

Research Article

Potentiometric Response Characteristics of Membrane-Based Cs⁺-Selective Electrodes Containing Ionophore-Functionalized Polymeric Microspheres

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Cs⁺-selective solvent polymeric membrane-based ion-selective electrodes (ISEs) were 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. A systematic study examining the effects of the membrane plasticizers bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (NPOE), and 2-fluorophenyl nitrophenyl ether (FPNPE) on the potentiometric response and selectivity of the corresponding electrodes was performed. Under certain conditions, P-EG-based ion-selective electrodes (ISEs) containing TFPB and plasticized with NPOE exhibited a super-Nernstian response between 1×10^{-3} and 1×10^{-4} M Cs⁺, a response characteristic not observed in analogous membranes plasticized with either DOS or FPNPE. Additionally, the performance of P-EG-based ISEs was compared to electrodes based on two mobile ionophores, a neutral lipophilic ethylene glycol derivative (ethylene glycol mono-octadecyl ether (U-EG)) and a charged metallacarborane ionophore, sodium bis(dicarbollyl)cobaltate(III) (CC). In general, P-EG-based electrodes plasticized with FPNPE yielded the best performance, with a linear range from 10^{-1} – 10^{-5} M Cs⁺, a conventional lower detection limit of 8.1×10^{-6} M Cs⁺, and a response slope of 57.7 mV/decade. The pH response of P-EG ISEs containing TFPB was evaluated for membranes plasticized with either NPOE or FPNPE. In both cases, the electrodes remained stable throughout the pH range 3–12, with only slight proton interference observed below pH 3.

1. Introduction

As a regulated environmental contaminant at nuclear processing facilities and as a possible constituent in radiological dispersal devices, ¹³⁷Cs is an important analyte for which early detection systems must be available. For aqueous systems, such as process effluent, municipal drinking water supplies, and natural waters, chemical sensors are an attractive option for Cs⁺ detection due to their low cost, reliable measurements, and in situ capabilities. One well-established class of electrochemical sensors that is capable of meeting these criteria and that has been widely used for measuring inorganic ions, including alkali metals, is the

solvent polymeric membrane-based ion-selective electrode (ISE) [1]. Typically, membrane-based ISEs are composed of a plasticized poly(vinyl chloride) (PVC) matrix that is incorporated with an ionophore and an ion exchanger.

In most cases, ISE membranes contain mobile active sensing components (e.g., ionophore). Unfortunately, over time, these components slowly leach from the membrane, resulting in decreased sensor performance [2]. It has been reported that the leaching rate of these active components is directly related to both the lipophilicity of the membrane and the lipophilicity of the sample [3]. In order to improve the robustness of ISEs, researchers have developed a variety of strategies, such as increasing the lipophilicity

of ionophores by adding long alkyl groups and by immobilizing the ionophore within the ion-selective membrane [4]. Several approaches have been used to immobilize ionophores, including copolymerizing the ionophore with comonomers to produce the principal polymer matrix [5–9], covalently attaching the ionophore to modified PVC [10, 11], and blending polymer-grafted ionophore with a traditional plasticized PVC matrix [6, 12, 13]. In addition to improving sensor longevity, ionophore immobilization has also resulted in other apparent advantages, such as improved lower detection limits [13], and elimination of dimer formation within ion-selective membranes based on metalloporphyrins [14].

One approach for immobilizing ion-selective ligands that is becoming increasingly more popular for chromatographic separations, but has yet to be studied for its applicability in ISEs, is grafting the ionophore onto cross-linked polymeric microspheres [15–17]. One concern that is associated with this approach is the impact that immobilization will have on the selectivity of the ionophore. Extraction experiments using a microsphere-immobilized Cs^+ -selective calix[4]arene have indicated that ionophore selectivity is indeed retained [15]; however, this behavior has not been confirmed for ISE applications.

In addition to ionophore immobilization, the chemical structure and polarity of the membrane plasticizer can also have a dramatic effect on electrode performance (e.g., selectivity) [18]. For example, apolar plasticizers such as bis(2-ethylhexyl) sebacate (DOS), that possess carboxylate functionalities are known to compete with the ionophore for ion complexation, thus decreasing the ionophore-mediated selectivity [19]. Additionally, the membrane plasticizer can also have a dramatic effect on both the upper and lower detection limits of ISEs [19]. Several studies have examined the effects of plasticizers on the potentiometric performance of ISEs [18, 20, 21].

Recently, we reported that ethylene glycol-functionalized cross-linked polystyrene microspheres (P-EG) can be used to produce Cs^+ -selective ISEs [22]. The work presented herein provides a more comprehensive investigation of this electrode configuration by examining the effect of various plasticizers and membrane compositions on the potentiometric performance of these new electrodes. The ISEs are evaluated in terms of sensitivity, selectivity, conventional lower detection limit, linear range, dynamic response, and pH response. In addition, P-EG-based electrodes are compared to both a new charged Cs^+ ionophore, bis(dicarbollyl)cobaltate(III) (cobalticborane, CC), and a lipophilic, mobile ethylene glycol derivative, ethylene glycol mono-octadecyl ether (U-EG).

2. Experimental

2.1. Reagents. For membrane preparation, high molecular weight PVC, 2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) sebacate, 2-fluorophenyl nitrophenyl ether (FPNPE), tetrahydrofuran (THF), and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (NaTFPB) were Selectophore grade from Fluka. Ethylene glycol mono-octadecyl

ether, ethylene glycol-functionalized polystyrene microspheres (200–400 mesh) cross-linked with 2% divinylbenzene, and alkali and alkaline earth metal chloride salts were puriss. p.a. quality from Fluka. Sodium cobalticborane was obtained in 99% purity from Aldrich. All sample solutions were prepared with distilled deionized Nanopure water (18 M Ω ·cm). The chemical structures of the ion-selective membrane components used in this work are shown in Figure 1.

2.2. Electrode Preparation and EMF Measurements. Ion-selective membranes approximately 200 μm in thickness were prepared by dissolving ~150 mg of membrane components in 1.5 mL of THF, casting the membrane cocktail into 22 mm i.d. glass rings that were affixed onto a glass plate, and allowing the THF to evaporate overnight. Disks 6 mm in diameter were cut from the elastic parent membrane and mounted into Philips-type electrode bodies (Fluka). Four electrodes were prepared for each membrane composition. In all cases, the data presented herein are the mean values obtained. For membrane compositions refer to Table 1.

Unbiased selectivity coefficients were determined using the modified separate solution method (SSM) according to the protocol introduced by Bakker [23]. 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 0.001–0.1 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. For pH response measurements, a solution of 0.01 M CsCl was adjusted to pH 2 with 1 M HCl and incrementally titrated with 1 M NaOH while concurrently measuring the solution pH with a combination pH electrode (Metrohm 6.0130.100).

The 16-channel custom-built data acquisition system used to perform potentiometric measurements has previously been described [22]. 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. 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

Of the alkali and alkaline earth metal cations, Cs^+ is known to possess the highest affinity for ethylene glycol moieties [24]. This has resulted in the development of several Cs^+ -selective extractants that contain pendant ethylene glycol functionalities [25]. Moreover, in its polymerized form, poly(ethylene glycol) has been used as a carrier in the universal (solvent) extraction (UNEX) process, which removes cesium and strontium isotopes from radioactive waste [26].

In this work, the suitability of ethylene glycol as a Cs^+ ionophore and the effects of using cross-linked polystyrene microspheres as the support for its immobilization were

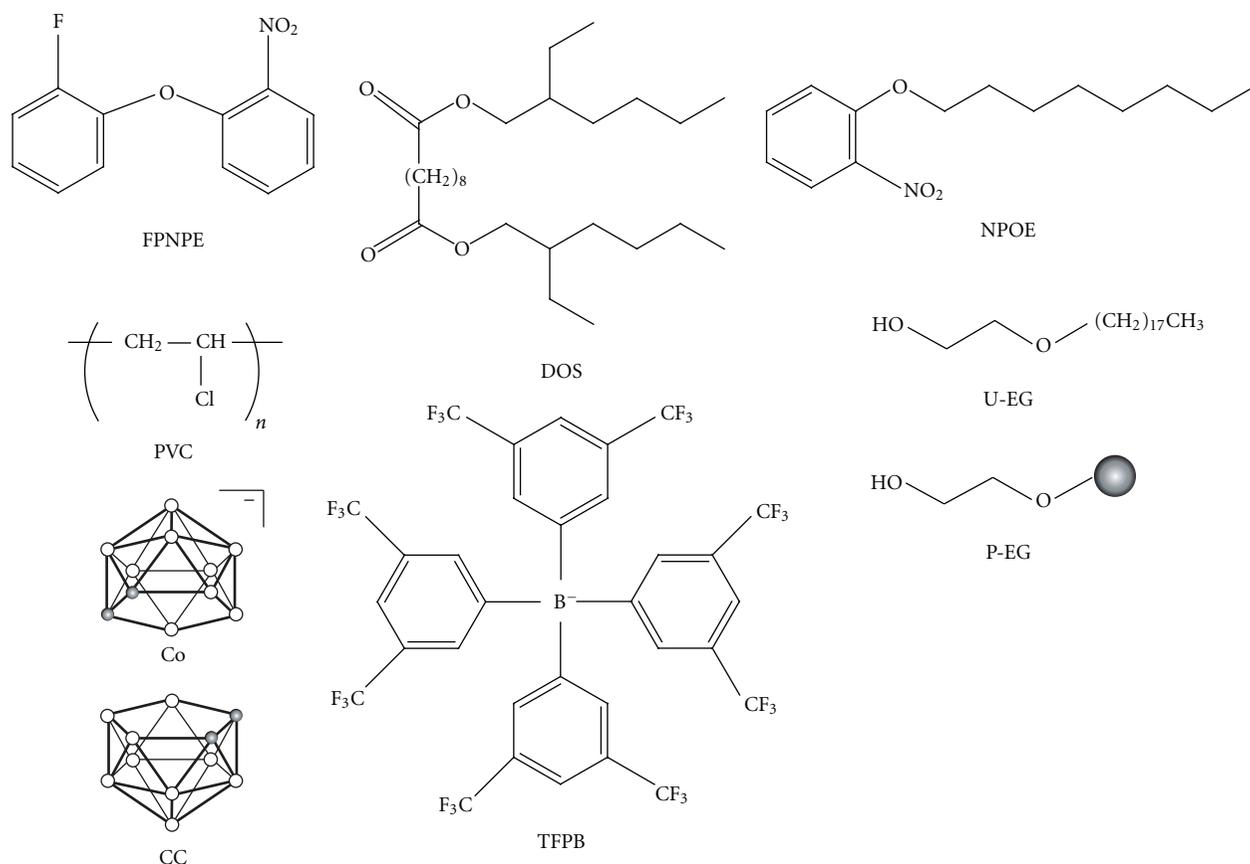


FIGURE 1: Chemical structures and nomenclature of the ion-selective membrane components used in this work. In the structure of cobalticborane, open circles and shaded circles denote boron atoms and carbon atoms, respectively. The shaded circle in the structure of P-EG represents a cross-linked polystyrene microsphere.

TABLE 1: Compositions of the Cs⁺-selective membranes studied in this work.

Membrane	PVC (% w/w)	NaTFPB (mmol/kg)	P-EG (% w/w)	U-EG (mmol/kg)	CC (mmol/kg)	DOS (% w/w)	NPOE (% w/w)	FPNPE (% w/w)
1	31.8	9.2	4.3			66.3		
2	32.0	9.8	3.4				63.7	
3	33.2	4.4	3.5				66.4	
4	27.8	9.2	3.7					67.7
5	33.1	5.6		12.3			66.2	
6	32.8	10.3			19.6		65.6	

evaluated using membrane-based ISEs. Polymeric membrane electrodes were prepared using poly(vinyl chloride) as the matrix, ethylene glycol-functionalized microspheres as the ionophore, TFPB as the ion exchanger, and DOS, NPOE, or FPNPE as plasticizer. Preliminary experiments to determine the optimum concentration of ethylene glycol-functionalized microspheres for ISE applications were performed for membranes loaded with 1, 2.5, 5, and 10 mg of P-EG. It was found that membranes containing 5 mg (3.5%

w/w) of P-EG yielded the best selectivity with respect to alkali and alkaline earth metal cations (data not shown) therefore, this concentration was used in subsequent studies. Moreover, membranes loaded with 10 mg of P-EG exhibited noisy potentials, inferior selectivity, and sluggish electrode responses, suggesting an increased membrane resistance relative to membranes containing ≤ 5 mg of P-EG.

Cs⁺ calibration curves obtained for ISEs containing P-EG are shown in Figure 2. Surprisingly, PVC-NPOE ISEs

containing 5 mg (3.5% w/w) of P-EG and 10 mmol/kg of TFPB consistently exhibited a super-Nernstian potential jump between 1×10^{-3} and 1×10^{-4} M Cs^+ (Figure 2(a), lower curve). A super-Nernstian response is usually caused by an inward flux of primary ions into the ion-selective membrane and a resultant depletion of sample ions in the diffusion layer at the sample-membrane phase boundary. This phenomenon is usually observed when there is a low concentration of primary ions in the inner filling solution (IFS) (e.g., $<10^{-3}$ M) [27]. However, this was not the case here, where the IFS was 0.01 M CsCl. Moreover, super-Nernstian potential jumps are typically observed at concentrations at or below 1×10^{-6} M, suggesting that the super-Nernstian response observed here may be caused by a different phenomenon. The Pretsch group has studied the influence of lipophilic silica gel particles on trans-membrane ion fluxes that occur in ISE membranes [28]. They concluded that a super-Nernstian electrode response could be eliminated if the ion-selective membrane was inverted, so that the particle layer was located on the sample side of the membrane. We tried this approach to suppress the super-Nernstian response obtained with PVC-NPOE membranes containing the ethylene glycol-functionalized particles; however the approach failed, providing additional evidence that a different phenomenon is most likely occurring. Nevertheless, suppression of the super-Nernstian response was achieved by reducing the ionic strength within the membrane as suggested by Ceresa et al. [27], which was accomplished by reducing the ion exchanger concentration to 5 mmol/kg (Figure 2(a), upper curve).

It is established that the chemical structure and polarity of the membrane plasticizer can have a dramatic effect on the partitioning of ions from the aqueous sample into the lipophilic ISE membrane [29]. Parameters such as ionophore diffusion coefficients [30] and membrane selectivity [4] are affected by the properties of the membrane plasticizer. Because NPOE is a rather polar plasticizer ($\epsilon = 24$) [18], it was expected that ISE membranes containing P-EG and other polar plasticizers of the same structural type (i.e., ethers) should also exhibit super-Nernstian behavior. In order to test this hypothesis, P-EG-containing ISEs were prepared with either a polar, FPNPE, or apolar, DOS ($\epsilon = 4$) [18], plasticizer. Surprisingly, in contrast to analogous membranes containing NPOE, both DOS- and FPNPE-plasticized membranes did not exhibit super-Nernstian behavior (Figure 2(b)).

In order to compare the potentiometric response characteristics of the P-EG-based ISEs with other ionophore-based electrodes, Cs^+ -selective membranes were prepared using two mobile ionophores, one a lipophilic ethylene glycol derivative, ethylene glycol mono-octadecyl ether, and the other a new charged Cs^+ ionophore, bis(dicarbollyl) cobaltate (III), also known as cobalticborane. The calibration curves for these electrodes are shown in Figure 2(c). In both cases, electrodes demonstrated Nernstian behavior with no unfavorable response characteristics. Previously, cobalticborane derivatives have been used as ion exchangers [31] and ionophores [32] in liquid-contact and solid-contact ISEs, respectively; however this work demonstrates, for the

TABLE 2: Response characteristics of the Cs^+ -selective electrodes studied in this work.

Membrane	Slope (mV/decade)	Detection limit (M)	Linear range (M)
1	60.4	2.3×10^{-5}	1.4×10^{-1} – 1.1×10^{-4}
2	59.9 ^a	1.0×10^{-3b}	1.4×10^{-1} – 6.1×10^{-3}
3	56.5	4.9×10^{-6}	1.4×10^{-1} – 1.1×10^{-5}
4	57.7	8.1×10^{-6}	1.4×10^{-1} – 1.1×10^{-5}
5	58.2	3.5×10^{-5}	1.4×10^{-1} – 1.1×10^{-4}
6	62.4	2.1×10^{-5}	1.4×10^{-1} – 1.1×10^{-4}

^aSuper-Nernstian response observed between 1×10^{-3} and 1×10^{-4} M Cs^+ .

^bDetermined according to the method recommended by Bakker et al. [33].

first time, the suitability of metallacarborane derivatives as charged ionophores for liquid-contact membrane-based electrodes. Attempts to evaluate the performance of CC-based electrodes containing the anion exchanger tridodecylmethylammonium chloride were unsuccessful due to its incompatibility with CC.

Table 2 summarizes the potentiometric response characteristics for all of the calibration curves shown in Figure 2. In most cases, near-Nernstian response slopes were obtained, with conventional lower detection limits in the micromolar range. The detection limit reported for the super-Nernstian P-EG electrode was calculated according to the recommendation of Bakker et al., which suggests that the useful detection limit for the sensor is the concentration at which the potential deviates from the Nernst function by a factor of $(RT/zF)\ln 2$, where R , T , and F are the universal gas constant, the absolute temperature, and the Faraday constant, respectively, and z is the charge of the measured ion [33].

In addition to sensitivity towards Cs^+ , ion-selective membranes containing ethylene glycol derivatives were evaluated in terms of selectivity. Figure 3 illustrates the selectivity behavior observed over alkali metal cations for three different Cs^+ -selective ISEs that contain either U-EG or P-EG as ionophore. In all cases, the calibration curves obtained for all of the ions measured were Nernstian, as indicated by the solid lines through the data. Additionally, all of the electrodes evaluated showed the highest selectivity for Cs^+ , and a selectivity pattern that directly reflects the hydration enthalpies of the ions measured. It should be mentioned that although the selectivity sequence of the ISEs follows the hydration enthalpies of the measured ions, the selectivity coefficients obtained are significantly better than those reported for analogous ion exchanger electrodes [22], indicating that ethylene glycol moieties possess ionophoric properties. Figure 3 also demonstrates that P-EG membranes plasticized with FPNPE exhibit the best selectivity over alkali metal cations relative to analogous membranes plasticized with NPOE. The selectivity coefficients of the membranes evaluated, calculated using the modified separate solution method (SSM) [23], are given in Table 3. From Table 3 it is apparent that the selection of plasticizer has a dramatic effect on the selectivity of ISEs based on P-EG. Membranes plasticized with DOS exhibited the worst selectivity, especially

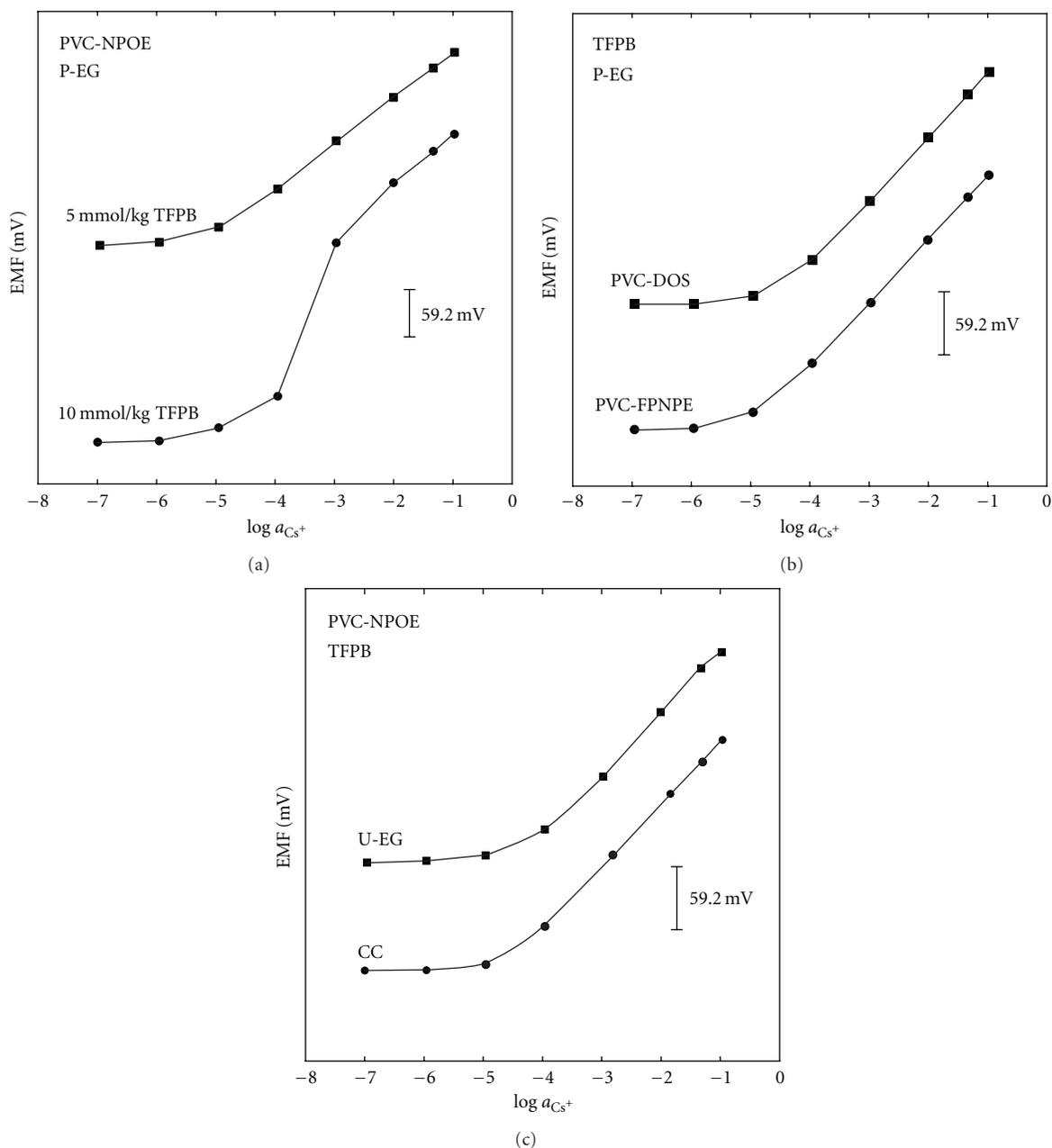


FIGURE 2: Mean potentiometric response curves of PVC-based Cs^+ -selective ISEs containing P-EG and TFPB and plasticized with NPOE (a) or either DOS or FPNPE (b). Mean potentiometric response curves of PVC-NPOE membrane containing TFPB and a mobile Cs^+ ionophore, either U-EG or CC, are also shown for comparison (c).

over alkali metal cations, compared to analogous membranes plasticized with NPOE and FPNPE. This result agrees with previous reports that suggest that the ester moieties found in DOS are capable of interacting with monovalent cations that are extracted into the sensing membrane, thus masking the true ionophore-mediated selectivity [19, 34]. Although the selectivity obtained for the covalently attached ethylene glycol derivative is only modest at best, it is substantially better with respect to Na^+ , Li^+ , and alkaline earth metal cations than membranes containing the

mobile ethylene glycol mono-octadecyl ether. This suggests that covalent immobilization of the ionophore onto cross-linked polymeric microspheres does not adversely affect sensor performance. This welcomed finding suggests that the approach of using ionophore-functionalized microspheres may be useful in designing new, more robust sensors, based on highly selective macrocycles.

Another metric for evaluating the potentiometric performance of ethylene glycol-based Cs^+ -selective ISEs is the dependence of the measured potential on the sample pH.

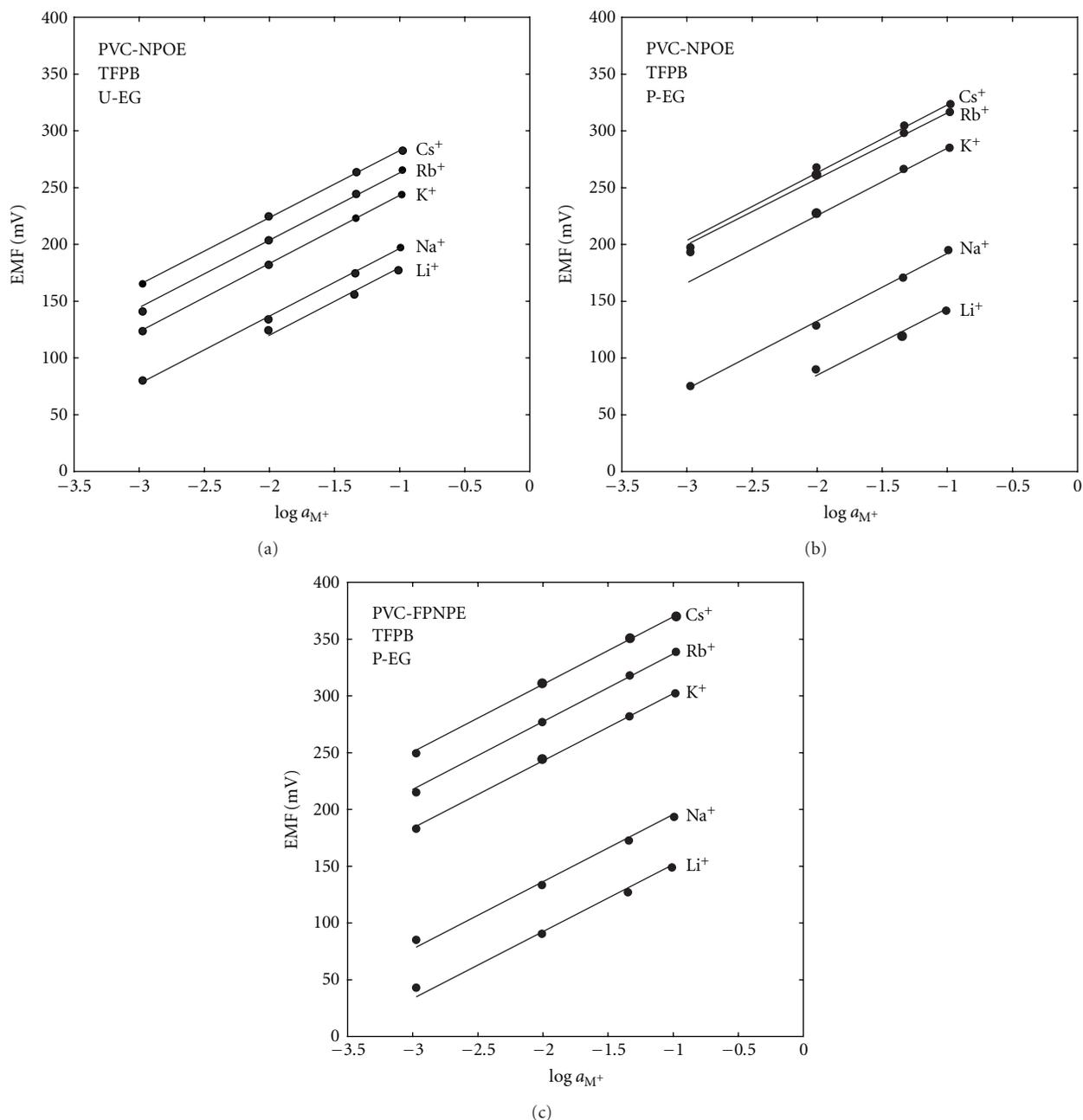


FIGURE 3: Mean potentiometric response towards alkali metal cations of PVC-NPOE membranes containing TFPB and either U-EG (a) or P-EG (b), or P-EG and TFPB plasticized with FPNPE (c). Solid lines denote a theoretical Nernstian slope.

Figure 4 shows the mean potential values observed for an FPNPE-plasticized ISE containing P-EG and TFPB. In the presence of 0.01 M CsCl, the measured electrode potential varied by only a few millivolts between pH 3–12. Below pH 3, however, a significant drop in the electrode potential occurs due to proton interference. A useful pH range of 3–12 was also observed under identical conditions for an analogous membrane plasticized with NPOE (data not shown). Stable electrode potentials at low pH are an important response characteristic due to the acidic conditions under which cesium separations typically occur [35].

4. Conclusion

In this work, Cs⁺-selective solvent polymeric membrane-based ion-selective electrodes have been described based on the use of ethylene glycol-type ionophores. It was demonstrated that the performance of ISEs containing a covalently attached ethylene glycol moiety as ionophore is not impaired relative to electrodes containing a mobile lipophilic ethylene glycol derivative, ethylene glycol mono-octadecyl ether. Furthermore, a new charged cesium ionophore, cobalt-carborane, was introduced and compared to P-EG-based

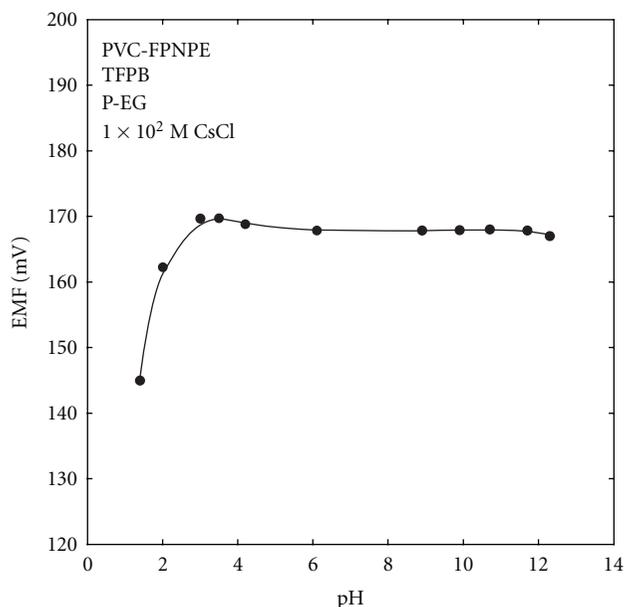


FIGURE 4: Mean potentiometric pH response of FPNPE-plasticized PVC ISEs containing P-EG and TFPB.

TABLE 3: Unbiased potentiometric selectivity coefficients, $\log K_{Cs,J}^{pot}$, of the Cs^+ -selective membranes evaluated in this work.

Ion	Membrane				
	1	2	4	5	6
Cs^+	0.0	0.0	0.0	0.0	0.0
Rb^+	0.1	-0.2	-0.5	-0.3	-0.2
K^+	< -0.1	-0.8	-1.2	-0.7	-0.5
Na^+	-0.6	-2.3	-3.1	-1.6	-2.0
Li^+	-0.7	-3.4	-3.9	-2.0	-2.8
Ba^{2+}	-2.7	-3.1	-3.0	-1.7	-2.2
Sr^{2+}	-3.0	-3.3	-3.5	-1.8	-2.6
Ca^{2+}	-2.7	-3.8	-3.5	-1.8	-2.7
Mg^{2+}	-2.8	-4.1	-3.7	-2.5	-3.0

electrodes. In general, P-EG membranes plasticized with FPNPE outperformed analogous electrodes plasticized with DOS and NPOE with respect to selectivity. This work demonstrates the potential for ionophore-grafted polymeric supports in designing more robust ion-selective sensors.

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