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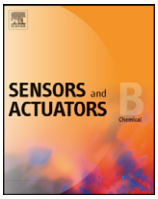

New silver selective electrode fabricated from benzothiazole calix[4]arene: Speciation analysis of silver nanoparticles

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ABSTRACT

A new calix[4]arene containing benzothiazolyl pendants was synthesized and used as an ionophore to fabricate macro- and micro-Ag^+ selective membrane electrodes. PVC membranes plasticized with NPOE provided better selectivity coefficient towards Ag^+ than those plasticized with DOS. The selectivity coefficients ($\log K^{pot}_{Ag,j}$) for macro- and microelectrode were, respectively, −2.8 and −2.5 for Hg(II) and lower than −4.0 and −3.5 for other cations tested. The fabricated electrodes can be used in a wide pH range (pH 2–8) with a response time less than 5 s. The electrodes exhibit near theoretical Nernstian slope ($59.7 \pm 0.8\,mV\,decade^{-1}$ for macroelectrode and $59.8 \pm 1.0\,mV\,decade^{-1}$ for microelectrode) with low detection limits (ca. 5.0×10^{-7} M) and wide linear working range (10^{-6} to 10^{-2} M). The electrodes were used as an indicator electrode for the argentometric titration of the mixture of Cl^- and Br^-. The fabricated electrodes were also used for the first time in speciation analysis of Ag nanoparticles with good accuracy and precision. This Ag-ISE should be beneficial to researches regarding Ag nanoparticles.

1. Introduction

It is well known that Ag ions and Ag-based compounds have strong antimicrobial effects [1]. Silver nanoparticles (AgNPs) are now received much interest in various applications including antibacterial clothes [2]. However, antimicrobial mechanisms of Ag ions and Ag nanoparticles are not well understood. Microbiologists have used a number of techniques to study the effects of Ag nanoparticles on microbial growth inhibition such as SEM, TEM [3] and ESR [4]. Ag^+ selective electrode may be a valuable tool for measuring concentration of Ag^+ to find a suitable condition for synthesizing desired silver nanoparticles and may be used to study antimicrobial properties of AgNPs.

Ion selective electrode (ISE) is an ion analysis technique that provides many unique characteristics. ISE may have response to ion activity change in the aqueous phase [5] based on the measurement of the phase boundary potential at the sample/membrane interface. Recently, backside calibration potentiometry has been demonstrated [6] as a new concept in the field of ISE, and further exploration to prove the validity of this technique has also been reported [7]. The principle of ISE, thus, still continues to develop to valuable applications.

The ionophore is one of the important compositions in a polymeric membrane ion selective electrode. The ionophore selectivity over the interfering ion is the concerning issue in ionophore discovery. Good selectivity resulted from a stronger complex between an ionophore and a detecting ion rather than a weaker complex of the ionophore and interfering ions. A number of Ag-ISE's have been reported during the past 10 years. PVC membranes based on macrocyclic compounds such as pyridine tetramide [8], calix[2]furano[2]pyrrole [9] and tris(pentafluorophenyl)corrole [10] were reported to give high selectivity towards Ag^+.

It is well known that sulfur containing ligands preferred to bind heavy metal ions such as Ag^+ and Hg^{2+}. Non-macrocyclic ionophores containing thiocarbamates [11,12], phosphorothiolates [13] and carboxythiophenoxy groups [14] have been reported to be selective ionophore for Ag^+. In addition, cyclic thioethers were also employed as ionophore in Ag-ISE's [15,16].

Calixarene is the most frequently employed building block for ionophores. Kimura and co-workers reported Ag^+ selective electrodes using π-coordinate calix[4]arene derivatives as soft neutral carriers in the membrane phase [17]. Bitter and co-workers have synthesized a variety of calix[4]arene derivatives containing sulfur donors and π-coordinate groups and studied their binding properties towards Ag^+ [18]. Pretsch and colleague,

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then, showed that selectivity coefficients of membranes containing π-coordinating calix[4]arene ionophores were worse than those containing calix[4]arene incorporating sulfur donors [19]. Demirel et al., reported that the Ag^+ selective PVC membrane using thiacrown-4 as an ionophore exhibited high selectivity towards Ag^+ over other ions [20]. Heterocyclic ionophores containing sulphur as donor sites were synthesized by Zhang's and He's groups [21–23]. They used two groups of thiobenzothiazole (four sulphur atoms in one molecule). This molecule exhibited good characteristics of Ag^+ ionophores. Recently, we have synthesized benzothiazole-derivatized calix[4]arenes by varying chain lengths of the benzothiazole tethers and *p-tert*butyl substituents on the calix[4]arene. It was found that calix[4]arene with shortest chain length and no substituents possessed the best characteristic of the Ag^+-ionophore [24]. In the light of this study, we synthesized a new calix[4]arene derivative containing two benzothiazole groups with a methylene tether and used the compound as an ionophore to make a Ag-ISE.

The principle of potentiometry states that potentiometry is less dependent on scaling laws. Recently, Bakker and co-workers have showed that they can successfully made solid-contact silver microelectrodes [25]. Therefore, a simple-to-make micropipettip electrode (microelectrode) and a conventional standard size electrode (macroelectrode) have been constructed using the synthesized calix[4]arene ionophore. We also demonstrated the use of our Ag-ISE's in the argentometric titration of the mixture of Cl^- and Br^-. According to aforementioned literatures, there is no report in uses of Ag-ISE's in analysis of Ag nanoparticles. Therefore, in this article we have shown that our Ag-ISE's can be used in speciation analysis of Ag nanoparticles.

2. Experimental

2.1. Reagents and general method

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 MHz nuclear magnetic resonance spectrometer. In all cases, samples were dissolved in deuterated chloroform. Chemical shifts were recorded in part per million (ppm) using a residue proton as internal reference. MALDI-TOF mass spectra were recorded on a Micromass Platform II. Calix[4]arene [26] as well as silver nanoparticles [27] were prepared by the previously published procedure.

High molecular weight polyvinyl chloride (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), bis (2-ethylhexyl)sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB) and tetrahydrofuran (THF) were purchased from Fluka with Selectophore® grade. Nitrate salts of cations were of analytical grade obtained from Merck, Fluka, Sigma–Aldrich, Reidel and Carlo Erba. The solution pH was adjusted by HNO_3 or NaOH. All solutions were prepared with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore).

2.2. Synthesis of the ionophore

2.2.1. Synthesis of 25,27-di(cyanomethoxy)-26,28-dihydroxycalix[4]arene (1)

In a 250 mL two-necked round bottom flask equipped with a magnetic bar, 25,26,27,28-tetrahydroxycalix[4]arene (5.00 g, 11.8 mmol), potassium carbonate (4.60 g, 33.2 mmol) and acetonitrile (120 mL) were stirred under nitrogen at room temperature for 1 h. Bromoacetonitrile (6.20 g, 51.6 mmol) was then added and the mixture was heated at reflux for 7 h. The mixture was cooled to room temperature and filtered. The filtrate was evaporated to reduce the volume of the solution. Methanol was then added to precipitate 25,27-di(cyanomethoxy)-26,28-dihydroxycalix[4]arene, **1**, as a white solid (3.60 g, 60%).

^1H NMR spectrum (400 MHz, $CDCl_3$): δ (in ppm) 7.13 (d, *J* = 7.2 Hz, 4H, *m*-*H*ArOH) 6.83 (d, *J* = 7.6 Hz, 4H, *m*-*H*ArOCH_2) 6.79–6.73 (m, 4H, *p*-*H*ArOH and *p*-*H*ArOCH_2) 6.02 (s, 2H, ArO*H*) 4.85 (s, 4H, CH_2CN) 4.26 (d, *J* = 13.6 Hz, 4H, Ar–CH_2–Ar) 3.52 (d, *J* = 13.6 Hz, 4H, Ar–CH_2–Ar).

2.2.2. 25,27-Di(benzothiazolyl)-26,28-hydroxycalix[4]arene (**CU1**)

Compound **1** (0.50 g, 1.0 mmol) was mixed with 2-aminothiophenol (0.34 mL, 2.3 mmol). The reaction mixture was heated at reflux and stirred for 3 h under nitrogen. The reaction mixture was then cooled to room temperature. Dichloromethane (50 mL) was added into the mixture, and methanol was subsequently added to precipitate 25,27-di(benzothiazolyl)-26,28-hydroxycalix[4]arene, **CU1**, as a white solid (0.58 g, 81%).

^1H NMR spectrum (400 MHz, $CDCl_3$): δ (in ppm) 8.05 (d, *J* = 8.4 Hz, 2H, BTAr*H*), 7.51 (t, *J* = 7.6 Hz, 2H, BTAr*H*), 7.43 (d, *J* = 8.4 Hz, 2H, BTAr*H*), 7.29 (t, *J* = 7.6 Hz, 2H, BTAr*H*), 7.25 (s, 2H, OH), 7.11 (d, *J* = 7.6 Hz, 4H, *m*-*H*ArOH), 6.89 (d, *J* = 7.6 Hz, 4H, *m*-*H*ArCH_2), 6.78 (t, *J* = 7.2 Hz, 2H, *p*-*H*ArOH), 6.72 (t, *J* = 7.4 Hz, 2H, *p*-*H*ArCH_2), 5.45 (s, 4H, ArOCH_2), 4.42 (d, *J* = 13.6 Hz, 4H, Ar–CH_2–Ar), 3.47 (d, *J* = 13.6 Hz, 4H, Ar–CH_2–Ar). *^{13}C NMR spectrum* (100 MHz, $CDCl_3$): δ (in ppm) 167.6, 153.2, 152.8, 151.4, 135.1, 132.7, 129.3, 128.7, 127.7, 126.2, 126.0, 125.2, 123.0, 122.0, 119.2, 75.5, 31.2 MALDI-TOF for $[C_{44}H_{34}N_2O_4S_2 + K]^+$, Anal calc: $m/z = 757.1$, Found: $m/z = 756.9$.

2.3. Membrane preparation

The membrane cocktail consisting of ionophore **CU1** (10 mmol kg^{-1}), KT*p*ClPB, 33 wt.% PVC and 66 wt.% plasticizer were dissolved in 2.5 mL of THF (total mass of 220 mg). The cocktail solution was then poured into a glass ring (30 mm i.d.) fixed on a glass plate. The solvent was allowed to evaporate overnight at room temperature to give a transparent membrane (thickness ~0.2 mm). The membrane was punched into small sizes (7.5 mm i.d.) and glued with a PVC/THF slurry on the top of PVC tube and connected to a micropipette tip as an electrode body. For microelectrodes, the tip of 1 mL micropipette (0.5 mm i.d.) was dipped into membrane cocktail for 3 s. It was left to stand in vertical position to allow the solvent to evaporate. The membrane thickness is around 0.5 mm. Membrane compositions and electrode response properties are collected in Table 1.

2.4. EMF measurements

The polymeric membrane electrodes were conditioned overnight in 0.01 M solution possessing identical composition as inner filling solution. Membrane potentials were measured in stirring solution at ambient temperature in the galvanic cell:

Ag, AgCl/3 M KCl//1 M LiOAc//sample solution/membrane/IFS/AgCl, Ag.

The reference electrode Ag/AgCl with double junction was used (type 6.0726.100, Metrohm AG, CH-9010 Herisau, Switzerland) with 1 M LiOAc as salt bridge electrolyte. Continuous EMF measurements were carried out with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA) while discrete EMF measurements were monitored by a pH meter (Orion Research Inc., Boston, MA 02129, USA). Activity coefficients of cations in aqueous solutions were calculated according to the Debye-Hückel approximation [28].