



SILVER ION SELECTIVE ELECTRODE BASED ON (2-PYRIDYLMETHOXY)-*P-T*-OCTYLCALIX[4]ARENE

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ABSTRACT

Calix[4]arene bearing pyridyl group at lower-rim has been used as an ionophore for silver ion-selective electrode. The electrode membranes containing different amount of potassium tetrakis(*p*-chlorophenyl)borate (KT*p*CIPB) were prepared to investigate the influence of KT*p*CIPB on potential response. The response behavior for membranes depends on the amount of KT*p*CIPB and dramatically changes from anion to cation response. The membrane containing 135 mol % with respect to ionophore gives linear response to Ag⁺ in the concentration range from 10^{-5.5} to 10⁻² M AgNO₃.

Keywords: ion-selective electrode, calix[4]arene, selectivity coefficient, anion effect

INTRODUCTION

Calixarenes are phenolic cyclic oligomers, obtained by the condensation of phenol and formaldehyde. Calixarenes have been studied as molecular recognition reagents in the field of analytical and separation chemistry. Calix[4]arene has the smallest cavity size and is capable of taking four conformational isomers. That are "cone", "partial cone", "1,2-alternate" and "1,3-alternate" [1]. Among these conformations, the "cone" is the most rigid conformation suitable for selective recognition, because it has a preorganized cavity to form complex. Although ion-selective electrodes using calixarene derivatives have been reported, most of them have treated with alkali and alkaline earth metal ions especially to sodium ion [2-4].

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Only a few studies on silver ion-selective electrode using calixarene derivatives have been reported [5,6]. As a result of our previous study, (2-pyridylmethoxy)-*p-t*-octylcalix[4]arene in cone conformation was found to possess good selectivity toward silver ion in solvent extraction [7]. In this paper, we report the silver ion-selective electrode based on (2-pyridylmethoxy)-*p-t*-octylcalix[4]arene and the influence of amount of lipophilic salt on potential responses.

EXPERIMENTAL

Reagents

The chemical structure of ionophore is shown in Fig. 1. Synthesis of 25,26,27,28-tetrakis(2-pyridylmethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (2Py) was described in the previous paper [7].

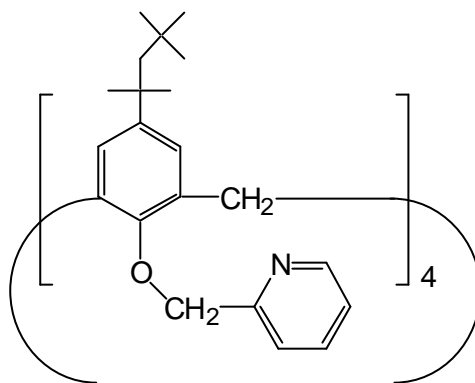


Fig. 1. Chemical structure of ionophore (2Py).

Polyvinyl chloride (PVC) with *ca.* 1100 degree of polymerization was purchased from Katayama Chemical (Osaka, Japan). Potassium tetrakis(*p*-chlorophenyl)borate (KT*p*CIPB) lipophilic salt and *o*-nitrophenyl phenyl ether (NPPE) plasticizer of PVC were supplied by Dojindo Laboratories (Kumamoto, Japan). Reagent grade tetrahydrofuran (THF) and metal nitrates were obtained from Wako Pure Chemical Industries (Osaka, Japan). All reagents were of analytical grade and were used without further purification.

Electrode membrane fabrication

Electrode membrane was prepared according to a procedure similar to that described by Ohki *et al.* [8]. Thus, PVC (50 mg), NPPE (100 mg), calix[4]arene derivative (5 mg) and various amounts of KT*p*CIPB were dissolved in 1.5 cm³ THF. The solution was poured dropwise onto a polytetrafluoroethylene membrane attached to a PVC tube; then the solvent was allowed to evaporate for 20 min. This procedure was repeated 10 times.

The resulting PVC tube was fixed on an electrode body (DKK7900, Tokyo, Japan). The membranes containing 0, 50 and 135 mol % $KTpCIPB$ with respect to the ionophore were abbreviated as membrane 1, 2 and 3, respectively.

Measurements

The electrode membranes were conditioned by soaking in a 1×10^{-3} mol dm^{-3} $AgNO_3$ solution for 12 h before measurements. All the potentiometric measurements were performed at 23-25 $^{\circ}C$ using DKK PHL-40, Tokyo, Japan pH meter. For measuring the electrode potentials, double junction Ag-AgCl type reference electrode was used.

The electrochemical cell is $Ag-AgCl | 1mmol\ dm^{-3}\ AgNO_3 | PVC\ membrane | sample\ solution | 0.1\ mol\ dm^{-3}\ NH_4NO_3 | 3\ mol\ dm^{-3}\ KCl | Ag-AgCl$.

RESULTS AND DISCUSSION

Electrode responses to silver ion

Electrode responses for the silver ion with the membrane containing 2Py as an ionophore and various amounts of $KTpCIPB$ are shown in Fig. 2.

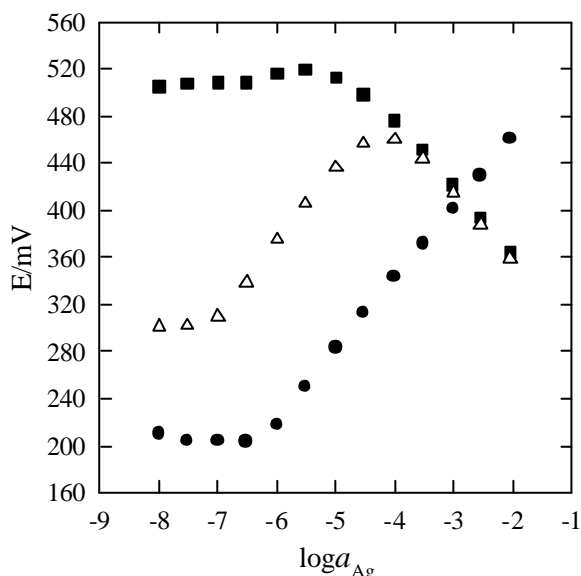


Fig. 2. Potential responses of silver ion with membrane containing various amount of $KTpCIPB$; (□) 0, (△) 50, (●) 135 mol % with respect to ionophore.

The activity coefficients were calculated by the Debye-Hueckel equation. As shown in Fig. 2, significant differences of the electrode responses with changes of $KTpCIPB$ content are observed. Membrane 1 did not respond to silver but responds to nitrate ion present as a counter anion. Membrane 1

responds to nitrate ion in the range from 10^{-5} M to 10^{-2} M. Membrane 2 responds to silver ion in the range from 10^{-7} M to $10^{-4.5}$ M with positive slope and responds to nitrate ion in the range from 10^{-4} M to 10^{-2} M with the same negative slope found for membrane 1 c.f. anion effect [9]. It means, that at high concentration of silver nitrate, ionophore 2Py extracts not only silver ion but also nitrate counter anion into membrane in agreement with the solvent extraction study [7]. Membrane 3 responds to silver ion in the range of $10^{-5.5}$ M to 10^{-2} M. Judging from this result, the addition of KTpCIPB improves the performance of the electrode membrane removing an anion effect.

Selectivity coefficients for silver ion against interfering ions

Since the membrane 3 gave good linear response, as mentioned above, the selectivity coefficients $k_{Ag,M}^{pot}$ for silver ion against various interfering ions were evaluated by mixed solution method [10]. In the method, the concentration of Li, K, NH_4 , Cu, Ni, Ca are 1.0×10^{-2} M; Co, Zn are 3.3×10^{-2} M, and Na is 1.0×10^{-1} M.

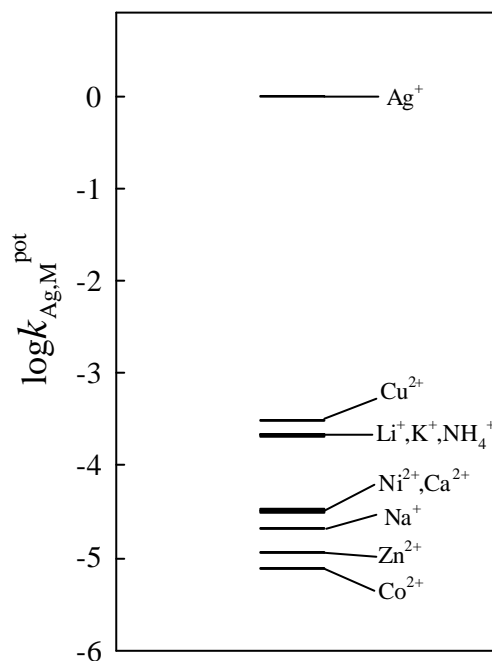


Fig. 3. Selectivity coefficients for silver ion against various cation ($\log k_{Ag,M}^{pot}$) for membrane 3.

Fig. 3 shows the logarithm of $k_{Ag,M}^{pot}$. Membrane 3 selectively responds to silver ion over high concentration range of interfering ions. For divalent metal ions, except for Cu, $\log k_{Ag,M}^{pot}$ reached better values than -4 and for

monovalent ions better than -3.5. In the case of Cu, the obtained value is not satisfactory compare to other divalent metal ions. It could be attributed to a competition of Cu^{2+} and Ag^+ in binding to soft pyridine units in 2Py. The $\log k_{\text{Ag,Na}}^{\text{pot}}$ equal -4.69 is a remarkable result. Generally, electrodes based on calix[4]arene derivatives suffer with interference of as their cavity size fits the size of sodium ions [6]. Therefore many calix[4]arenes are used as ionophores for sodium selective electrodes. In the case of 2Py ionophore, the electrode 3 does not distinguish monovalent ions of different radii (Li^+ , K^+ , NH_4^+).

CONCLUSIONS

2Py has been used as an ionophore for silver ion-selective electrode. The influence of the ratio of ionophore to KTpCIPB on electrode properties has been investigated. It was found that membrane containing 135 mol % of KTpCIPB membrane 3 responds to silver ion; membrane 1 without KTpCIPB responds to nitrate anion. The observed influence of interfering ion on electrode responses agrees with solvent extraction study. In such experiments 2Py extracts only silver ion.

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