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Amperometric Ion Detector for Ion Chromatography

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A new type of amperometric detector for nonredox ions based on ion-transfer reactions at the water|2-nitrophenyl octyl ether−poly(vinyl chloride) gel microinterface has been developed. The polarized interface between water and a polymer composite membrane that can incorporate ionophores such as dibenzo-18-crown-6 and valinomycin provides a selective transducer for an amperometric detection of nonredox ions under flow conditions. Such a sensor is employed as a detector for cation-exchange ion chromatography and shows detectability similar to that obtained with a conductivity detection. The main advantage of this approach is that selectivity can be tailored by the choice of the ionophore and by the polarization potential. As an example, we show how to detect ammonium in the presence of an excess of sodium.

The most ubiquitous detection method in ion-exchange chromatography (IC) is undoubtedly conductometry. Based on the measurement of the conductivity of the electrolytes separated by an ion-exchange column, this method is both accurate and reliable.[1] The accuracy of these detectors is now such that some manufacturers of ion chromatography systems recommend in certain cases not to use suppressor systems. However, the main drawback of a conductometric detector is its total lack of selectivity when compared with an optical or a direct amperometric detector. Of course, direct amperometric detection based on solid electrodes is restricted to redox species.[2−4]

The purpose of this paper is to show, using the recent advances of electrochemistry at polarized liquid|liquid interfaces, that it is now possible to design amperometric detectors for ionic nonredox species such as the alkali metal ions.

Over the last thirty years, our understanding of ion-transfer reactions across the interface between two immiscible electrolyte solutions (ITIES) has reached a point where these reactions can be used for analytical purposes.[5] The principle of an electrochemical ion-transfer reaction, from an analyte to an organic phase, is to provide the ion with the Gibbs energy of transfer required by polarizing the interface. The rate of ion-transfer reactions is extremely fast, and for most purposes, it can be considered to be diffusion controlled. Consequently, if one polarizes an ITIES with a linear sweep of potential as in cyclic voltammetry, the current response will be exactly the same as for a diffusion-controlled reaction on a solid electrode. The equivalent of the standard redox potential is the standard transfer potential, which is the Gibbs energy of transfer expressed in a voltage scale. Of course, a free-standing interface between an analyte and an organic solution cannot be used as a detector.

A lot of work has been dedicated to gelify the organic phase to make it more convenient to use as a detector.[6−20] Our group has recently developed a polymer composite membrane comprising a thin inert polymer layer which is microperforated and covered by a poly(vinyl chloride)−2-nitrophenyl octyl ether (PVC−NPOE) electrolyte gel.[21−23] This electrolyte gel is somewhat similar to those used for the manufacturing of an ion-selective electrode. This approach affords the amperometric detection of ion by classical electrochemical methodology.

The potential window at an ITIES is limited by the Gibbs energy of transfer of the aqueous supporting electrolyte if a hydrophobic salt is used as supporting electrolyte in the PVC−NPOE gel. In the case of cation transfer from water to the organic phase, it is possible to shift the Gibbs transfer energy by incorporating ionophores in the PVC−gel electrolyte phase.[21] Indeed, the ionophore lowers the solvation energy in the gel and the shift of Gibbs energy is equal to $RT \ln K_c$, where K_c is the complexation constant in organic phase. In this case, we shall speak of facilitated ion-transfer reactions. In the present paper, we shall report three cases of ion-transfer reactions and show how

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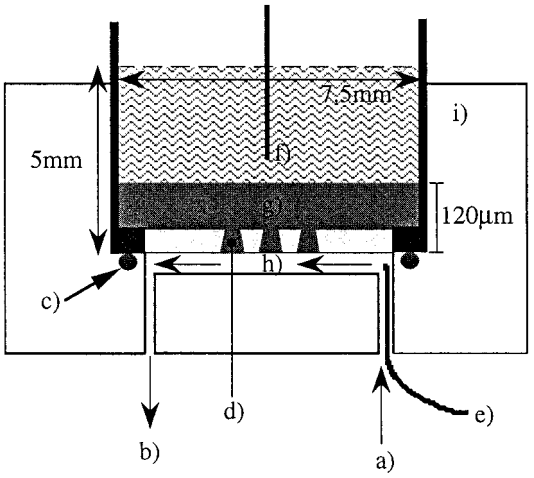

Figure 1. Simplified diagram of setup for flow experiments: (a) inlet, (b) outlet, (c) O-ring, (d) drilled PET film containing PVC−NPOE gel in microholes, (e) Ag|AgCl wire, (f) TBA^+ ISE, (g) PVC−NPOE organic gel, (h) aqueous solution, and (i) Perspex flow cell.

they can be applied to an amperometric detection in ion chromatography: (1) direct ion transfer, (2) facilitated transfer with a nonspecific ionophore, and (3) facilitated ion transfer with an ionophore highly specific for potassium and ammonium over other alkali metal ions.

EXPERIMENTAL SECTION

Chemicals. The aqueous- and organic-phase solvents are deionized water (Milli-Q, Millipore) and NPOE (Fluka), respectively. Dibenzo-18-crown-6 and valinomycin are supplied by Fluka. Lithium, sodium, and potassium nitrate salts together with ammonium chloride are purchased as ion chromatography standard solution (Fluka). High-molecular-weight poly(vinyl chloride) is supplied by Sigma. Tetrabutylammonium tetrakis(4-chlorophenyl) borate (TBATPBCl) and bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl) borate (BTPPATPBCl) are prepared as described elsewhere.[21] All other chemicals used are analytical grade or better.

MicroMachined Composite Polymer Membrane. The membrane consists of two polymer layers. A supporting film of poly(ethylene terephthalate) (23 μm thick, Melinex type S from ICI Films) with a microhole array of 66 holes (11 × 6) ablated by a UV excimer laser acts as a supporting film for a plasticized ion-conducting PVC gel which is prepared by dissolving PVC (2.8% m/m) in a solution of TBATPBCl (10 mM) in NPOE. The thickness of the composite polymer membrane is ~100 μm. The procedures of the laser micromachining of the polyester and the casting of the PVC gel layer are described in a previous paper.[23] Due to the laser fabrication method, the holes are conical with a larger diameter of 20 μm and a smaller diameter of 10 μm.[24]

Electrochemical Measurements. For experiments with a flow cell (see Figure 1), a Teflon cylinder and a corresponding sealing cap with a diameter of 0.75 cm are used. The organic gel is cast on the perforated PET film on the side exposing the smaller diameter. The gel fills the conical holes so that we can obtain an array of microdisk interfaces having a diameter of 20 μm and exposed to the flowing aqueous solution. The reference electrode for the organic phase consists of a tetrabutylammonium ion-selective electrode (TBA^+ ISE) comprising an aqueous solution of TBA-Cl and Ag|AgCl reference electrode. A TBA^+ ISE is added on the top of the composite polymer membrane having a total thickness of ~5 mm. Electrochemical measurements are performed in a two-electrode mode. The ion chromatography, the pump, and the autosampler used are models 690, 697, and 698, respectively, from Metrohm. The separation column is a Metrosep cation 1-2 column (6.1010.000IC column) also from Metrohm. The ion chromatograms are recorded on an analog *XY* recorder (Advanced Bryans). Cyclic voltammetry, chrono-amperometry and pulse amperometry are performed using a computer controlled potentiostat (Sycopel Scientific Ltd., and Tacussel Pol 150 T) from which the data are acquired using Windows-driven software. The galvanic potential difference across the polarized gel interface is expressed in the TATB scale and given by

$$\Delta_o^w \phi = E_{\text{appld}} - [\Delta_o^w \phi_{1/2,\text{TMA}^+_{(\text{exp})}} - \Delta_o^w \phi_{1/2,\text{TMA}^+}]$$

where the half-wave potential of TMA^+ ion ($\Delta^w_{o\,1/2,\text{TMA}^+}$) is 214 mV in TATB scale.[21] The sweep rate in the cyclic voltammetry is 10 mVs^{-1} (unless otherwise specified). All the above experiments are carried out at a room temperature of 23 ± 2 °C.

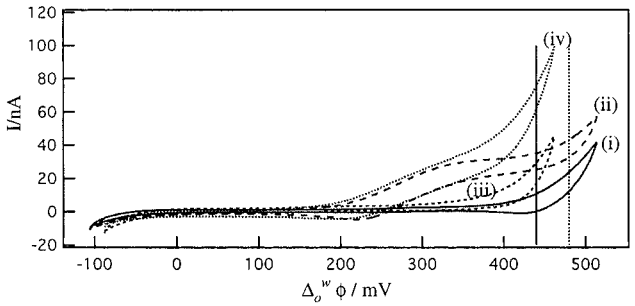

Figure 2. Cyclic voltammograms of choline ion transfer into PVC−NPOE gel membrane. The potential is referred to the TATB scale using cell I: (i) 1 mM LiCl potential window, (ii) 0.1 mM choline ion in 1 mM LiCl, (iii) 5 mM tartaric acid, and (iv) 0.1 mM choline ion in 5 mM tartaric acid.

RESULTS AND DISCUSSION

Direct Ion Transfer of Monovalent Cations. As an example, the transfer of choline ion from an aqueous supporting electrolyte of either LiCl or tartaric acid to a PVC gel membrane has been studied by cyclic voltammetry, and the results obtained using cell I (see Chart 1) are shown in Figure 2. The transfer of choline ion occurs within the polarized potential window and the half-wave potential of choline ion transfer is found to be 263 mV in the TATB potential scale. The potential window is limited at positive potentials either by the transfer of Li^+ from water to the PVC gel or by the transfer of protons.

To test the device in a flow channel, different concentrations of choline are injected into a flow of 1 mM LiCl (flow rate 0.8 $mL \cdot min^{-1}$) using an automated sampler (10-μL injection). The sample is prepared by dilution within the eluent (1 mM LiCl) and then filtered with a Spritzen filter (0.20 μm from Semadeni). The test flow system is simply obtained by disconnecting the ion-

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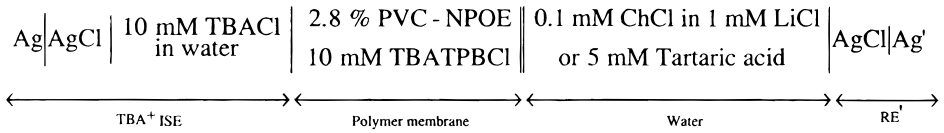
Chart 1. Cell I



exchange column and the conductometric detector and by connecting directly the micromachined polymer composite membrane mounted in its holder as shown in Figure 1. The distance between the amperometric detector, and the injection valve is ~18 cm. For choline ion analysis, a constant-potential operation mode maintaining the analyte|PVC gel interface polarized at 480 mV is used and the current is measured with a sampling rate of 10 Hz.

Figure 3 shows the current response to a flow injection for different concentrations of choline. It can be seen that a stable baseline and high sensitivity are obtained mainly because choline ion transfers within the potential window. The small oscillations on the baseline are caused by the pump in the absence of the ion-exchange column. The response of the amperometric detector is found to be linear over the concentration range studied of 7.5−250 μM within experimental error (5% of mean values), and the detection limit (signal-to-noise ratio of 3:1) of membranes measured for choline ion is found to be ~7.5 μM.

When using the cation-exchange column, the composition of the aqueous phase should follow the manufacturer's recommendation, and to comply with the requirements of the Metrosep column, a 5 mM tartaric acid is used as eluent (pH 2). As far as the amperometric detection of cations is concerned, the nature of the anions has no influence on the gel detector so this eluent was used for the whole experiment. As shown in Figure 2, a relatively low pH shortens the potential window, but the presence of acids cannot be avoided in cation-exchange chromatography. To compare the ion amperometric detector to the classical conductometry detector, two types of amperometric methods have been used, namely, constant-potential chronoamperometry at 480 mV and pulse amperometry. In the case of the pulse amperometry mode, between 190 mV where no ion transfers and 440 mV where mainly choline ion transfers are used, the pulse period is 140 ms and the current recorded is the difference between the current at the end of the pulse at 440 mV (40 ms) and that at the end of the period at 190 mV (100 ms).

Figure 4 shows the comparison between a conductometric and an amperometric detection in constant-potential amperometry or pulse amperometry. In all cases, the broadening of the choline ion peak is mainly due to a long retention time and the severe asymmetry of the peak is also obtained due to the column overloading, which causes the concentration to be in the nonlinear region of the convex ion-exchange isotherm. The results of Figure 4 show that pulse amperometry yields results of the same quality as conductometry. Constant-potential amperometry is much less sensitive by 1 order of magnitude compared to pulse amperometry. This can be explained by the concentration profiles of the transferring ion in the aqueous phase for the two diffusion conditions, but also by the fact that keeping the interface polarized for long periods at 480 mV may alter its chemical composition. These results clearly demonstrate that the microgel membrane can be used as an effective amperometric detector for ionic species having a relatively small Gibbs energy of transfer between water and NPOE, i.e., for ionic species crossing within the potential window.

Figure 5 shows cyclic voltammograms for the transfer of the monovalent cations (lithium, sodium, ammonium, potassium) across the PVC−NPOE gel membrane in the TATB potential scale using cell II (Chart 2). From the voltammograms, it can be seen that each cation is itself a potential-limiting species. For these ions, the amperometric detection methods described above become problematic because there is interference between the

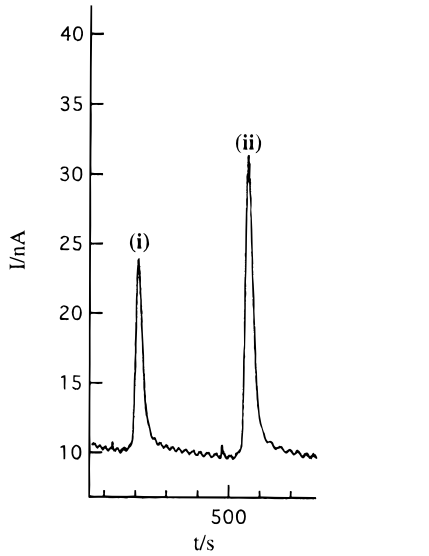


Figure 3. Chronoamperograms recorded for the detection of choline ion using the PVC−NPOE gel membrane at the constant potential of 480 mV shown in Figure 2. Flow rate is 0.8 mL·min^{-1}. The concentration is (i) 0.2 and (ii) 0.3 mM.

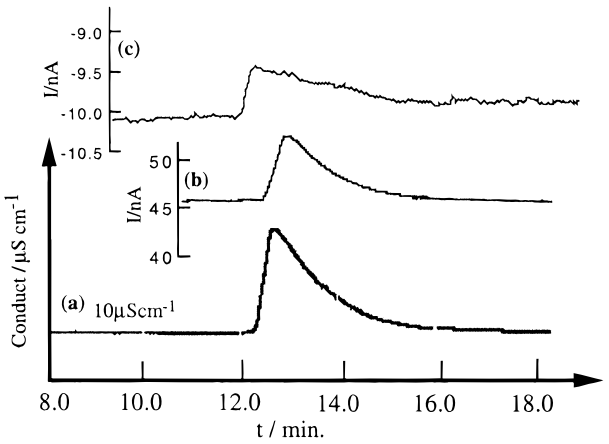


Figure 4. Comparison of IC conductometric and microgel detectors for the detection of choline ion using ion-exchange chromatography: (a) chromatogram for choline ion based on a conductometric detector, (b) pulse amperogram, and (c) chronoamperogram recorded for the detection of choline ion using the PVC−NPOE gel membrane. Flow rate is 0.85 mL·min^{-1}. Choline ion concentration is 1 mM; 5 mM tartaric acid is used as an eluent.

Chart 2. Cell II

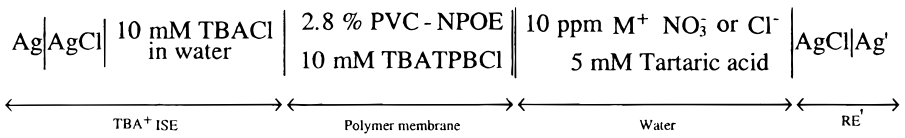
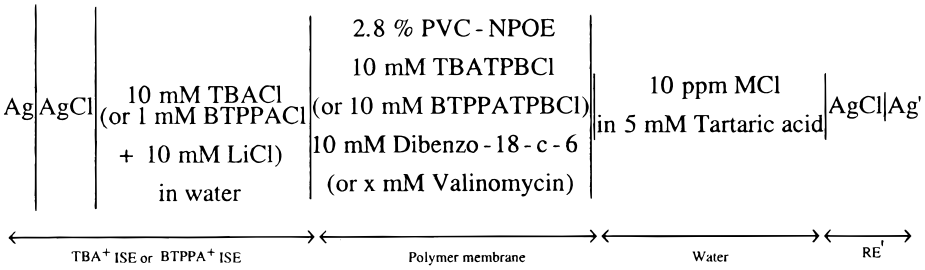


Chart 3. Cell III



target ion transfer and the transfer of the protons from the eluent occurring in the same potential domain. Figure 6a shows a chromatogram obtained by chronoamperometry in a constant-potential mode at 500 mV. It is clear that the response behavior of microgel membranes is somewhat similar to that obtained by the conductometric detector (Figure 6b) but that the baseline is too poor to be of any analytical use. In the case of pulse amperometry, interferences from the proton do not allow any quantitative analysis either.

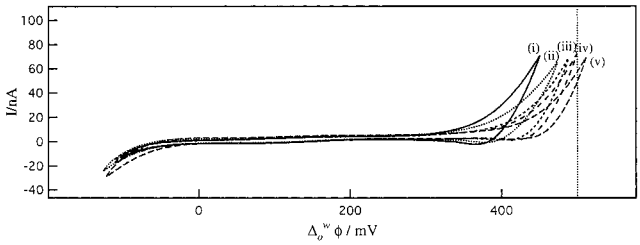


Figure 5. Cyclic voltammograms of monovalent cations transfer into PVC−NPOE gel membrane. The potential is referred to the TATB scale using cell II: (i) 10 ppm NH_4Cl, (ii) 10 ppm KCl, (iii) 10 ppm LiCl, (iv) 10 ppm NaCl, and (v) 5 mM Tartaric acid. sweep rate 10 mV·s^{-1}.

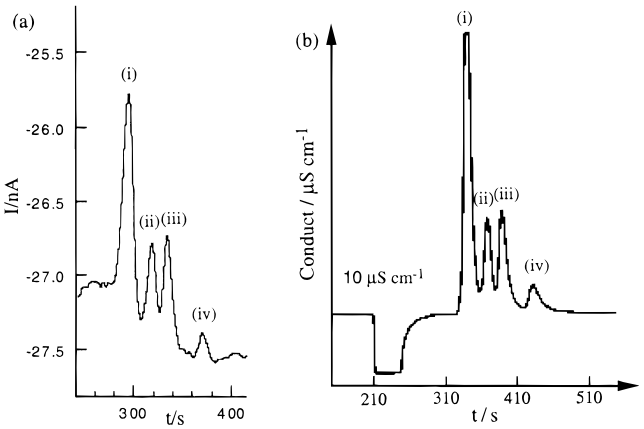


Figure 6. Comparison of IC conductometric and microgel detectors for the detection of cations using ion-exchange chromatography: (a) chronoamperogram recorded for the detection of monovalent cations studied using the PVC−NPOE gel membrane; (b) chromatogram obtained for the monovalent cations based on a conductometric detector. (i) Li^+, (ii) Na^+, (iii) NH_4^+, and (iv) K^+. Flow rate is 0.85 mL·min^{-1}. Each cation concentration is 10 ppm; 5 mM tartaric acid is used as an eluent.

To circumvent these problems, we have to lower the Gibbs energy of transfer of these monovalent ions and the best way to achieve this is to add ionophores to the organic phase.

On-Line Amperometric Detection of Facilitated Monovalent Cations by DB18C6. The transfer of alkali metal ions can be facilitated by ionophores such as di-benzo-18-crown-6 (DB18C6) introduced in the 2.8% PVC−NPOE gel. Figure 7 shows cyclic voltammograms of the facilitated transfer of proton, sodium, ammonium, and potassium in 5 mM tartaric acid eluent across the PVC−NPOE gel membrane using cell III with the potential scale referred to the TATB transfer potential (Chart 3).

Pulse amperometry can now be used with an initial potential where no ion transfers across the membrane ($E_i = -70$ mV) and a transfer potential value of 280 mV as shown in Figure 7. The pulse time characteristics are identical to those used before. Figure 8a presents a pulse amperometric detection at 280 mV of a mixture of Na^+, K^+, and NH_4^+ separated by the Metrosep column. The presence of the ionophore clearly enables the detection of these species in a satisfactory manner compared to the conductometric detection shown in Figure 8b. The dependence of corresponding charges (Q), over the concentration in the aqueous phase is linear for the range studied (0.2−20 ppm)

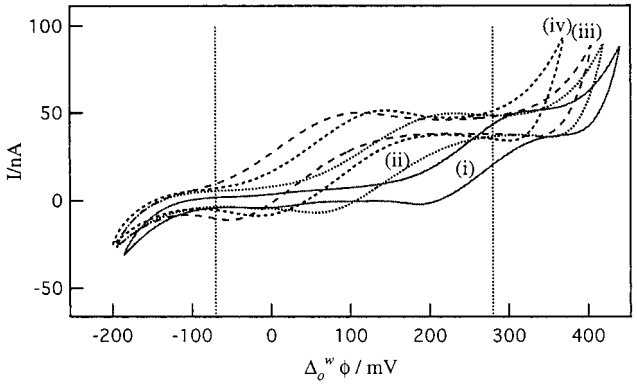


Figure 7. Cyclic voltammograms of monovalent cation transfer into PVC−NPOE gel membrane facilitated by 10 mM DB18C6. Cell III is used and potentials are referred to the TATB scale: (i) H^+ in 5 mM tartaric acid, (ii) Na^+, (iii) NH_4^+, and (iv) K^+. Each cation concentration is 10 ppm.

Table 1. Amperometric Detection Response from Calibration Plots Obtained either without an Ionophore Using Constant-Potential Chronoamperometry at 500 mV or with 10 mM DB18C6 as an Ionophore in the Gel Using Pulse Amperometry between −70 and 280 mV

	Na^+/ nC·μM^{-1}	NH_4^+/ nC·μM^{-1}	K^+/ nC·μM^{-1}	Li^+/ nC·μM^{-1}
without ionophore	0.0028	0.0029	0.0042	0.0039
with 10 mM DB18C6	0.222	0.681	1.298	

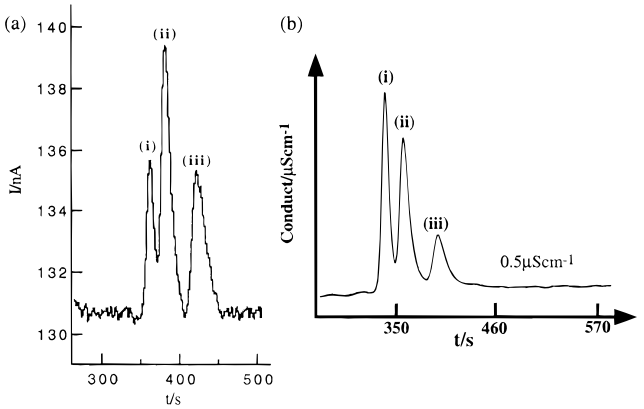


Figure 8. (a) pulse amperogram recorded for the detection of monovalent cations studied using the PVC−NPOE gel membrane at the final potential of 280 mV. (b) chromatogram recorded for the monovalent cations based on conductometric detector. Flow rate is 0.85 mL·min^{-1}. Each cation concentration is 1 ppm. (i) Na^+, (ii) NH_4^+, and (iii) K^+; 5 mM tartaric acid is used as an eluent.

for all three cations. At higher concentrations, deviation from linear behavior is observed for ammonium. Excellent reproducibility is achieved for various chromatographic runs. The detection limit (signal-to-noise ratio of 3:1) of the amperometry is estimated as 100 ppb for K^+, 50 ppb for Na^+, and 200 ppb for NH_4^+ when a 10-μL sample volume is used. Compared to the detection limit of the conductometry measurement, which is estimated as 50 ppb for those ions, it can be said that the microgel membrane with DB18C6 can be used as an alternative detection method.

Table 1 compares the sensitivity of the membrane for the determination of monovalent cations using constant-potential chronoamperometry in the case of direct ion transfer and pulse amperometry in the case of facilitated ion transfer. The different values obtained reflect the different diffusion coefficients and the standard transfer potential of the different species.

A water sample from Lake Geneva has also been prepared by filtering twice with the filter paper (5892 white ribbon from Scheicher & Schuel) and prepared in the eluent, 5 mM Tartaric acid, without dilution. After that it is filtered again with a Spritzen filter (0.20 μm from Semadeni). The standard addition curves and the calibration curves are constructed with the concentration ranges between 0.5 and 20 ppm for all the cations studied. The concentrations of monovalent cations determined from the lake water by both standard addition and calibration methods are found to be 67 (±3) ng of sodium, 3 (±0.5) ng of ammonium, and 15 (±1) ng of potassium. These values are in good agreement with the results obtained by the conductometric detection using the same experimental conditions 63 (±3) ng of Na^+, 2 (±0.5) ng of NH_4^+, and 12 (±1) ng of K^+.

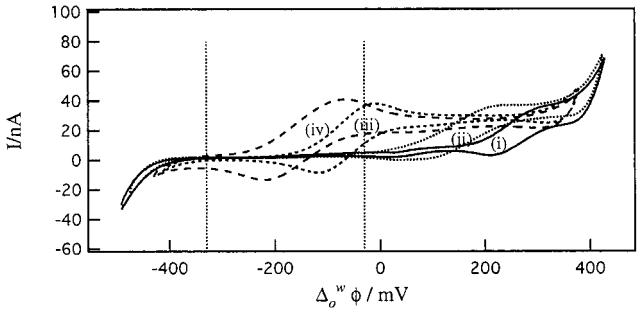


Figure 9. Cyclic voltammograms of the monovalent cation transfer into PVC−NPOE gel membrane facilitated by valinomycin (x = 10 mM). Cell III is used and potentials are referred to the TATB scale. $BTPPA^+$ cation as the organic supporting electrolyte. Each cation concentration is 1 ppm. (i) H^+ in 5 mM tartaric acid, (ii) Na^+, (iii) NH_4^+, and (iv) K^+.

Ammonium-Selective Detection Based on Facilitated Transfer by Valinomycin. The detection of ammonium in an excess of sodium and that of sodium in an excess of ammonium has proved to be a difficult task in conventional ion-exchange chromatography when conductometric detectors are used. The ion transfer facilitated by valinomycin as an ionophore can be used to increase the selectivity of ammonium ion transfer over that of sodium. Valinomycin has been used as a potassium ion-selective ionophore[25,26] and is also a well-known ionophore for the facilitated transfer of ammonium. Valinomycin has a similar association constant for both potassium and ammonium.[21,27] The ISEs detectors based on valinomycin have already been developed for the potentiometric sensing of alkali and alkaline metal ions[28] and previously employed as potentiometric detectors in ion chromatography.[29]

Figure 9 shows cyclic voltammograms of the facilitated transfer of proton, sodium, ammonium, and potassium in 5 mM tartaric acid using 10 mM valinomycin in the PVC−NPOE gel membrane. From this figure, the potentials −330 and −30 mV are taken, respectively, as the initial potential where no ion transfers and the final potential where the ammonium ion mostly transfers for the pulse amperometric detection. Figure 10a shows amperograms obtained for the concentration range of (A) (i) 100 ppm Na^+, (ii) 0.5 ppm NH_4^+, and (iii) 0.5 ppm K^+; (B) (iv)100 ppm Na^+, (v) 1 ppm NH_4^+, and (vi) 1 ppm K^+; and (C) (vii) 20 ppm Na^+, (viii) 4 ppm NH_4^+, and (ix) 4 ppm K^+ in the presence of 1 mM valinomycin in the gel membrane. Here TBA^+ is used as the organic supporting electrolyte cation to improve the stability and endurance of the membrane. The signals obtained from a conductometric detection are also shown in Figure 10b over the same concentration range. It can be seen that the selectivity of the membrane for the ammonium ion increases dramatically even if the concentration of sodium ion is over 3 orders of magnitude in excess. Furthermore, low-ppm levels of ammonium ion can be effectively detected over 200 times excess of Na^+ ion (see Figure 10a(A)).

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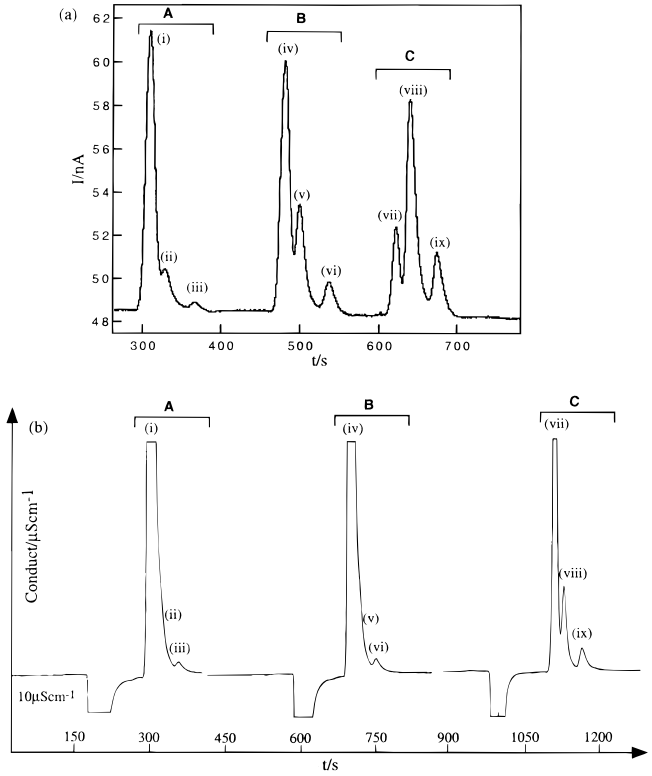

Figure 10. Pulse amperograms recorded for (a) monovalent cations facilitated by 1 mM valinomycin using the microgel membrane and TBA^+ cation in the organic supporting electrolyte. (b) Chromatogram obtained for the monovalent cations based on a conductometric detector. The concentrations of the standard solutions are (A) (i) 100 ppm Na^+, (ii) 0.5 ppm NH_4^+, and (iii) 0.5 ppm K^+; (B) (iv) 100 ppm Na^+, (v) 1 ppm NH_4^+, and (vi) 1 ppm K^+, and (C) (vii) 20 ppm Na^+, (viii) 4 ppm NH_4^+, and (ix) 4 ppm K^+. Flow rate is 0.85 mL·min^{-1}, and 5 mM tartaric acid is used as an eluent.

Table 2. Amperometric Detection Response from Calibration Plots Obtained at Various Concentrations of Valinomycin Using Pulse Amperometry between −330 and −30 mV

$c_{valinomycin}$/ mM	Na^+/ nC·μM^{-1}	NH_4^+/ nC·μM^{-1}	K^+/ nC·μM^{-1}
1	0.016	0.380	0.370
10	0.021	0.401	0.329

The calibration curves for each cation analyzed are displayed in Figure 11. It is observed that the response of the membrane is linear over the concentration range studied. The selectivity and sensitivity of membranes are similar for both ammonium and potassium ions as a result of their high association constants, i.e., 14.6 for NH_4^+ and 16.0 for K^+.[21] Correspondingly, a decrease of the sensitivity of the membrane for sodium ion is observed due to a smaller association constant. The similar performances of the membranes for 1 and 10 mM valinomycin (see Table 2) indicate that the faradaic signal is determined by the diffusion flux of cations to the interface. The detection limit (signal-to-noise ratio of 3:1) obtained for both potassium and ammonium is ∼50 ppb.

It should also be mentioned that when measurements of the current for monovalent cations are carried out, not in the absence of the other analyte ions, but on a mixed matrix, the response of the membrane is not linear over either high or low concentration. This nonlinearity may reflect a competition between the various cations for the interfacial complexation despite the separation by the cation column.

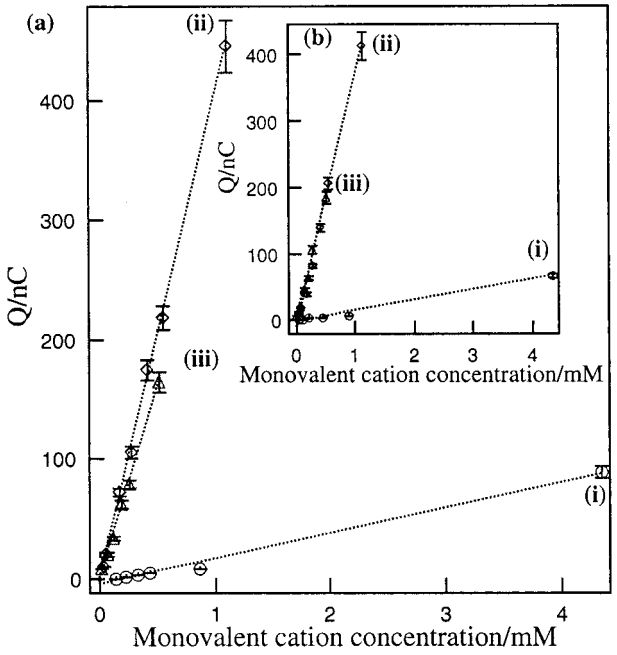

Figure 11. Corresponding charges versus concentrations of monovalent cations using (a) 10 mM valinomycin and (b) 1 mM valinomycin for the membrane: (i) Na^+, (ii) NH_4^+ and (iii) K^+. (- - -) represents the best fit. These calibration plots are obtained in the absence of other analyte ions.

CONCLUSIONS

The experimental results show that the composite polymer membranes can be employed as an effective detector for monovalent cations in a conventional ion chromatographic column. The sensitivity and selectivity of the membrane can be significantly increased by introducing an ionophore such as DB18C6 in the gel phase. The selectivity of the membranes toward ammonium in the presence of an excess of sodium can be substantially increased by introducing an ammonium-selective ionophore such as valinomycin in the gel membranes. Furthermore, the methodology can be extended to detect other ions such as lithium and alkali earth metal ions by selecting appropriate ionophores.

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