Communications

Lipophilic Pyrrole-Based Tetraazacrown Ether as Neutral Carrier for Silver Ion-Selective Electrode

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Crown ethers have been extensively applied as neutral carriers for metal ion-selective electrodes.[1] Especially nitrogen or sulphur-containing crown ethers have been applicable to electrodes for heavy metal ions.[2] However, there have been very few neutral carrier-type Ag^+-selective electrodes. Also, in previous Ag^+ electrodes based on mono- and dithiacrown ethers, acyclic dithia benzene derivatives, and calixarene derivatives, serious interference by Hg^{2+} was observed.[3]

We report here a high performance Ag^+-selective electrode which employs lipophilic tetraazacrown ether of 16-membered rings with four pyrrole units (Ionophore I). The ionophore I was synthesized by the acid-catalyzed condensation of pyrrole and cyclohexanone as shown in Scheme 1.[4] The crude product was purified by column chromatography on silica gel using chloroform/hexane (40 : 60). The product was finally recrystallized from a 50 : 50 mixture of chloroform/hexane to give a white solid powder (yield 9.0%); mp 195-197 ℃. Anal. Calcd. for $C_{40}H_{52}N_4$ (mol. wt. 588.9): C, 81.59; H, 8.9; N, 9.51. Found: C, 80.62; H, 8.41; N, 9.42; IR (KBr) 3440, 2980, 1578, 1416, 1050 and 782 cm^{-1}; ^1H NMR (δ) 1.40-1.52 (m, 24H), 1.93 (t, 16H), 5.90 (d, 8H) and 7.04 ppm (s, 4H).

The typical membrane consisted of 1.5 wt.% the ionophore I, 33 wt.% poly(vinyl chloride) (PVC), 65 wt.% plasticizer, 2-nitrophenyl phenyl ether (NPPE) or bis(2-ethylhexyl) adipate (BEHA), and 0.5 wt.% potassium tetrakis (*p*-chlorophenyl) borate(KTpClPB). The membranes were prepared as previously described[5] and were mounted in home-made Ag/AgCl electrode body.[6(b)] After filling with a solution of
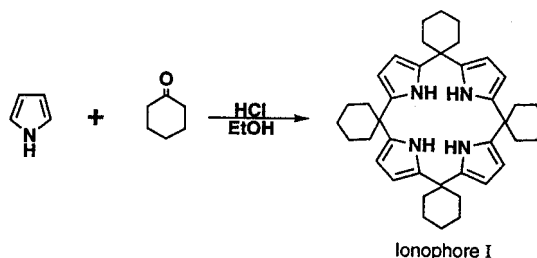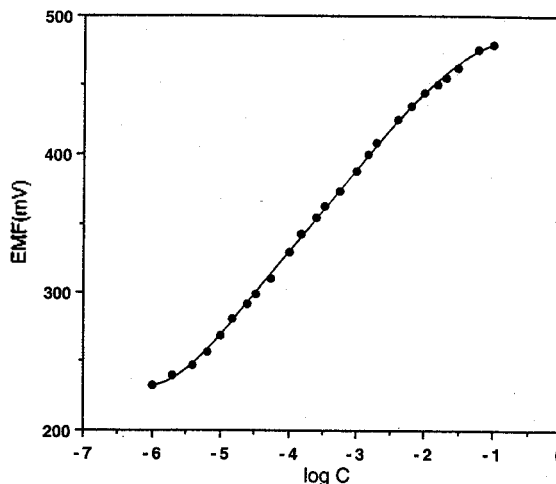
Scheme 1.

Figure 1. Calibration plots of membrane electrode for silver ion based on ionophore I/NPPE.

10^{-2} M $AgNO_3$ as internal solution, the electrodes were conditioned for 2 days by soaking in a 10^{-2} M $AgNO_3$ solution. The electrochemical cell for the e.m.f. measurements was as follows: Ag; AgCl/3M KCl/0.1 M NH_4NO_3/test solution//membrane//10^{-2} M $AgNO_3$/AgCl; Ag. Further experimental details have been described previously.[3,6]

A typical calibration curve and response characteristics for the Ag^+-selective PVC membrane electrodes based on the ionophore I are reported in Figure 1 and Table 1. Response characteristics of a commercial crystalline silver-selective electrode (Orion 94-16 Ag_2S electrode) are also shown in

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Table 1. Characteristics and selectivity coefficients of home-made Ag^+-selective membrane electrodes based on ionophore I and Orion 94-16 Ag_2S electrode
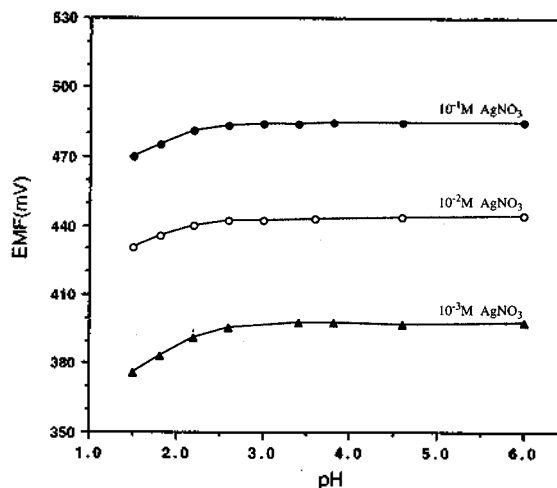
	PVC membrane		Ag_2S
	Ionophore I/NPPE	Ionophore I/BEHA	electrode[a]
Detection limit (M)	$1.0×10^{-5}$	$1.0×10^{-5}$	$1.0×10^{-6}$
Slope (mV/dec)	56.7	54.0	59.4
Response time (s)[b]	30	50	30
Effective pH range	2.5-6.0	2.5-6.0	
Selectivity coefficients, $K^{pot}_{Ag,M}$			
Hg^{2+}[c]	$1.32×10^{-2}$	$1.95×10^{-1}$	$1.95×10^{-1}$
H^+	$2.75×10^{-2}$		
Fe^{3+}	$8.51×10^{-5}$	$1.20×10^{-3}$	$5.37×10^{-5}$
Na^+	$8.32×10^{-5}$	$4.57×10^{-4}$	$5.62×10^{-5}$
K^+	$8.32×10^{-5}$	$9.77×10^{-4}$	$6.31×10^{-5}$
Ca^{2+}	$1.91×10^{-5}$	$8.51×10^{-6}$	$1.17×10^{-5}$
Mg^{2+}	$9.12×10^{-6}$	$6.76×10^{-6}$	$1.58×10^{-5}$
Co^{2+}	$7.24×10^{-6}$	$7.08×10^{-6}$	$1.17×10^{-5}$
Pb^{2+}	$7.59×10^{-6}$	$6.31×10^{-5}$	$5.37×10^{-5}$
UO_2^{2+}	$5.75×10^{-4}$		
La^{3+}	$6.03×10^{-4}$		

[a] Orion 94/16 Silver/Sulfide electrode (Orion Research Incorporated). [b] Time required to obtain steady potential within $±0.1$ mV fluctuation when the cationic concentrations change from 10^{-4} to 10^{-5} M. [c] For the preparation of mercuric nitrate solution, see reference 7.

Table 1. The electrodes exhibit linear responses of 56.7-54 mV per decade at 25 °C within the concentration range of 10^{-2}-10^{-5} M $AgNO_3$. The detection limits for all electrodes were *ca.* $1×10^{-5}$ M. The response time of the electrodes was reasonably fast as it reached stable potentials within 30 to 50 sec. The potentiometric selectivity coefficients $(k^{pot}_{Ag,M})$ were determined by the separate solution method (SSM)[8] using 0.01 M solutions. Table 1 gives the Ag^+ selectivities of the electrode against alkali metal ions (Na^+, K^+), alkaline-earth metal ions (Ca^{2+}, Mg^{2+}), other heavy metal ions (Hg^{2+}, Fe^{3+}, Co^{2+}, Pb^{2+}), UO_2^{2+} and La^{3+}. The interference by the other metal ions except Hg^{2+} is negligible. Even the Ag^+ selectivity against Hg^{2+} was improved as compared to those of the commercial Ag_2S-based crystalline electrode (Table 1) and previously reported Ag^+-selective liquid membrane electrodes based on monothiacrown ether $(K^{pot}_{Ag,Hg}=1.6×10^{-2})$,[3(a)] dithiacrown ether $(K^{pot}_{Ag,Hg}=0.87)$[3(b)] and a calixarene derivative $(K^{pot}_{Ag,Hg}=85.1)$.[3(c)]

Although Hg^{2+} provides some interference, the selectivities are good enough to assure technical applications.

In water and other highly solvating media, the charged complex and counter anions are separately solvated, and no anion effect on complex stability is expected. However, in poorly solvating media such as the solvent polymeric membranes, complexed ion pairs or ligand-separated ion pairs are formed. The solubility factors are extremely important for the dissolutions of the complex in membrane solvent media.[9] Among these PVC membrane electrodes based on ionophore

Figure 2. Effect of pH on the EMF response of ionophore I-based NPPE/PVC membrane electrode. HNO_3 was used to change the pH value.
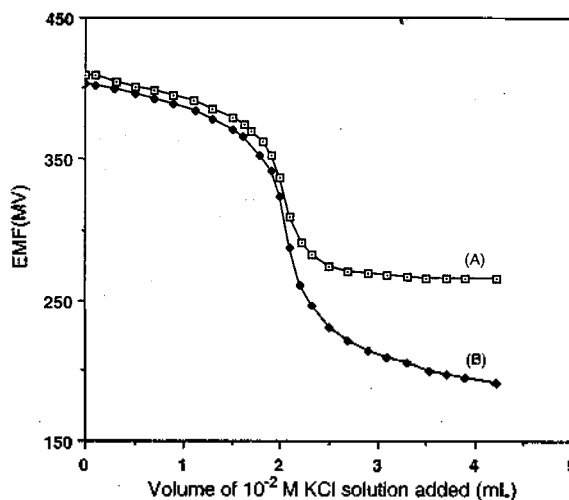
Figure 3. Potentiometric titration curves of 20 mL of $9.5×10^{-2}$ M $AgNO_3$ solution for (A) ionophore I/NPPE electrode, (B) Ag_2S membrane electrode (Orion 94-16).

1, the NPPE ($\varepsilon=23.58$[9(c)]) plasticized membrane having high dielectric constant proved more successful than BEHA ($\varepsilon=6.00$[9(a)]) plasticized membrane having low dielectric constant.

The pH-dependence of the electrode was studied for the pH range 1.5-6.0. The pH of the solution was adjusted by addition of nitric acid solution with the same silver concentration as the test solution. In basic solutions, silver reacts with hydroxide ions to form a precipitate of Ag_2O.[10] It is seen from Figure 2 that hydrogen ions do not interfere in silver estimation in the pH range 2.5 to 6.

The ionophore I/NPPE-based membrane electrode has also been used as an end-point indicator electrode in the potentiometric titration of Ag^+ ion. The titration curves (Figure 3) are of nearly classical type which further confirms that the electrode is specific toward silver.

It is, therefore, concluded on the basis of present investigations that the ionophore I-based electrode is of analytical use in the estimation of silver in the presence of various

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other ions. Further study is currently under way.

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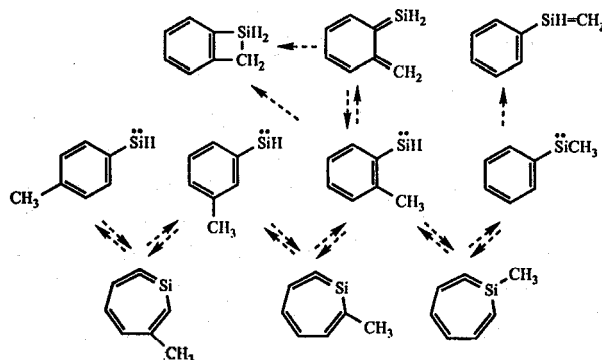
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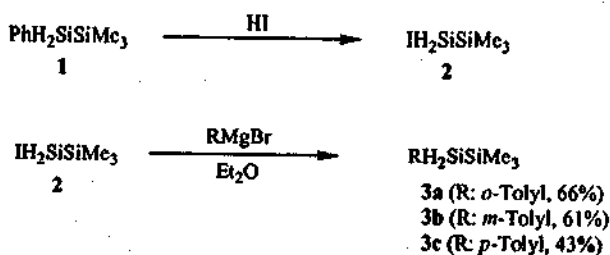
Generation and Reactivity of Tolylsilylenes

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The isomeric tolylmethylenes have been studied in considerable detail over the past two decades.[1-3] Much of the impetus for these works came from mechanistic studies of the interconversion to give the benzocyclobutene and styrene. However, tolylsilylenes, analogues of tolylmethylenes have apparently not been reported. In this context, we thought it might be of some interest to study the reactivities of the *o*-, *m*-, and *p*-tolylsilylenes in comparison with those observed on chemistry of isomeric tolylmethylenes (Scheme 1).[2,3]

The following synthetic scheme, including the acid-cleavage of 2-phenyldisilane with HI,[4] was adopted to obtain the required tolylsilylene precursors.

Flow vacuum pyrolyses (FVP) of **3a-c**[5] at 600 ℃ in the presence of a 30-fold excess of 2,3-dimethylbutadiene as the trapping agent gave 1-silacyclopent-3-ene derived from the addition of tolylsilylenes to the diene in 52, 24, and 48% yields, respectively.[6] When the precursors **3a-c** were pyrolyzed in the absence of trapping agent, benzosilacyclobutene (**12a**)[7] *via* the intramolecular γ C-H insertion of *o*-tolylsilylene was obtained in 70% yield, but in case of *m*- and *p*-tolylsilylenes, the formation of benzosilacyclobutene due to the interconversion *via* methylsilacycloheptatetraene intermediate shown in Scheme 1 was not observed. In the presence of triethylsilane as a trapping agent, the pyrolysis of **3b-c** gave 1,1,1-triethyl-2-(*m*-tolyl)disilane, **5b** and 1,1,1-triethyl-2-(*p*-tolyl)disilane, **5c** in 40% and 37% yields, respectively.[8] Interestingly, the pyrolysis of **3a** gave 1,2-benzo-3-sila-1-cyclobutene, **12a** and no **5a** was observed. This result strongly suggested that an intramolecular C-H insertion reaction of *o*-tolylsilylene was much favor over an intermolecular Si-H insertion.

It was also interesting to note that tolylsilanes, **11a-c**[7] were obtained in 19, 39 and 48% yields, respectively, which were presumably formed due to the intramolecular β C-H insertion.

Scheme 1. The Possible Isomerization of Tolylsilylenes.

Scheme 2.