

Use of a Silver Ion Selective Electrode for the Determination of Stability Constants of Metal Complexes

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The potential response of a sulfide-based silver ion selective electrode was examined in various metal buffer solutions. In every system tested, the potential response of the electrode was rapid and the electrode potential correctly reflected the free silver ion concentration in the solution. The stability constants of silver complexes with seven ligands were determined. This electrode was used also to measure the free cyanide ion concentration in the solutions containing silver, cyanide and a second metal ion. The stability constants of zinc and cadmium cyano complexes were obtained. The behavior of the silver ion selective electrode is discussed in contrast to that of the mixed sulfide membrane electrodes.

Keywords Silver ion selective electrode, stability constant, metal buffer, ligand buffer

The response of the copper, lead and cadmium ion selective electrodes has been studied in various metal buffer solutions.¹⁻³ The active materials of these electrodes consist of mixed sulfides of silver and one of these metals. In many metal buffer systems, they gave correct potentials reflecting the free metal ion concentrations even at very low levels, and can be used for the determination of the stability constants of these metal complexes. In the cases of aminopolycarboxylates such as EDTA and CDTA⁴, however, the response was extremely slow and the potential was extraordinarily high. Some reasons for these abnormalities have been discussed.¹⁻³ Even in these cases, reasonable potentials were obtained by the use of ligand buffer systems.^{5,6}

Sulfide-based silver ion selective electrodes have been used to monitor silver or sulfide ion in unbuffered solutions. These electrodes have been used also for the potentiometric titration of cyanide and sulfide with silver ions.⁷⁻¹⁴ In these titrations, the solution is a silver ion buffer before the equivalence point, but no quantitative interpretation has been presented. This paper deals with the response of a sulfide-based silver ion selective electrode in various metal buffer solutions. The performance of the silver ion selective electrode was compared with that of copper, lead and cadmium ion selective electrodes. Furthermore, an excess of the second metal, such as zinc or cadmium, was introduced in the silver-cyanide system to make a cyanide buffer. The free cyanide concentration in equilibrium with the second metal ion and its cyanide complexes was measured with this electrode.

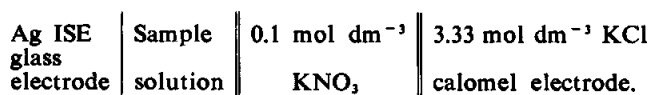
Experimental

Reagents

A 0.03 mol dm⁻³ silver ion solution was prepared by dissolving the nitrate and was standardized against sodium chloride solution potentiometrically. The solution was stored in a cool and dark place, and diluted just before use.¹⁵ Zinc and cadmium ion solutions were prepared from their nitrates and standardized against EDTA. All the ligands were of analytical-reagent grade, and cyanide and thiosulfate were standardized against silver ion potentiometrically. Potassium nitrate was recrystallized twice. Carbonate-free potassium hydroxide was prepared as described previously.¹⁶

Procedure

All the measurements were done in an air-bath thermostated at 25±0.5°C. The ionic strength was kept at 0.10 mol dm⁻³ KNO₃. The electro-chemical cell used was



The silver ion selective electrode (AgISE) was a Denki Kagaku Keiki Co. (DKK, Tokyo) type 7080 electrode, of which active membrane was prepared by pressing silver sulfide powder. The surface of the electrode was repeatedly rinsed before use and the e.m.f. was read with a DKK ion meter IOC-10 to 0.1 mV. Hydrogen ion concentration was determined with a Radiom-

eter PHM-64 pH meter equipped with a Radiometer glass electrode(G202C). A 1.00×10^{-3} mol dm $^{-3}$ silver solution and a 1.00×10^{-2} mol dm $^{-3}$ nitric acid solution were used as the potential standards of pAg(= $-\log[\text{Ag}^+]$)=3.00 and $-\log[\text{H}^+]$ =2.00, respectively. The change in liquid-junction potential with hydrogen ion concentration was taken into account.³

For cyanide and thiosulfate systems, solutions containing silver ion were titrated with ligand solutions. For other systems, solutions containing silver ions, an excess of a ligand and nitric acid were titrated with a potassium hydroxide solution. The silver ion concentration was monitored as a function of hydrogen ion concentration (see Table 1 for experimental conditions). The total concentration of silver ion was decreased in the case of bpy because of the low solubility of its bis complex.

For ligand buffer systems 2-(*N*-morpholino)ethane-sulfonic acid solutions containing 0.5–1.0 mmol dm $^{-3}$ silver ion, an excess of cyanide and a second metal ion (0.4–0.5 mmol dm $^{-3}$ for zinc and 0.5–1.0 mmol dm $^{-3}$ for cadmium) were titrated with a cyanide solution up to 2–4 mmol dm $^{-3}$. The titration was continued until the contribution of the hydrolyzed species of the second metal ion ceased to be negligible.

Results and Discussion

Calibration curve

The silver ion selective electrode was calibrated with several silver nitrate solutions between 10^{-2} – 10^{-7} mol dm $^{-3}$ made by serial dilution of the stock solution. Nernstian response with a 59 mV slope was obtained down to 10^{-6} mol dm $^{-3}$. Below this level the potential was very unstable and depended largely on the concentration of silver ion in the preceding measurement. After the electrode was rinsed repeatedly with water, the solution containing no silver ion showed a potential around 50 mV, which corresponded to

around 10^{-8} mol dm $^{-3}$ free silver ions.

Potential response in metal buffer systems

The potential response of the silver ion selective electrode was examined in the seven silver buffer solutions listed in Table 1. The ligands having various donor atoms were chosen so as to provide different complexation characteristics, *i.e.* aromatic nitrogen (py and bpy), aliphatic nitrogen (NH $_3$), aliphatic nitrogen and oxygen (EDTA and CDTA), sulfur (S $_2$ O $_3^{2-}$) and carbon(CN $^-$).

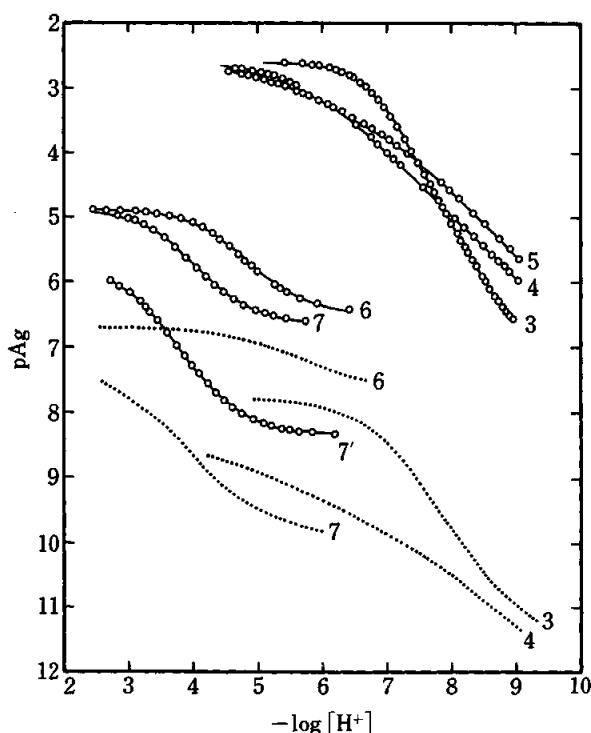


Fig. 1 Electrode response in silver buffer solutions. See Table 1 for identification of curves and experimental conditions. Solid lines: curves calculated with the constants obtained. Dotted lines: detection limit in each ligand solution (see text for details).

Table 1 Experimental conditions and stability constants of silver complexes

No.	Ligand	$C_{\text{Ag}}/\text{mol dm}^{-3}$	$C_{\text{L}}/\text{mol dm}^{-3}$	Stability constants					
				log β_1	log β_2	log K^a	log β_1	log β_2	log K^a
1	CN $^-$	2.558×10^{-3}	vary	—	20.61	—	—	20.44 ^b	—
2	S $_2$ O $_3^{2-}$		vary	9.52	13.08		9.23 ^b	12.50 ^b	
3	NH $_3$		9.190×10^{-2}	3.41	7.26		3.40	7.40	
4	EDTA		5.002×10^{-3}	7.32		6.19	7.31		6.49
5	CDTA		4.882×10^{-3}	8.40		6.74	8.41		—
6	py	1.445×10^{-5}	6.394×10^{-2}	2.33	4.13		1.90	4.25	
7	bpy	1.259×10^{-5}	3.112×10^{-3}	3.44	6.78				6.8
7'	bpy	1.413×10^{-6}	7.056×10^{-3}						

a. $K = [\text{AgHL}]/[\text{AgL}][\text{H}]$.

b. Under different conditions.

c. L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes, and Supplement No. 1" The Chemical Society, London, 1964 and 1971.; IUPAC, "Stability Constants of Metal-ion Complexes, Part A and B", Pergamon, Oxford, 1979 and 1982.

The decrease in the potential of the silver ion selective electrode by complexation was rapid in every system and at any $-\log[H^+]$. The pAg value calculated from the equilibrium potential was plotted against $-\log[H^+]$ in Fig. 1.

The detection limit of the electrode was also measured in the solution containing the same ligand and no silver ions^{1,2}, and converted to pAg as shown by dotted lines in Fig. 1. The limit depends very much upon the ligand and $-\log[H^+]$. In each system the pAg vs. $-\log[H^+]$ curve of the detection limit is similar to that of the metal buffer system in shape but shifted far below. The shift is large compared with that in the case of mixed sulfide electrodes.^{1,2} The curve of the detection limit corresponds to that of the hypothetical metal buffer solution containing 10^{-6} to $10^{-8.5}$ mol dm⁻³ silver ion.

If AgL_n is mainly formed with the overall stability constant, $\beta_n = [AgL_n]/[Ag][L]^n$ (charges are omitted), the following relation holds:

$$pAg = -npL + (\log \beta_n - \log C_{Ag}).$$

Then a plot of pAg against pL ($-\log[L]$) should give a straight line with a slope of $-n$.

The experimental results are shown in Fig. 2. The stability constants obtained from the intercept of the tangent to the curves were refined to make $U = \sum(pAg_{\text{obsd}} - pAg_{\text{cald}})^2$ minimum. Very close values were obtained in the case of bpy even under very different conditions

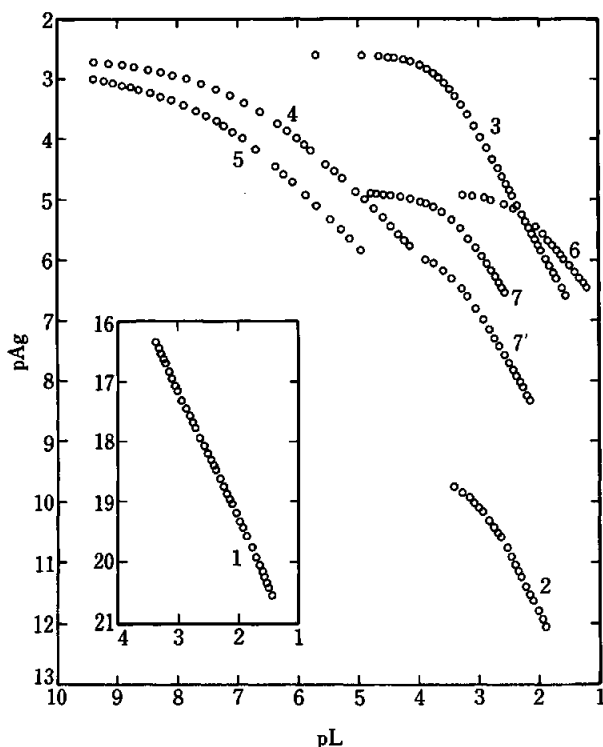


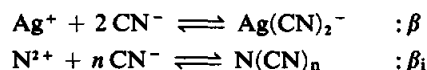
Fig. 2 Plot of pAg vs. pL. See Table 1 for identification of curves and experimental conditions.

($\log \beta_1: 3.43$ for 7, 3.45 for 7'; $\log \beta_2: 6.74$ for 7, 6.81 for 7'). These values are summarized in Table 1 together with those reported in the literature. The calculated curve using the constants obtained are shown as solid lines in Fig. 1.

In EDTA or CDTA system, reasonable potentials were observed at any $-\log[H^+]$ in contrast to copper, lead and cadmium ion selective electrodes.¹⁻³ The stabilities of the silver complexes with these ligands are not so high, and the pAg value does not decrease so much. On the other hand, copper, lead and cadmium form more stable complexes with these ligands. The potential of the mixed-sulfides membrane electrodes in the metal buffer solutions containing these ligands is limited by the silver ions which originate from the electrode material; this could be the reason for the abnormally high potential.¹⁻³

Potential response in ligand buffer systems

The potential response of the silver ion selective electrode in ligand buffer systems and its application to the determination of the stability constants were examined. In the system consisting of silver, cyanide and a second metal ion N such as Zn^{2+} or Cd^{2+} , cyanide preferentially coordinates to silver ion, because the silver complexes are more stable than those of the second metal. Excess cyanide reacts with the second metal ion.



As $[Ag(CN)_2^-] = C_{Ag}$, $[CN^-]$ can be calculated with $[Ag^+]$, which is obtained from the electrode potential.

$$[CN^-] = (C_{Ag}/\beta[Ag])^{1/2}$$

The average number of cyanide ions bound to the second metal N, \bar{n} , can be calculated

$$\bar{n}_{\text{obsd}} = \frac{C_{CN} - [CN^-] - [HCN] - 2[Ag(CN)_2^-]}{C_N}$$

where C_N and C_{CN} are the total concentrations of the second metal and cyanide ion, respectively.

The plot of \bar{n} vs. $-\log[CN^-]$ is shown in Fig. 3. The function did not shift by changing the total concentration of the second metal ion. On the other hand, the \bar{n} value is written as

$$\bar{n}_{\text{cald}} = \frac{\sum i\beta_i[CN^-]^i}{\sum \beta_i[CN^-]^i}$$

where β_i is the overall stability constant of $N(CN)_i$. These constants were refined to give the minimum error square sum, $U = \sum(\bar{n}_{\text{cald}} - \bar{n}_{\text{obsd}})^2$. The constants thus obtained are in good agreement with the literature values (Table 2).

The silver ion selective electrode gave the Nernstian

Table 2 Logarithmic overall stability constants of metal cyanide complexes

Metal ion	β_1	β_2	β_3	β_4	Temp.	Medium	Reference
Zn^{2+}	5.64	11.04	16.38	21.42	25°C	0.1 KNO ₃	this work
		11.07	16.05	19.62	25°C	dil	a
	5.3	11.0	16.7	21.6	25°C	3 NaClO ₄	b
Cd^{2+}	5.76	10.75	15.72		25°C	0.1 KNO ₃	this work
	5.8	11.1			30°C	0.1 NaClO ₄	c
	5.62	10.8	15.7	19.2	25°C	3 NaClO ₄	b

a. R. M. Izatt, J. J. Christensen, J. W. Hansen and G. D. Watt, *Inorg. Chem.*, **4**, 718 (1965).

b. H. Persson, *Acta Chem. Scand.*, **25**, 543 (1971).

c. H. E. Hellwege and G. K. Schweitzer, *J. Inorg. Nucl. Chem.*, **27**, 99 (1965).

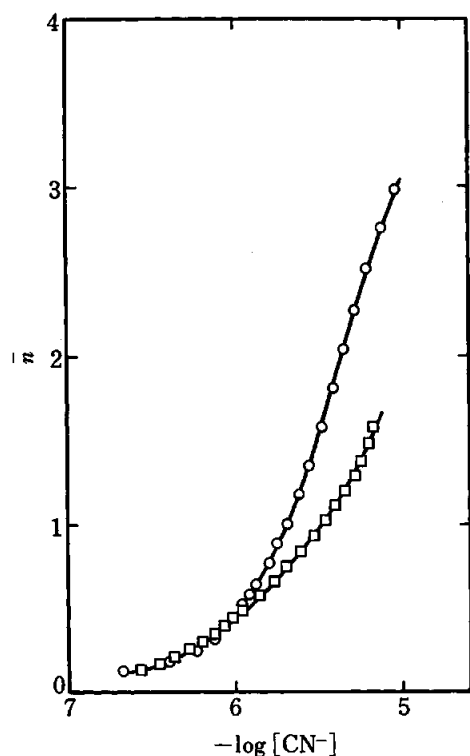


Fig. 3 Plot of \bar{n} vs. $-\log [CN^-]$.

○, Zn^{2+} ; □, Cd^{2+} . The solid lines are curves calculated with the constants obtained.

response to sulfide ion in the absence of silver ion⁷⁻⁹, but not to cyanide ion in the absence of $Ag(CN)_2^-$.¹³ For example, Fleet and von Storp reported that the Nernstian response holds between $10^{-4.7}$ and 10^{-4} mol dm^{-3} cyanide with the expected slope around 120 mV¹¹ in the presence of 10^{-3} mol dm^{-3} $Ag(CN)_2^-$. The standard addition method has been reported efficient for the determination of cyanide ion below 10^{-6} mol dm^{-3} .¹² In this study, the excess cyanide ion was buffered with the second metal, and the electrode proved to work properly even at the 10^{-7} mol dm^{-3} free cyanide level.

Leden first used the silver/silver chloride electrode in the same way for the determination of the stability constants of cadmium sulfato complexes.¹⁷ But the application is limited to moderately stable complexes such as those with phenanthroline and bipyridine, because of the large solubility of $AgCl$.^{18,19} The silver

ion selective electrode is suitable for the determination of the stability constants of the complexes with stronger complexing agents.

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