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Cs^+-selective membrane electrodes based on ethylene glycol-functionalized polymeric microspheres

Shane Peper*, Chad Gonczy, Wolfgang Runde

Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract

A new strategy for improving the robustness of membrane-based ion-selective electrodes (ISEs) is introduced based on the incorporation of microsphere-immobilized ionophores into plasticized polymer membranes. As a model system, a Cs^+-selective electrode was developed by doping ethylene glycol-functionalized cross-linked polystyrene microspheres (P-EG) into a plasticized poly(vinyl chloride) (PVC) matrix containing sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (TFPB) as the ion exchanger. Electrodes were evaluated with respect to Cs^+ in terms of sensitivity, selectivity, and dynamic response. ISEs containing P-EG and TFPB that were plasticized with 2-nitrophenyl octyl ether (NPOE) yielded a linear range from 10^{-1} to 10^{-5} M Cs^+, a slope of 55.4 mV/decade, and a lower detection limit ($\log a_{Cs}$) of -5.3. In addition, these membranes also demonstrated superior selectivity over Li^+, Na^+, and alkaline earth metal ion interferents when compared to analogous membranes plasticized with bis(2-ethylhexyl) sebacate (DOS) or membranes containing a lipophilic, mobile ethylene glycol derivative (ethylene glycol monooctadecyl ether (U-EG)) as ionophore.

Keywords: Cesium; Ion-selective electrode; Ethylene glycol; Immobilized ionophore

1. Introduction

In order to simplify the handling and ultimate disposal of nuclear material, it is necessary to separate the radionuclides that contribute the highest thermal load, namely ^{137}Cs and ^{90}Sr. This scientific challenge has prompted researchers to develop a variety of partitioning techniques for selectively removing Cs^+ and Sr^{2+} from actinides and other fission products. The most common approaches are based on liquid–liquid extraction [1], supported-liquid-membrane (SLM) extraction [2], and ion exchange processes [3]. All of these techniques rely upon the use of highly selective organic ligands, which, in the case of column separations, can be covalently bound to a polymeric support.

In order to evaluate the extraction efficiency of prospective ligands, it is necessary to have a variety of detection methods available for accommodating the broad range of potential sample matrices. One approach that offers rapid, reliable measurements in aqueous environments is the use of polymeric membrane ion-selective electrodes (ISEs). Analogous in many ways to SLM extractions, these electrochemical sensors contain an ion-selective membrane that is in contact with two aqueous phases: the inner filling solution and the sample. The durable, elastic sensing membrane employed is traditionally composed of a plasticized poly(vinyl chloride) (PVC) matrix that is impregnated with a lipophilic, ion-selective ligand (ionophore) and an ion exchanger. Originally developed to determine clinically relevant ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-, ISEs have been used to measure many other analytes [4]. In recent years, theoretical advances and changes in experimental protocols have made it possible for ISEs to be used in process monitoring and for trace-level detection of environmental contaminants, including Pb^{2+} [5], Cd^{2+} [6], and Ag^+ [7].

For decades, a variety of substituted macrocyclic polyethers (e.g., crown ethers) have been reported as selective ionophores for ISEs [8,9]. In contrast, however, their acyclic

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* Corresponding author. Tel.: +1 505 667 7078; fax: +1 505 665 4955.
E-mail address: speper@lanl.gov (S. Peper).

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analogs have not been well studied for ISE applications. To date, only two ISEs of this type have been reported, a Ca^{2+}-selective electrode based on poly(propylene glycol) [10] and a K^+-selective electrode based on a disubstituted diphenyl glycolic ether [11]. Of the alkali and alkaline earth metal cations, Cs^+ possesses the highest affinity for ethylene glycol functionalities [12]. This has prompted the development of ethylene glycol-functionalized cesium extractants [13] and has resulted in the use of poly(ethylene glycol) as a synergistic agent in the universal (solvent) extraction (UNEX) process [14]. For membrane-based Cs^+-sensing applications, several types of macrocyclic ionophores have been reported, including the antibiotic cephalexin [15], crown-formazanes [16], crowned benzoquinones [17], macrocyclic diamides [18], lactones and lactonelactams [19], and various calix[4]arene [20], and calix[6]arene derivatives [21]. Prior to the advent of ionophore-based sensors, Cs^+-selective electrodes were solely based on an ion exchanger, exploiting the inherently low hydration enthalpy of cesium relative to other alkali and alkaline earth metal ions [22].

Due to the chemical diversity of potential sample matrices in which an ISE can be used, it is necessary to understand the processes that may contribute to decreased sensor lifetime or performance. In particular, a significant amount of research has been done studying the effects of plasticizer, ionophore, and ion exchanger loss from ISE membranes [23–25]. As expected, the loss of each component has a detrimental effect on sensor behavior. For example, because of its role as an organic solvent, plasticizer exudation results in decreased solubility of the active components, resulting in a marked decrease in both sensor sensitivity and selectivity [26]. In addition, ionophore loss is known to result in decreased sensor selectivity [24], while a significant decrease in ion exchanger causes a dramatic increase in the lower detection limit [27]. Numerous approaches have been employed to address these shortcomings, such as the use of self-plasticizing polymer matrices [28–30], photopolymerization of the plasticizer with the polymer matrix [31], the blending of ionophore-immobilized polymers with plasticized PVC [32–34], the covalent attachment of ionophores [35–38] and ion exchangers [39–41] to the principal polymer matrix, and the use of chemically robust ion exchangers for acidic samples [42].

All of the aforementioned ISEs reported for improving sensor lifetime or performance are based on conventional ISE membrane formulations, which use a homogeneous solvent-soluble matrix. Some reports, however, have also explored the use of suspended particles within plasticized polymer membranes. For Cs^+ determination in particular, inorganic zeolite particles have been used as an ionophoric material within non-PVC-based polymer membranes [43]. Moreover, for blood electrolyte analyses, lipophilic sol–gel particles have been used as supports for covalently immobilizing active sensing components [44]. Another approach describes the use of a conventional ion exchange resin to produce a functional Ni^{2+} ISE [45]. In this instance, however, no exogenous ion exchanger was used, resulting in a sensor with a narrow dynamic range and poor selectivity. In addition to using particles as an ionophoric matrix (e.g., zeolites) or as a support for immobilizing active sensing components, recent work by Pretsch and co-workers [46] has demonstrated that the presence of lipophilic silica gel particles within ISE membranes can suppress super-Nernstian electrode responses and ultimately lead to improved lower detection limits. This effect is due to a decrease in transmembrane ion fluxes, which are now known to dictate the lower detection limit of ISEs [47].

In this work, a new strategy for improving ISE longevity and performance based on the use of ionophore-functionalized cross-linked polymeric microspheres embedded within plasticized PVC membranes is presented. As a model system, ethylene glycol-functionalized microspheres are used to demonstrate the proposed approach and to evaluate ethylene glycol for its efficacy as a Cs^+-selective ionophore. The effect of ionophore immobilization on sensor performance is assessed in terms of electrode sensitivity, selectivity, and response time. The behavior of the resultant ISEs is also compared to ion exchanger-type membranes and to analogous electrodes containing a mobile ethylene glycol derivative, ethylene glycol monooctadecyl ether.

2. Experimental

2.1. Reagents

For membrane preparation, high molecular weight poly(vinyl chloride), 2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) sebacate (DOS), tetrahydrofuran (THF), and sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB) were Selectophore grade from Fluka. Ethylene glycol monooctadecyl ether (U-EG), ethylene glycol-functionalized polystyrene microspheres (200–400 mesh) cross-linked with 2% divinylbenzene (P-EG), and alkali, and alkaline earth metal chloride salts were puriss quality from Fluka. All sample solutions were prepared with distilled deionized Nanopure water (18 MΩ cm).

2.2. Electrode preparation and emf measurements

Ion exchanger membranes containing no ionophore consisted of TFPB (10 mmol/kg), either DOS or NPOE (66 wt.%), and PVC (33 wt.%). Membranes containing ethylene glycol monooctadecyl ether as ionophore consisted of U-EG (20 mmol/kg), TFPB (10 mmol/kg), NPOE (66 wt.%), and PVC (33 wt.%), while membranes containing the polymer-grafted ethylene glycol (P-EG) as ionophore consisted of P-EG (5 mg), TFPB (10 mmol/kg), DOS (66 wt.%), and PVC (33 wt.%). In order to eliminate a super-Nernstian response in P-EG membranes containing TFPB and NPOE, the TFPB concentration was reduced to 5 mmol/kg, while keeping all other components at the concentrations stated above. ISE membranes (∼200 μm in thickness) were prepared by dissolving (with the exception of the suspended cross-linked P-EG microspheres) ∼150 mg of total membrane components into 1.5 mL of THF and pouring the resultant solution into 2.2 cm glass rings affixed onto a glass plate. Disks 6 mm in diameter were cut from the parent membrane and mounted into Philips-type electrode bodies (Fluka). Four electrodes were prepared for each membrane composition studied.

Unbiased selectivity coefficients were determined using the modified separate solution method (SSM) according to the protocol introduced by Bakker [48]. Electrodes were conditioned overnight in 0.01 M NaCl and contained 0.01 M NaCl as the inner filling solution (IFS). Interfering ions were measured from the most to the least discriminated ion and selectivity coefficients were determined for each interfering ion from the Nernstian electrode slope, typically from 10^{-3} to 10^{-1} M, extrapolated to 1 M sample activity. To generate Cs^+ calibration curves, the electrodes were conditioned overnight in 0.01 M CsCl and contained 0.01 M CsCl as the IFS. All emf measurements were conducted in unstirred solutions and taken against an Ag/AgCl reference electrode (IFS, 3 M KCl) (Metrohm, 6.0729.100) with 1 M LiOAc as bridge electrolyte. Potentiometric measurements were conducted using a desktop computer operating LabView® Express Version 7.0 software. Electrodes were connected via a high-impedance interface (World Precision Instruments) to a 16-channel BNC block (National Instruments) that was coupled to a 16-bit PCI-type data acquisition board (National Instruments). Potentials were taken at 1 s intervals and averaged ($N = 250$). Measured values were corrected for liquid junction potentials using the Henderson formalism and ion activities were calculated according to the Debye–Hückel approximation.

3. Results and discussion

In this work, two ethylene glycol derivatives were evaluated for their applicability as Cs^+-selective ionophores for use in carrier-based ion-selective electrodes. One derivative was a mobile, lipophilic ether, ethylene glycol monooctadecyl ether, and the other was immobilized ethylene glycol that was covalently grafted onto the surface of cross-linked polystyrene microspheres. Polymeric membrane electrodes were prepared using a plasticized poly(vinyl chloride) matrix that contained one of the ethylene glycol derivatives and an ion exchanger, tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate. The mean potentiometric Cs^+ response of four electrodes for each membrane composition is shown in Fig. 1. This figure suggests that both ethylene glycol derivatives are capable of binding Cs^+, with corresponding electrodes yielding a Nernstian response. The mean slopes obtained for NPOE-plasticized PVC ISEs containing TFPB and either U-EG or P-EG were 58.9 and 55.4 mV/decade, while the conventional lower detection limits were $\log a_{Cs+} = -4.4$ and -5.3, respectively.

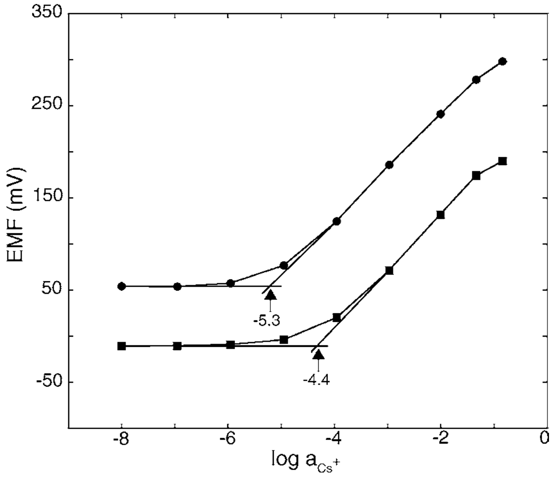

Fig. 1. Mean potentiometric response ($N = 4$) of Cs^+-selective polymer membrane electrodes containing TFPB and either (■) unbound ethylene glycol monooctadecyl ether (U-EG) or (●) polymer-bound ethylene glycol (P-EG) in PVC–NPOE.

In order to eliminate the possibility that the Cs^+ response was caused by the ion exchanger, it was necessary to evaluate the selectivity of both ion exchanger and ionophore-based electrodes. Fig. 2 illustrates the mean selectivity observed for both types of electrodes. It is apparent that each of the electrodes containing an ethylene glycol-type ionophore yields a selectivity pattern that is distinctly different from the DOS and NPOE-plasticized ion exchanger membranes, especially with respect to alkaline earth metal cations. It should be mentioned that in all cases near-Nernstian response slopes were observed for the interfering ions, indicating that the selectivity differences shown in Fig. 2 among similarly plasticized membranes are indeed true selectivity differences. Interestingly, electrodes containing U-EG exhibited comparable selectivity over Rb^+ and K^+ to analogous membranes containing the polymer-bound ethylene glycol derivative, meanwhile demonstrating inferior

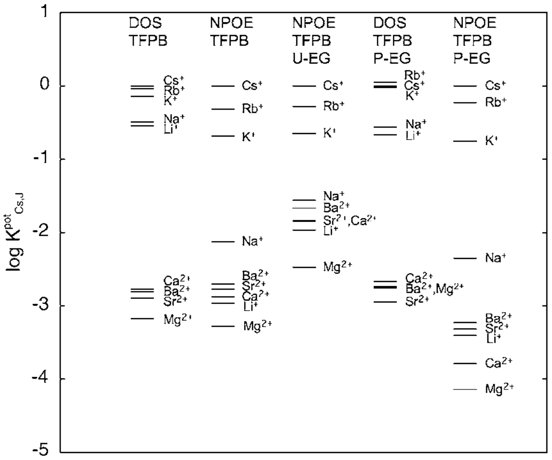

Fig. 2. Mean potentiometric selectivity coefficients ($N = 4$), $\log K^{pot}_{Cs,J}$, of plasticized PVC membranes containing only an ion exchanger, TFPB, or containing an ethylene glycol derivative and TFPB.

selectivity over Na^+, Li^+, and all divalent cations studied. In order to make a direct comparison between the selectivity coefficients of the U-EG and P-EG membranes, one must assume that the ion–ionophore complex stoichiometry and the ionophore to ion exchanger mole ratio are the same in both cases. This is unlikely, since the surface area of the microspheres, which has some degree of variability, governs the ligand concentration in the P-EG membranes. Therefore, the selectivity comparison between the immobilized and mobile ethylene glycol derivatives should be merely qualitative.

In addition to the mobility of the ionophore, the type of plasticizer used also had a dramatic effect on the selectivity. The less polar plasticizer of the two, DOS ($\varepsilon = 4$) [49], induced decreased selectivity over alkali metal cations, this is often due to the pseudo-ionophoric binding properties of the ester oxygen atoms present in the plasticizer. This phenomenon is well known and has been reported in other instances [28,50]. It is also apparent from Fig. 2 that the best selectivity is observed with the microsphere-bound ethylene glycol ionophore in an NPOE-plasticized matrix. Although the selectivity of the NPOE-plasticized P-EG ISEs is rather modest, it is important to note that the immobilization of the ligand does not seem to adversely affect sensor selectivity (relative to U-EG membranes). The retention of ionophore selectivity suggests the potential applicability of ionophore-immobilized microspheres as stationary phases for column and chromatographic separations.

The response time of an ISE is an important parameter that must be considered if the sensor is going to have any type of practical utility. The dynamic response of ionophore-based ion-selective electrodes has been studied for many years [51,52]. For conventional membrane-based ISEs, the potentiometric response is due to the phase-boundary potential that results at the sample–membrane interface when activity changes occur in either surface layer [53]. It has been suggested that other time-limiting processes may occur in non-traditional ISE matrices, such as silicone rubber [30]. In order to confirm that the P-EG electrodes functioned in a rapid manner according to theory, experimental time traces were recorded. Fig. 3 depicts the mean experimental time trace of PVC–NPOE electrodes containing P-EG and TFPB. It is evident from this figure that the use of microsphere-immobilized ionophores does not induce a sluggish electrode response. In addition, the stable, low-noise emf values indicate a low membrane resistance, which is a desired characteristic for optimal sensor performance.

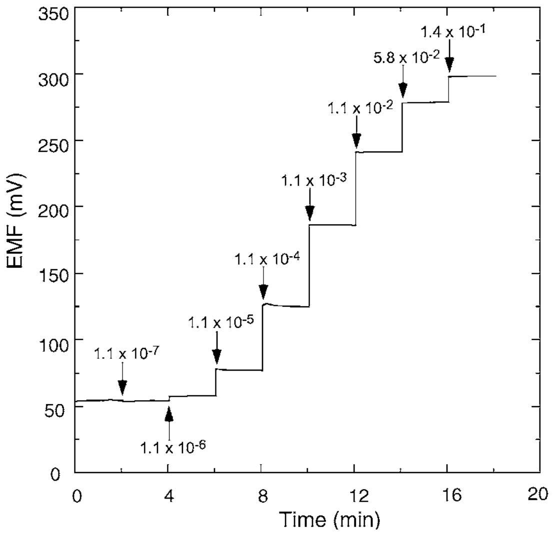

Fig. 3. Mean experimental time trace ($N = 4$) of the emf values obtained at the indicated molar concentration changes for a Cs^+-selective PVC–NPOE membrane electrode containing polymer-bound ethylene glycol (P-EG) and TFPB.

4. Conclusions

In this work, Cs^+-selective solvent polymeric membrane electrodes have been introduced that contain ethylene glycol-type ionophores. It was demonstrated that the covalent attachment of ethylene glycol onto cross-linked polystyrene microspheres does not adversely affect the ability of this ionophore to coordinate Cs^+ in membrane-based ion-selective electrodes. This method of ionophore immobilization offers a new route for potentially improving sensor lifetimes without causing deleterious effects on sensor sensitivity, selectivity, and dynamic response. This work also demonstrated that polymer-bound ethylene glycol electrodes fabricated with NPOE resulted in improved selectivity over Li^+, Na^+, and alkaline earth metal cations when compared to both analogous DOS electrodes and electrodes containing an ion exchanger only.

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