16.36 | 16.24 |
| 20 | Mn^{2+} | 0.987 | 4.62 | 2.35 | 14.24 | 14.05 |
| 21 | Ca^{2+} | 0.926 | 8.02 | 5.81 | 10.78 | 10.78 |
| 22 | Mg^{2+} | 9.800 | — ^e | | | |

a, Ref. 10, 11; b, $C_{Cu} = 1.014 \times 10^{-3}$ mol dm^{-3} , $C_L = 1.019 \times 10^{-3}$ for No. 3 and 8, 2.227×10^{-3} for No. 5 and 10, and 1.113×10^{-3} mol dm^{-3} for others; c, $C_{Pb} = 0.958 \times 10^{-3}$ mol dm^{-3} , $C_L = 1.113 \times 10^{-3}$ mol dm^{-3} ; d, $C_{Cd} = 0.988 \times 10^{-3}$ mol dm^{-3} , $C_L = 1.113 \times 10^{-3}$ mol dm^{-3} ; e, no constant pM value.

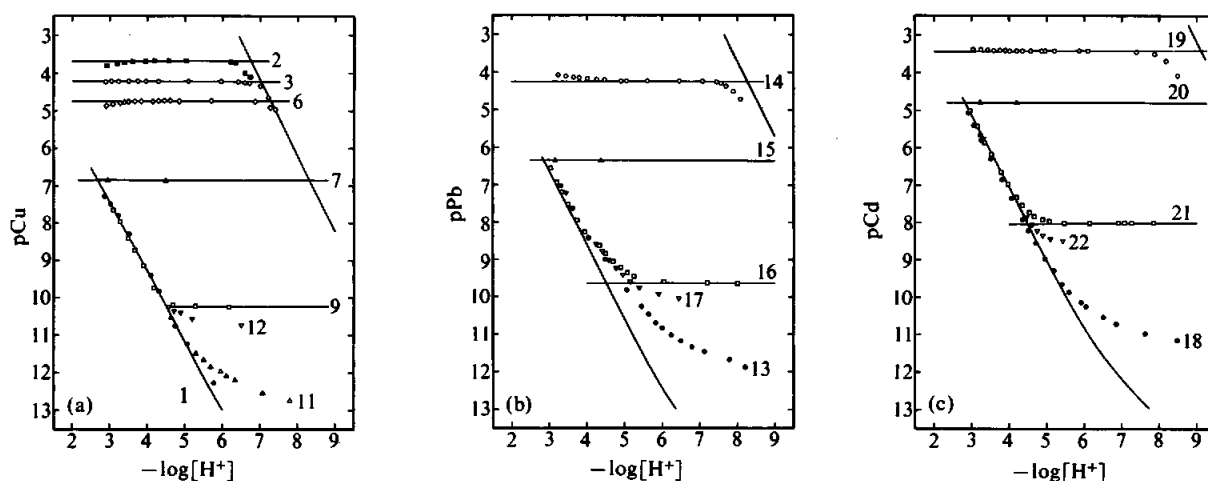


Fig. 1 $pM \sim -\log[H^+]$ diagram for EDTA system.

M: Cu^{2+} for (a), Pb^{2+} for (b), Cd^{2+} for (c). See Table 1 for identification of curves and experimental conditions.

the electrode potentials and the potentials are determined by K_{ML} , $[ML]/[L]$ and pH.

$pM \sim -\log[H^+]$ diagram for EDTA system

The logarithmic concentration of free metal ion, pM , was measured as a function of $-\log[H^+]$ with various second metal ions. Experimental conditions are summarized in Table 1. Figure 1(a) shows the $pCu \sim -\log[H^+]$ diagram. The solid circles are the data obtained with the solution containing no second metal ion. Experimental pCu values deviated from the calculated curve at $-\log[H^+] > 5$. The electrode correctly responded to pCu up to higher $-\log[H^+]$ than that in the previous work^{1,2}, because in this study the ratio of C_L/C_{Cu} was kept at 1.1 instead of 2, and the pCu value was at a lower level. The stability constant of copper-EDTA complex was obtained from the pCu values in the $-\log[H^+]$ range of 4-5 (Table 1).

On the addition of an excess of a second metal ion N, pCu values were buffered at a certain low level and became independent of $-\log[H^+]$. The larger the stability constant of EDTA complex with the second metal was, the lower the pCu value of the flat portion. When lead, cadmium or zinc was used as a second metal ion, small deviations in pCu values from horizontal lines were observed in a low $-\log[H^+]$ range ($-\log[H^+] < 3$). These are quantitatively explained by considering the formation of the protonated EDTA complexes of copper and these metal ions, $\log K_{MLH}^H$: 3.00 for copper, 2.83 for lead, 2.93 for cadmium and 3.00 for zinc.

The effect of the $[N]/[NL]$ ratio on the response of the copper ion-selective electrode was examined with zinc and calcium, by changing C_L and C_N , while keeping C_{Cu} constant. The pCu value of the flat portion should decrease by one if the $[N]/[NL]$ ratio is increased by one order. When C_L became close to C_M , the

value of K_{CuL}/K_{NL} was subject to much error simply because of the large error in the evaluation of $[NL]$ from the difference between C_L and C_M (No. 3 and 8 in Table 1). In the case of zinc ion, correct pCu values and hence K_{CuL}/K_{ZnL} were obtained over a wide range of the $[N]/[NL]$ ratio. In the case of calcium ion, however, a good result was obtained only at $[N]/[NL]$ ratio around 10. At the ratio around unity, the pCu value was located beyond the dynamic pCu range of the copper ion-selective electrode. In the case of magnesium ion, no flat portion was obtained even at $[N]/[NL]=100$.

Figures 1(b) and 1(c) represent the $pM \sim -\log[H^+]$ diagrams for lead and cadmium ion-selective electrodes. The results summarized in Table 1 show that the method is very useful for the determination of the stability constants of metal complexes.

Determination of the stability constants of HEDTA complexes

Since pM is independent of $-\log[H^+]$ in ligand buffer systems, the solution containing copper(II) ion and an excess ligand (EDTA, HEDTA) was titrated with various second metal ions at $-\log[H^+] = 5.80$, and the pCu values were measured with a copper(II) ion-selective electrode. The potential response was fairly fast (within 10 min) in the range $C_N > (C_L - C_M)$.

The ratio of K_{CuL}/K_{NL} was calculated from pCu according to Eq. 6. The results for EDTA were in good agreement with those obtained from $pM \sim -\log[H^+]$ diagram. For HEDTA, no consistent value was obtained in the case of calcium ion under the conditions examined.

From the measurements in the metal buffer solution of HEDTA, K_{CuL} was determined to be $10^{17.36}$. This value is in good agreement with that given by Moeller and Ferrus ($10^{17.40}$)¹², and is reliable enough to be used as a basis for the calculation of K_{NL} . The

Table 2 Determination of the stability constants of HEDTA complexes

| Metal ion N | log (K_{CuL}/K_{NL}) | log K_{NL} | |
|------------------|--------------------------|-----------------------|---|
| | | Measured ^a | Literature |
| Pb ²⁺ | 1.77 | 15.59 | 15.5 ^b |
| Zn ²⁺ | 2.77 | 14.59 | 14.5 ^b , 14.5 ^c |
| Co ²⁺ | 2.87 | 14.49 | 14.4 ^c |
| Cd ²⁺ | 3.12 | 14.24 | 13.0 ^c , 13.6 ^d 14.27 ^e |
| Mn ²⁺ | 5.95 | 11.41 | 10.7 ^c |

a, Using log K_{CuL} = 17.36; b, J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960); c, S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955); d, Y. Koike and H. Hamaguchi, *J. Inorg. Nucl. Chem.*, **29**, 473 (1967); e, ref. 3.

stability constants of the other metal complexes were calculated from K_{CuL}/K_{NL} and K_{CuL} (Table 2). These constants are in good agreement for Pb²⁺, Zn²⁺ and Co²⁺ with those in the literature and for Cd²⁺ with that determined in metal buffer solutions by the use of a cadmium ion-selective electrode.³

In conclusion, use of ligand buffer systems provides a simple and reliable method for the determination of the stability constants of metal complexes with ion-selective electrodes. By selecting large [N]/[NL] ratios, pM can be measured even for the second metal ions which have relatively small stability constants. A copper ion-selective electrode is widely applicable because of its large selectivity toward other metal ions. Schmid and Reilley employed a mercury electrode for the same purpose.⁹ Ion-selective electrodes have advantages for the measurements in the presence of easily oxidizable complexes such as Co(II),

Fe(II) and Mn(II).

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