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Neutral Carrier-Type Silver Ion-Selective Electrode Based on Lipophilic Monothiacrown Ether

Masatoshi OUE,* Keiichi KIMURA,† Kazuhiro AKAMA,† Minoru TANAKA,† and Toshiyuki SHONO†

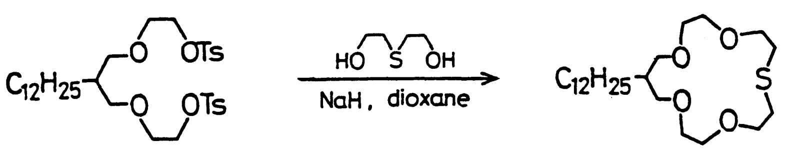
Department of Chemical Engineering, Nara National College of Technology, Yata, Yamato-Kōriyama, Nara 639-11

†Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

Dodecyl-16-crown-5, which contains one sulfur and four oxygen atoms, was synthesized and tested for its usefulness as a neutral carrier for Ag^+-selective electrodes. The resulting ion-selective electrodes exhibited Nernstian response to Ag^+ in a wide activity range. The ion selectivities against other heavy metal ions and alkali and alkaline-earth metal ions were quite excellent.

Crown ethers, which have good affinities to alkali and alkaline-earth metal ions, have been utilized as neutral carriers in metal ion-selective electrodes. Especially in the electrodes based on bis(crown ether) derivatives, high selectivities for alkali metal ions have been realized.[1-3] However, there are very few neutral carrier-type Ag^+-selective electrodes. Also, in previous Ag^+ electrodes based on dithiacrown ether derivatives,[4] serious interference by Fe^{3+} and Hg^{2+}(selective coefficients of about 1) was observed. We report here a high-performance Ag^+-selective electrode using a lipophilic monothiacrown ether.

Monothiacrown ether **1** was synthesized from bis(2-hydroxyethyl)sulfide and 5-dodecyl-3,7- dioxanonane-1,9-diol ditosylate as shown in the scheme.[5,6] The compound was purified by silica gel column chromatography (Ethyl acetate/hexane = 1/10) to yield a colorless oil(25%) : Found:C,66.31;H,11.12%; M^+,418. Calcd for $C_{23}H_{46}O_4S$: C,65.99;H,11.08%; M^+,418.



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The electrode membranes were prepared by a previously-reported method,[1] and contained PVC(27.6 wt%), the neutral carrier(2.8 wt%), DOP(dioctyl phthalate)(69.1 wt%), and dipicrylamine sodium salt(0.5 wt%). After injecting 1 M(1 M=1 mol·dm^{-3}) KNO_3 aqueous solution as the internal filling solution, the electrodes were conditioned by soaking them in 10^{-3} M $AgNO_3$ for 3 days. The electrochemical cell for the e.m.f. measurements was as follows: Ag-AgCl/4 M KCl/0.1 M NH_4NO_3/ sample solution/membrane/1 M KNO_3/AgCl-Ag

A typical e.m.f. response of the **1**-based ion-selective electrode to Ag^+ is shown in Fig. 1. An ideal Nernstian slope(59 mV/decade) for Ag^+ was attained in the Ag^+ activity range of 10^{-5} — 10^{-2} M. The response time of the **1**-based Ag^+-selective electrode was within 30 s. The electrode properties were hardly changed for at least 3 months. The high selectivity and durability of the electrode might be attributed partly to the high lipophilicity of the thiacrown ether. Thus, the Ag^+-selective electrode based on **1** is quite promising for practical applications. Figure 2 gives the Ag^+ selectivities of the electrode against other heavy metal ions, alkali and alkaline-earth metal ions, and NH_4^+. The interference by the metal ions except Hg^{2+} is negligible. Even the Ag^+ selectivity against Hg^{2+} (k_{AgHg}^{Pot} = 1.6×10^{-2}) was drastically improved as compared to that (k_{AgHg}^{Pot} = 0.77) of the previous thiacrown ether-based electrodes.[4] Furthermore, the **1**-based Ag^+-selective electrode is definitely superior to popular Ag_2S-based Ag^+electrodes in the Hg^{2+} interference, since coexistence of Hg^{2+} in measuring solutions never be allowed in the Ag_2S-based electrode system. Further study is currently under way.

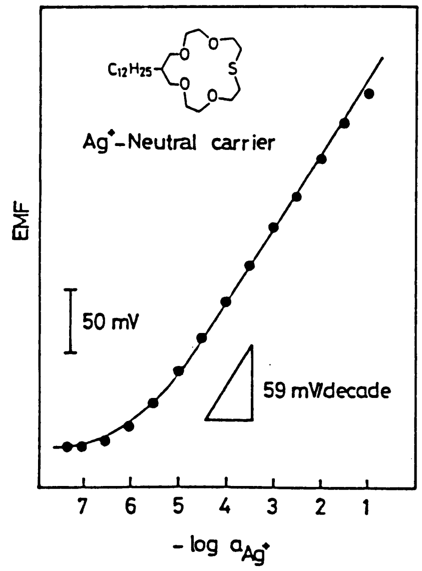
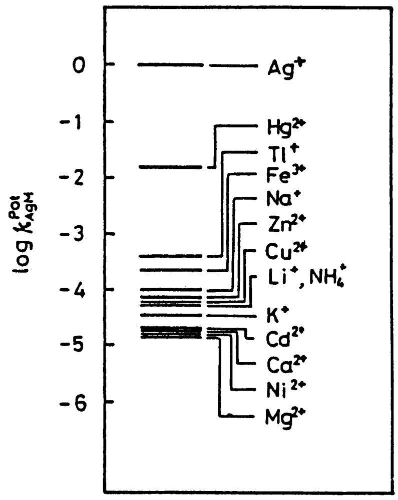


Fig. 1. Calibration plots for Ag^+-selective electrode based on **1**.(left)

Fig. 2. Selectivity coefficients log k_{AgM}^{Pot}. (Determined by FIM) (right)



References

1) K. Kimura, T. Maeda, H. Tamura, and T. Shono, J. Electroanal. Chem. Interfacial Electrochem., 95, 91(1979).

2) T. Shono, M. Okahara, I. Ikeda, K. Kimura, and H. Tamura, J. Electroanal. Chem. Interfacial Electrochem., 132, 99(1982).

3) S. Kitazawa, K. Kimura, H. Yano, and T. Shono, J. Am. Chem. Soc., 106, 6978(1984).

4) M. T. Lai, and J. S. Shih, Analyst(London), 111, 891(1986).

5) D. Ammann, R. Bissig, M. Guggi, E. Pretsch, and W. Simon, Helv. Chim. Acta, 58, 1535(1975).

6) H. Sakamoto, K. Kimura, Y. Koseki, M. Matsuo, and T. Shono, J. Org. Chem., 51, 4974(1986).

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