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Super High Sensitivity of CuSe–Ag_2S Solid Membrane Copper(II) Ion Selective Electrode in Several Metal Buffer Solutions

Yoshio UMEZAWA,* Yuichiro IMANISHI, Katsuhiko SAWATARI,
and Shizuo FUJIWARA
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

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Synopsis. A CuSe–Ag_2S solid membrane Cu(II) ion electrode in certain metal buffer solutions gave detection limit of free Cu(II) ion as low as 10^{-18}M.

Nakagawa and his coworkers observed extremely high sensitivity of copper(II) ion selective electrodes(ISE) in metal buffer solutions with the use of a CuS–Ag_2S solid membrane.[1] Similar phenomena have also been observed with the same type of electrodes by Ishibashi and Jyo.[2] It has been believed that the actual sensitivity of a cupric ion selective electrode is determined by the residual concentration of Cu(II) and Ag(I) ions at the interface.[3] Therefore, if we can lower this residual concentration as low as possible by complex formation of Cu(II) and Ag(I) ions with added ligand species, the concentration of the detection limit of the electrode may possibly be descreased. However, an inherent reaction of solid membrane itself with ligand species was found to be taken into consideration.[1] Unwanted reactions between the solid membrane and solution species may cause slow and unstable response of the ISE.

In the present study, the effect of several ligand species on the response of a CuSe–Ag_2S solid membrane Cu(II) ISE was studied with a view to examine whether or not similar phenomenon to CuS–Ag_2S is observed even with the different solid membrane material in order to generalize the behavior of the ISE in metal buffer solutions.

Experimental

The solid membrane used for a Cu(II) ISE is of CuSe–Ag_2S, where the ratio of CuSe to Ag_2S is several %. A reference used is an Ag/AgCl electrode of TOA Dempa Co. Water used is deionized and distilled. Chemicals were of analytical reagent grade. The electrochemical cell assembly employed is as follows:

$$\text{CuSe–Ag}_2\text{S}\left|\begin{array}{c}\text{Test solution}\\ \mu=0.1(\text{NaNO}_3)\end{array}\right|\text{KCl(sat.)}\,\Big|\,\text{AgCl}\,\Big|\,\text{Ag}$$

Potential-time profiles of the ISE were recorded using an on-line computer controlled ISE measuring system described elsewhere,[4] where the potential from the electrode is first converted into frequency in order to increase the precision of the voltage measurement. The response time for the electrode is slowed down appreciably upon addition of certain types of ligand species in aqueous Cu(II) solution. Therefore, we employed 30 minutes waiting time for the measurement of an equilibrium potential. By doing so, the equilibrium is nearly attained in most cases except for the case of EDTA. The measurement was performed in a room thermostated at 20±0.5 °C. The solution was stirred with a magnetic stirrer.

Procedure

The procedure employed is as follows : First of all, an empirical relation between the Cu(II) concentration and the observed frequency (potential) is obtained through the calibration curve in standard Cu(II) solution,

$$f = 3.16461 \log[\text{Cu}] + 39.7125 \quad (\text{kHz}), \qquad (1)$$

where f is the frequency which is one to one equivalent to the observed potential, and [Cu] the activity of Cu(II) solution. With the use of Eq. 1, the activity of Cu(II) ion [Cu] was calculated from the observed potential values of the Cu(II) ISE in each ligand solution. Values thus obtained are compared with the theoretical one, where the latter is simply calculated from β_n through the relations as follows :

$$\frac{[\text{CuL}_n]}{[\text{Cu}][\text{L}]^n} = \beta_n,$$

$$p[\text{Cu}] = \log\beta_n + n\log[\text{L}] - \log[\text{CuL}_n],$$

$$[\text{L}] = \frac{C_\text{L}}{\alpha_{\text{L(H)}}},$$

where [L] is a function of pH and is obtained using the total concentration of the ligand C_L, and the side reaction coefficient $\alpha_{\text{L(H)}}$ which is calculated from the concentration of proton ion in the solution and the acid dissociation constants of the ligand(1,5).

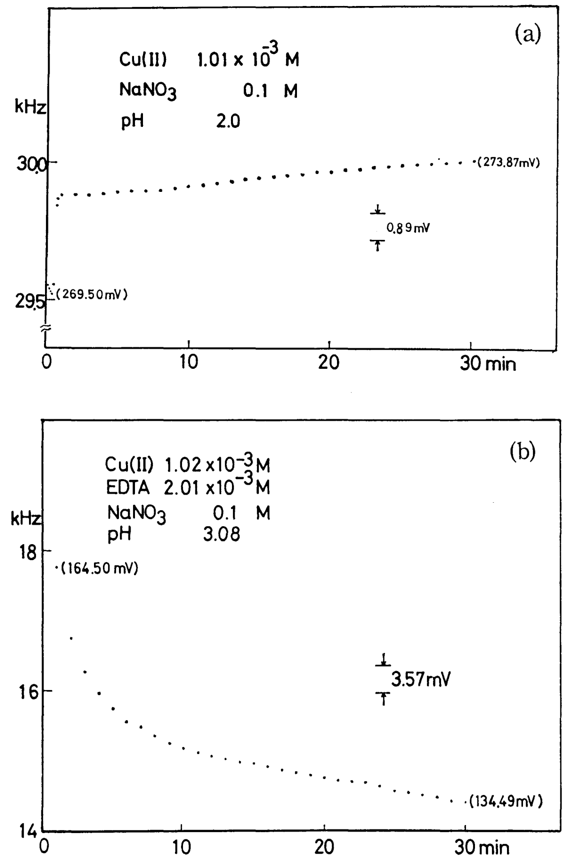
Results and Discussion

In Table 1, the extremely low activity of Cu(II) ions determined by the response of a CuSe–Ag_2S Cu(II) ISE is compared with those calculated using the reported data of stability constants of Cu(II) complexes in each ligand. In most cases except EDTA, the agreement is fairly well indicating that the copper(II) ISE of the present study is actually responding to such low activities as 10^{-15} M, for example, of free Cu(II) ions. This result is to be compared with similar results obtained by Nakagawa *et al.*, where CuS–Ag_2S is used instead of CuSe–Ag_2S for the cupric ion selective electrode. In the case of EDTA as a ligand, the agreement is not good, probably due to some unknown reactions between the CuSe–Ag_2S solid membrane itself and EDTA molecules. This is partly supported by the result in Fig. 1 where the potential-time profile for the copper(II) ISE in 1×10^{-3} M Cu(II) aqueous solution is extremely slowed down by the addition of certain amount of EDTA, indicating the non-equilibrium reaction, if any, between EDTA and solid membrane material itself. Appa-

Table 1. Extremely low activities of Cu(II) ions obtained by CuSe–Ag_2S solid membrane Cu(II) ion selective electrode

	C_{Cu}	C_L	pH	Cu(II) calculated from $\beta_n(\mu=0.1)$	$\log \beta_n$ [a]	Cu(II) observed
en	1.01×10^{-3} M	4.24×10^{-3} M	10.47	8.5×10^{-19} M	19.72 (β_2)	5.4×10^{-18} M
NH_3	1.01×10^{-3} M	6.8×10^{-1} M	11.41	2.9×10^{-16} M	13.23 (β_4)	4.6×10^{-16} M
bpy	9.94×10^{-4} M	1.00×10^{-3} M	5.47	1.0×10^{-5} M	8.00 (β_1)	1.4×10^{-5} M
bpy	1.01×10^{-3} M	4.30×10^{-3} M	6.30	4.1×10^{-12} M	17.08 (β_3)	1.1×10^{-13} M
edta2Na	1.02×10^{-3} M	2.01×10^{-3} M	3.08	2.4×10^{-19} M	18.80 (β_1)	7.5×10^{-9} M

a) Taken from Ref. 5. Abbreviations: en; ethylenediamine, NH_3; ammonia, bpy; α,α′-bipyridine, edta; ethylenediaminetetraacetic acid.



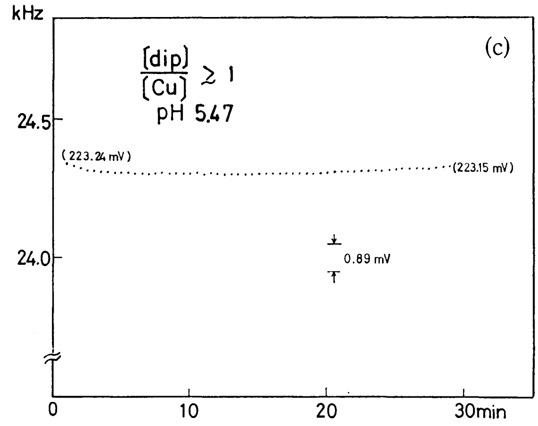


Fig. 1. Potential(Frequency)-time profiles of a CuSe-Ag_2S solid membrane Cu(II) ion selective electrode in different buffer solutions.

(a) Cu(II) ion 1.01×10^{-3} M, $NaNO_3$ 0.1 M, pH 2.0.

(b) Cu(II) ion 1.02×10^{-3} M, edta·2Na 2.01×10^{-3} M, $NaNO_3$ 0.1 M, pH 3.08.

(c) Cu(II) ion 0.99×10^{-3} M, bpy 1.00×10^{-3} M, $NaNO_3$ 0.1 M, pH 5.47.

Frequency f in kHz is equivalent to the potential E in mV as the following : $E=8.9287f+5.9184\pm2.679\times10^{-1}$.

rently, this reaction does not seem to have reached equilibrium during 30 min waiting time (Fig. 1). Also, it is interesting to note that although the activity of Cu(II) ion is generally decreased with the addition of any ligand species, the resulting response time is not necessarily slowed down and is specific to the kind of ligand species as shown in Fig. 1. Therefore, the reason why the response time is slowed down only in certain types of ligand species is attributed to some specific interaction of unknown nature between the ligand species and solid membrane materials rather than simply being due to the decrease in the activity of Cu(II) ions.

In conclusion, the CuSe–Ag_2S solid membrane electrode responds similar manner to the CuS–Ag_2S electrode in that both electrodes have the detection limit well lower than 10^{-15} M of Cu(II) ion activity in certain metal buffer solutions. Also, the response time in extremely low activity solution is not necessarily slow and is dependent on some specific chemical interaction between the ligand species and the solid membrane materials.

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