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Short communication

Neutral carrier-based ion-selective electrode with similar sensitivity to different monovalent cations as a detector in ion chromatography

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Abstract

A variety of neutral carrier-type ionophores were employed to prepare cation-selective electrodes for use as a detector in single-column ion chromatography. A polymer membrane electrode doped with a new siloxane-based bis-crown ether exhibited similar selectivity to ammonium and all alkali metal ions except lithium. The lithium ion selectivity was induced by further incorporating an appropriate amount of lithium ionophore ETH 1810 into the bis-crown ether-doped membrane. A single-ionophore membrane electrode doped with monensin methyl ester, known as a sodium ionophore, was shown to exhibit the most comparable sensitivity towards all alkali metal ions and ammonium ion.

1. Introduction

There is a growing interest in polymer membrane ion-selective electrodes (ISEs) to be used in flow-through detectors in ion chromatography (IC) [1–7]. These devices may offer the advantages of rapid and reproducible response, low detection capabilities, and ease of fabrication and miniaturization. Unlike conductometric detectors, the response of the potentiometric ISE detectors does not depend on the area of the electrode [4]. This will be a useful property in situations where a small detector is necessary, such as in capillary IC.

However, direct application of common potentiometric membrane electrodes to IC systems does not allow the detection of different ions with comparable detectabilities. Most of these ISEs are highly selective for specific ions, and exhibit negligible response toward other ionic species. Therefore, the design of ISEs with similar selectivity to many different ions is one essential aspect in the use of such potentiometric detectors for chromatographic applications. Recently, several research groups have examined various approaches to employ neutral carrier-based ISEs in chromatographic detectors [1–7]. For instance, four different cation ionophores (i.e., valinomycin, benzo-15-crown-5, nonactin and tetranactin) were examined to prepare chro-

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matographic ISE detectors [1]. In this study, single-ionophore membrane electrodes were prepared by incorporating each of these ionophores into poly(vinyl chloride) (PVC)-matrix membranes and employed as monovalent cation detectors in IC. Of these neutral carriers, tetranactin provided a membrane with the most similar sensitivity to alkali metal and ammonium ions. Another effort to balance the detectability of different ions includes the use of multiion-selective membranes incorporating several different ionophores [5,6]. The detection characteristics of the multiionophore membranes are controlled by the amounts and ratios of the ionophores incorporated in the membranes.

The aim of this work is to examine a wider range of neutral carrier-doped ISEs as monovalent cation detectors in IC. These neutral carriers include compounds known as sodium ionophores (i.e., ETH 157, ETH 2120, Fluka sodium ionophore VI and monensin methyl ester), lithium (ETH 1810), ammonium (nonactin) and potassium (valinomycin) ionophores, crown ethers (dibenzo-18-crown-6, benzo-18-crown-6 and benzo-15-crown-5), and a siloxane-based bis-crown ether recently synthesized by Chang and Kim [8].

2. Experimental

2.1. Reagents

PVC, bis(2-ethylhexyl) adipate (DOA), 2-nitrophenyl octyl ether (NPOE), potassium tetrakis(*p*-chlorophenyl) borate (KTpClPB), nonactin, N,N′-dibenzyl-N,N′-diphenyl-1,2-phenylenedioxydiacetamide (ETH 157), N,N,N′,N′-tetracyclohexyl-3-phenylenedioxydiacetamide (ETH 2120), bis[(12-crown-4)methyl] dodecylmethyl malonate (sodium ionophore VI), N,N-dicyclohexyl-N′,N′-diisobutyl-*cis*-cyclohexane-1,2-dicarboxamide (ETH 1810), and benzo-15-crown-5 were obtained from Fluka (Switzerland). Monensin methyl ester was purchased from Calbiochem-Novabiochem (La Jolla, CA, USA) and valinomycin from Sigma (St. Louis, MO, USA). A new bis-crown ether compound connected through a siloxane chain, 1,1,3,3,5,5-hexamethyl-1,5-dipentaoxacyclohexadecamethyl trisiloxane (BCE 11), was a gift from Professor Seung Hyun Chang, Taegu University, South Korea. It was prepared according to the procedure published previously elsewhere [8].

All other chemicals used were analytical-reagent grade. Standard solutions and buffers were prepared with the use of deionized water.

2.2. Ion-selective membrane electrodes

The polymeric membrane composition was 1% (w/w) neutral carrier, 33% (w/w) PVC and 66% (w/w) plasticizer (DOA or NPOE) except the membrane for sodium ionophore VI [6.5% (w/w) ionophore, 26.8% (w/w) PVC and 66.7% (w/w) plasticizer]. DOA was used for membranes doped with valinomycin, nonactin, ETH 159 and ETH 2120, and NPOE for membranes with ETH 1810, sodium ionophore VI, monensin methyl ester, benzo-15-crown-5 and BCE 11. Membranes with monensin methyl ester and ETH 1810 further incorporated 0.35 and 0.4% (w/w) of KTpClPB, respectively.

All membranes were cast as described elsewhere [9]. Smaller disks were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasbläserei Möller, Zürich, Switzerland). For all types of electrodes, 0.1 *M* KCl was employed as the internal filling solution. The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02).

Initial potentiometric evaluation of various membranes was conducted by employing a static arrangement. Electrodes were connected through a high impedance amplifier to an IBM AT-type computer equipped with an analog-to-digital converter. The cell potentials were measured at ambient temperature (22°C) by immersing ISEs and the reference electrode in a beaker containing 200 ml of the working buffer (0.05 *M* Tris–HCl, pH 7.2), and the calibration data were obtained from additions of standard solutions. The solutions were magnetically stirred through-out and equilibrium potentials were recorded. Selectivity coefficients were determined by using the separate solution-matched potential method [10–12] at an interfering cation concentration of 0.1 *M*. The detection limits of the membrane electrodes were obtained from the calibration curves as described elsewhere [10].

2.3. Ion chromatography

Chromatographic measurements were carried out using a HPLC pump (Model CCPD; Tosoh, Japan), a sample injector (Model 7125; Rheodyne, Cotati, CA, USA) equipped with a 20-μl sample loop, a cation separation column (Shodex IC Y-521; Showa Denko, Tokyo, Japan), a column heater (CH-30; Eppendorf North America, Madison, WI, USA), and an ISE detector. The design used for incorporating ISEs into a flow-through detection unit was a large volume wall-jet cell electrode design described elsewhere [6,13]. In addition to the HPLC pump, a peristaltic pump (Ismatech Model 7331-00, Zürich, Switzerland) was placed behind the outlet of the column to help maintain a constant level of effluent in the wall-jet detector cell. Electrodes were connected to an Accumet pH-mV meter (Model 925; Fisher Scientific, Romulus, MI, USA), and analog outputs were recorded on an integrator (HP 3394A; Hewlett-Packard, Avondale, PA, USA).

The eluent used was 2 m*M* nitric acid, and the column temperature was maintained at 40°C. For an optimal performance of the wall-jet electrode detector, the eluent stream (1.5 ml/min) from the outlet of the column was merged with a buffer stream (2.0 ml/min) of 0.05 *M* Tris–HCl, pH 9.0 and through a coiled length (35 cm × 0.81 mm I.D.) of PTFE tubing to the detector.

3. Results and discussion

Preliminary potentiometric evaluation of membranes doped with various types of neutral carriers was conducted by employing the static arrangement. Table 1 summarizes the results. For comparison purposes, the data values are presented with respect to potassium (i.e., as the primary ion) for all types of membranes. The more positive the value of log $k^{\mathrm{pot}}_{K^+,j}$ [10], the greater the electrode's response for the interfering ion. When the value of log $k^{\mathrm{pot}}_{K^+,j}$ is zero, the membrane electrode exhibits equal sensitivity

Table 1
Electrochemical characteristics of cation-selective membranes doped with various types of neutral carrier

Neutral carrier	Slope (*mV/dec*)	Selectivity coefficient (log $k^{\mathrm{pot}}_{K^+,j}$					*Detection limit* (*M*)
		Li^+	Na^+	NH_4^+	Rb^+	Cs^+	
Valinomycin	55.4	−4.96	−4.48	−2.01	0.42	−0.49	$7.4 \cdot 10^{-7}$
Nonactin	53.2	−4.13	−2.15	0.87	−0.60	−1.77	$3.0 \cdot 10^{-6}$
Dibenzo-18-crown-6	53.9	−4.86	−2.20	−1.79	−0.79	−0.22	$1.5 \cdot 10^{-6}$
Benzo-18-crown-6	49.1	−4.85	−2.21	−1.57	−1.01	−1.41	$2.5 \cdot 10^{-6}$
Benzo-15-crown-5	51.1	−3.54	−2.15	−1.62	−0.67	−1.15	$3.8 \cdot 10^{-6}$
ETH 157	43.1	−1.46	0.40	−0.63	−0.53	−0.94	$2.0 \cdot 10^{-5}$
ETH 2120	31.3	0.33	1.48	−0.25	−0.61	−0.41	$3.7 \cdot 10^{-5}$
Sodium ionophore VI	33.3	−1.28	1.87	−1.39	−0.38	−0.11	$2.6 \cdot 10^{-5}$
Monensin methyl ester	52.8	−0.28	0.79	−1.14	−0.88	−1.16	$4.9 \cdot 10^{-6}$
ETH 1810	24.0	2.71	0.35	−0.09	−0.09	0.09	$4.6 \cdot 10^{-5}$
BCE 11	52.1	−3.52	−1.07	−0.90	0.27	−0.82	$1.7 \cdot 10^{-6}$
BCE 11/ETH 1810[a]	50.9	−1.13	−0.96	−0.87	0.26	−0.85	$2.3 \cdot 10^{-6}$

Selectivity coefficients and detection limits calculated with respect to K^+ by employing a static arrangement (see the Experimental section and Refs. [10–12] for details).

[a] Prepared with 1% (w/w) of BCE 11 plus 1% (w/w) of ETH 1810.

toward the primary (potassium) and interfering ions. When the value of log $k^{\mathrm{pot}}_{K^+,j}$ is positive, the electrode exhibits even greater response toward the interfering ion than toward potassium. Therefore, more universal non-selective chromatographic detectors can be devised with ISEs having their log $k^{\mathrm{pot}}_{K^+,j}$ values closer to zero. In Table 1, the detectability of the electrode for different ions may be estimated roughly by comparing its selectivity coefficients, knowing the detection limit [10] of the electrode for potassium.

Valinomycin and nonactin are now commonly used for preparing potassium and ammonium-selective membrane electrodes, respectively. In addition to sodium ionophore VI, ETH 157, ETH 2120 and monensin methyl ester are used for sodium-selective electrodes, and ETH 1810 for lithium. The crown ether-type compounds have been examined for their cation selectivities, previously [7,14,15]. The selectivity values listed for the ionophores in Table 1 are in accordance with those previously reported elsewhere [11,16]. It can be seen that all neutral carriers resulted in membranes with a negligible response toward lithium, except monensin methyl ester which provided the membrane with similar sensitivity toward all monovalent cations including lithium.

The electrochemical properties of the PVC membranes doped with the siloxane-based bis-crown ethers such as 1,3-bis(trimethylsiloxyl)-1,3-dimethyl-1,3-dipentaoxacyclohexadecamethyl disiloxane (BCE 9) and BCE 11 have been reported previously [7]. Interestingly, the membranes doped with such bis-crown ether compounds as the ionophore exhibited quite a similar selectivity toward ammonium and all alkali metals except lithium. In this work, the BCE 11 membrane was employed for comparison purposes. When the BCE 11 membrane was further incorporated with ETH 1810 to induce selectivity toward lithium, the resulting BCE 11/ETH 1810 membrane achieved a comparable response toward all alkali metals and ammonium ion (see Table 1).

The use of multiple ionophores for a single membrane matrix is thought to be beneficial in that the selectivity of the membrane can be controlled by varying the types and amounts of ionophores incorporated [5,6]. The previous $K^+/NH_4^+/Na^+/Ca^{2+}$ ion-selective membrane electrode employs four different ionophores (i.e., valinomycin, nonactin, ETH 2120 and ETH 129) [6]. Because of their different lipophilicity values, the ionophores in this membrane will leach at different rates, with the membrane lifetime being determined by the one which leaches most rapidly. Furthermore, different leach rates of the ionophores can alter the initial selectivity of such membrane electrodes since the selectivity of the multiple-ionophore membrane electrodes depends upon the amount and ratio of the ionophores present in the membrane phase. The BCE 11/ETH 1810 membrane employed in this study incorporates only two different ionophores for multiion selectivity. This membrane maintained its initial response slope and selectivity at least for 40 days when stored in buffer. The reproducibility of the characteristics in these multiion membranes seems to be a function of our ability to control the exact quantities of ionophores incorporated into the membrane phase, just as is the case in conventional single-ionophore membranes.

Fig. 1 compares typical ion chromatograms obtained by using ISE detectors with some of the membrane electrodes listed in Table 1. Potentiometric detection was carried out with the wall-jet flow-injection system described in the Experimental section. The chromatograms were obtained by injecting 20 μl of standard mixture containing monovalent cations (Li^+, Na^+, NH_4^+, K^+, Rb^+ and Cs^+) in an equal concentration of 1.0 m*M*. In this study, an additional buffer stream was merged with the eluent stream to help maintain a constant level of effluent in the wall-jet detector cell, and to increase the pH of the eluent stream for an optimal performance of the ISE detectors. It should be noted, however, that a post-column addition of buffer and a mixing coil employed in the experimental set-up will have an adverse effect on chromatographic efficiency (i.e., band dispersion, a reduced signal magnitude due to dilution, etc.).

In static measurements, the electrode response was reasonably rapid, with equilibrium reached

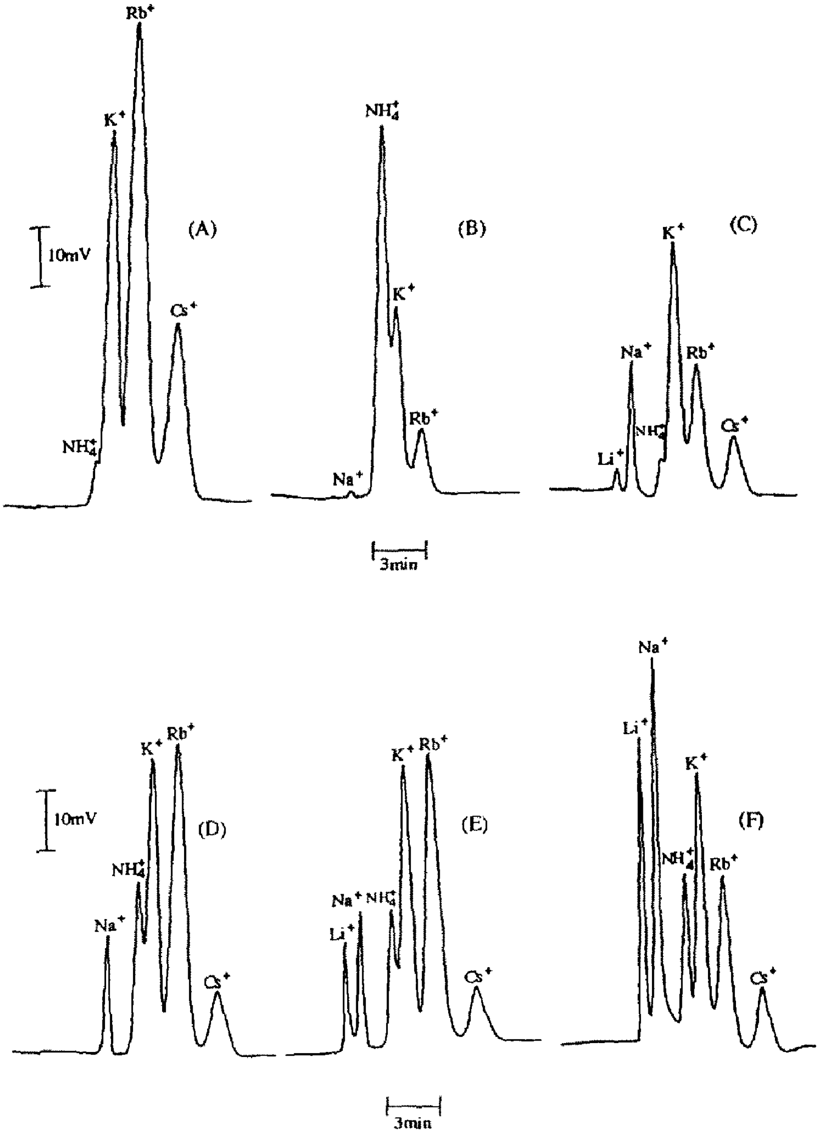

Fig. 1. Ion chromatograms obtained by using ISE detectors doped with (A) valinomycin, (B) nonactin, (C) benzo-15-crown-5, (D) BCE 11, (E) BCE 11 plus ETH 1810 and (F) monensin methyl ester: eluent, 2 m*M* HNO_3, pH 2.5, 1.5 ml/min; sample, 1.0 m*M* each cation (Li^+, Na^+, NH_4^+, K^+, Rb^+ and Cs^+); injection volume, 20 μl.

in less than 10 s; but a large tailing peak was observed in the chromatogram when a sample was injected at a very high concentration, but in most cases the response returned reasonably fast to the baseline level previously observed.

As can be seen in Fig. 1, the response magnitude of the detector was related basically to the selectivity sequences of the ISE employed. A significant response to Li^+ was observed only with the ISE detectors based on ETH 1810, BCE 11/ETH 1810 and monensin methyl ester. Compared to other single-ionophore detectors (e.g., valinomycin, nonactin, lithium and sodium ionophores except monensin methyl ester), all crown ether-based detectors showed better sensitivities toward most of the injected cations. Among the detectors examined, the BCE 11/ETH 1810 and monensin methyl ester electrodes exhibited most balanced detectability for the cations. However, it should be mentioned that even a highly selective ISE system with less universal detection capability may prove useful for a particular application in IC. For instance, the chromatographic determination of Na^+ and K^+ in the human serum matrix (i.e., a high-sodium and low-potassium medium) was reported by Watanabe et al. [4], employing an ISE detector of which the selectivity is higher for K^+ and lower for Na^+.

It is a very common opinion that the logarithmic nature of the response limits the precision of the ISE measurements; a 4% error results from an uncertainty of ± 1 mV with a monovalent ion and 8% for a divalent ion. However, calibration curves of the ISE detector employed in this study were still quite useful because of their good reproducibility. The response of the electrodes doped with BCE 11/ETH 1820 or monensin methyl ester is linear when plotted against logarithmic concentrations of the monovalent cations.

Since the BCE 11/ETH 1810- and monensin methyl ester-based ISE detectors were found to provide universal detection capabilities for monovalent cations, the detection limits were estimated from the calibration plots obtained for the chromatographic system employed. The amplitude of the baseline noise (0.42 mV) was compared with the signal magnitude obtained for the injection of the examined ions. The evaluation was made by assuming that, in the range of small potential changes, the peak height is linearly related to the concentration of injected cations [1–4]. For a signal-to-noise ratio of 2 and a sample volume of 20 μl, the detection limits were as follows: BCE 11/ETH 1810-based, 28 μM (3.9 ng) for Li^+, 4.2 μM (1.9 ng) for Na^+, 21 μM (7.6 ng) for NH_4^+, 2.8 μM (2.2 ng) for K^+, 2.8 μM (4.8 ng) for Rb^+ and 42 μM (110 ng) for Cs^+; monensin methyl ester-based, 1.2 μM (0.17 ng) for Li^+, 0.42 μM (0.19 ng) for Na^+, 4.2 μM (1.5 ng) for NH_4^+, 2.8 μM (2.2 ng) for K^+, 4.2 μM (7.2 ng) for Rb^+ and 84 μM (220 ng) for Cs^+. In this study, no direct comparison was made between ISE and conductometric detection methods. However, it has been reported that, in certain instances, the detectabilities obtainable with potentiometric ISE detection are comparable to those with conductivity detection in single column (non-suppressed) chromatography [1,3,6]. The detectability obtained in this work, without any preconcentration step, is considered to be also satisfactory.

In summary, cation-selective electrodes doped with a variety of neutral carrier-type ionophores were examined for application in flow-through detectors in ion chromatography. The ISE detectors prepared with both monensin methyl ester and a new siloxane-based bis-crown ether compound achieved a comparable response for different alkali metal and ammonium ions. Such ISE detectors could be used as alternative detectors for eluting monovalent cations in IC.

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