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Monomer and polymer quinoxaline derivatives for cationic recognition

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Abstract Monomeric and polymeric 5-nitroquinoxaline derivatives disubstituted in the 2 and 3 positions with 2-pyrrolyl (A), 2-furyl (B) and 2-thienyl (C) groups were prepared and characterized. The substituted 5-nitroquinoxalines were used as active components in poly(vinyl chloride)-membrane and electropolymerized electrodes that were then tested as possible sensors for various cationic species. In contrast to the difurylnitroquinoxaline-based systems, the monomeric and polymeric dipyrrolyl- and dithienylquinoxaline electrodes displayed a good selectivity for Ag^+ ions, providing a near-Nernstian response in the 10^{-5} to 10^{-2} mol L $^{-1}$ concentration range. The similar potentiometric behavior displayed by the monomeric and polymeric forms of systems A and C supports the contention that the main binding modes displayed by the monomeric forms are retained in the corresponding polymeric structures.

Keywords Nitroquinoxaline · Ion-selective electrode · Cationic selectivity

Introduction

The ongoing quest for receptors capable of recognizing selectively charged species has stimulated advances across a broad array of research fields [1, 2]. Recent developments in the area of electrochemical sensors and, in particular, ion-selective electrodes (ISEs) have played an important role in this process [3]. Endowed with a range of advantageous properties, including ready modification and

stability, electropolymerized electrodes have proved particularly instrumental in advancing the ISE area [4, 5, 6]. Unfortunately, our current understanding of response mechanism, as well as the origins of selectivity is extremely limited in the case of electropolymerized electrodes. Ion-exchange mechanisms, acting in concert with selective complexation processes involving specific analytes, might be responsible for the selectivity displayed by certain electropolymerized electrodes [4]. However, other factors, including the structure of the polymer, temperature, pH, and ion strength are also likely to be important. One way of gaining further insights into electropolymerized electrodes and their function would be to compare the electrochemical behavior of monomeric and polymeric forms of the same receptor immobilized on the surface of the electrode. To the best of our knowledge, however, this has not previously been done. Accordingly, we report here the characterization of several 2,3-disubstituted 5-nitroquinoxalines bearing 2-pyrrolyl (A), 2-furyl (B) and 2-thienyl (C) substituents (Fig. 1), as well as their use as active components in poly(vinyl chloride)-membrane and electropolymerized electrodes.

The ability of quinoxaline derivatives to coordinate various anionic species such as F^- , Cl^- and H_2PO_4^- has been described recently [7, 8]. Nitro substitution of the core quinoxaline has been found to increase the affinity of dipyrrolylquinoxalines for anions. In the course of prepar-

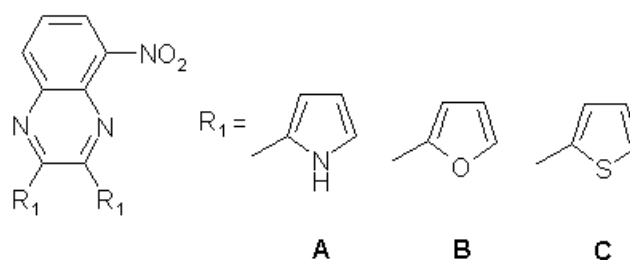


Fig. 1 Structures of 5-nitroquinoxaline derivatives substituted in the 2 and 3 positions with 2-pyrrolyl (A), 2-furyl (B), and 2-thienyl (C) groups

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ing polymeric films derived from nitroquinoxalines, we discovered that electrochemical reduction on the solid surface effects conversion of the nitro substituent into the corresponding primary amine [9]. The presence of this latter functionality could, we reasoned, lead to different selectivity for the polymeric electrodes compared to those based on their constituent monomers, especially in the case of cation recognition where the presence of extra lone pair donors would be potentially beneficial. In this study, we demonstrate for the first time the cation recognition capability of quinoxaline-derived ion-selective electrodes in both monomeric and polymeric forms and provide evidence that the factors influencing binding affinity in these two states are essentially the same.

Experimental

Materials

2,3-Disubstituted-5-nitroquinoxalines were prepared in accord with the general procedure described elsewhere [8]. Nitrate salts of the cations used in this study (Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , Pb^{2+} , Hg^{2+} , and Ag^+) were obtained from Lachema, Brno, Czech Republic. Poly(vinyl chloride) (PVC, high molecular weight type), 2-nitrophenyl octyl ether (o-NPOE), sodium tetraphenylborate (TPB) and tetrahydrofuran (THF) were obtained from Fluka, while dioctyl phthalate (DOP) was obtained from Aldrich. All aqueous solutions were prepared using distilled water unless noted otherwise.

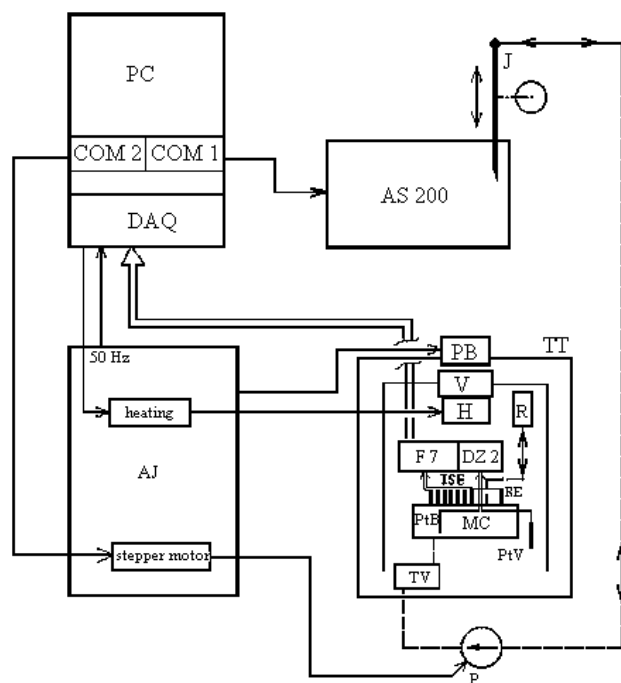


Fig. 2 Schematic representation of the flow-through cell. AS200, autosampler; P, peristaltic pump; AJ, analog unit box; TT, hot-air thermostat; COM 1 and COM 2, computer serial ports; DAQ, data-acquisition card PC 516; J, sampling needle; MC, measuring cell; V, ventilator; H, heating; PB, cooler; R, solution reservoir; PtB and PtV, platinum thermometers; DZ 2, two differential amplifiers; ISE, tested electrodes; RE, reference electrode (Ag/AgCl electrode ($3 \text{ mol L}^{-1} \text{ KCl}$)); F7, amplifiers

Instrumentation

Electropolymerization experiments were performed using a polarographic analyzer PA 2 (Laboratory Devices, Prague, Czech Republic) bearing a cyclic voltammetric adapter (Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Czech Republic) connected to an XY-recorder BAK 5T (Aritma, Prague, Czech Republic). A three-electrode system with a platinum-wire working electrode, a platinum plate counter electrode and an Ag/AgCl ($3 \text{ mol L}^{-1} \text{ KCl}$) reference electrode was used to effect polymerization.

The potentiometric response of the various experimental electrodes produced during the course of the present study was monitored at a temperature of $25.00 \pm 0.01 \text{ }^\circ\text{C}$ using a custom seven-channel flow-through cell that was built in house (cf. Fig. 2).

The pH was monitored using a glass electrode Type SEUJ 212 (Electrochemical Detectors, Turnov, Czech Republic) in conjunction with a Type OP-201/2 pH-Meter (Radelkis, Hungary).

Electrode preparation

PVC-membrane electrodes

PVC-membrane electrodes were prepared in accord with procedure used elsewhere [10]. In the present study, 0.7 mL THF was used to dissolve approximately 100 mg of a mixture composed of 3 wt% of the ionophore in question, 50 mol% (relative to the ionophore) of an anionic lipophilic additive (TPB), of PVC and plasticizer (o-NPOE or DOP) in a 1:2 (w/w) ratio. Control electrodes were prepared using similar procedure with no ionophore added [10]. The resulting membrane electrodes obtained after evaporation of THF were mounted into the flow-through cell.

Electropolymerized electrodes

Prior to polymerization the working solutions were purged with nitrogen for 10 min. Also, before effecting electropolymerization, the 5-nitroquinoxaline species were specifically reduced to the corresponding 5-aminoquinoxaline derivatives. These reductions were carried out using $10^{-2} \text{ mol L}^{-1}$ solutions of the 5-nitroquinoxaline in question made up in a 20:1 (v/v) mixture of 99.5% glacial acetic acid and $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and subjected to a -1.5 V (vs. Ag/AgCl ($3 \text{ mol L}^{-1} \text{ KCl}$)) potential over the course of 1 h. The polymerization itself was performed in a three-electrode cell by repeated scanning of the working electrode potential from -0.3 to 1.25 V at 100 mV s^{-1} in a cyclic fashion for 30 min [9]. The electrodes produced in this way were washed thoroughly with distilled water and stored in AgNO_3 solution (ca. $10^{-6} \text{ mol L}^{-1}$).

Potentiometric measurements

For measurements involving the poly(vinyl chloride) electrodes, the working solutions were prepared by diluting stock solutions ($10^{-1} \text{ mol L}^{-1}$) of the cationic species in question with water. For studies of the electropolymerized electrodes, the relevant working solutions were prepared by diluting stock solutions of the cationic species with a mixture consisting of $10^{-5} \text{ mol L}^{-1} \text{ LiNO}_3$ and $5 \times 10^{-5} \text{ mol L}^{-1} \text{ HNO}_3$, pH 4.5.

Linear concentration working ranges and detection limits (c_{min}) were measured and calculated in accord with the IUPAC recommendation [11].

The selectivity coefficients $\log K_{\text{Ag}^+/\text{j}}^{\text{Pot}}$ were determined using the fixed interference method and AgNO_3 solutions with a constant ionic background of the interfering salt (10^{-5} and $10^{-3} \text{ mol L}^{-1}$ for Hg^{2+} and $10^{-3} \text{ mol L}^{-1}$ for Mg^{2+} , Cu^{2+} , Co^{2+} , Pb^{2+} , Zn^{2+} , Na^+ , K^+) [12]. This procedure was used for the PVC-membrane electrodes as well as the electropolymerized electrodes.

The pH-sensitivity was studied in the pH range 2–9.

Results and discussion

The first goal of this study was to prepare and characterize ion-selective electrodes based on monomeric 5-nitroquinoxaline derivatives bearing 2-pyrrolyl (A), 2-furyl (B) and 2-thienyl (C) groups in the 2 and 3 positions and to compare their selectivities towards various cationic species. Here, the electrodes were made up using PVC-membranes containing either DOP or o-NPOE as plasticizers. In addition to these components and the quinoxaline ionophore, sodium tetraphenylborate (50 mol% relative to the ionophore) was incorporated into the membranes.

PVC-membrane electrodes

In the initial experiments, a PVC/o-NPOE control membrane electrode containing no ionophore was tested for its response to various cations. Such a membrane, which does contain tetraphenylborate, was found to be selective towards monovalent cations, e.g., Na⁺ (24 mV decade⁻¹, 10⁻² to 10⁻¹ mol L⁻¹), K⁺ (38 mV decade⁻¹, 10⁻³ to 10⁻¹ mol L⁻¹), Rb⁺ (37 mV decade⁻¹, 10⁻³ to 10⁻¹ mol L⁻¹), Cs⁺ (37 mV decade⁻¹, 10⁻³ to 10⁻¹ mol L⁻¹). However, in the case of divalent cations, no response was observed. Such findings are consistent with the logical assumption that, in the absence of a ionophore, the selectivity of the control membrane is determined by the hydration energy of the cations.

In the case of the PVC membranes based on the monomeric substituted nitroquinoxalines, it was found that the nature of the substituent has a great effect on the observed sensitivity. For instance, the PVC/o-NPOE membranes

based on A and C showed a sub-Nernstian response towards monovalent cations (Table 1), whereas those based on B displayed a weak affinity towards all tested cationic species. It is well known that oxygen-containing groups are hard Lewis bases and generally stabilize complexes containing hard cations (i.e., those of the alkali and alkaline earth series). It was thus expected that membranes containing the monomeric, difuryl-substituted receptor B would have a good response towards alkaline earth cations. However, this did not prove to be the case, as underscored by the lack of response observed for such electrodes. Presumably, this latter lack of response reflects the absence of a preorganized cavity for cation binding or the presence of one whose electrostatic character is not well-suited for accommodating positive charges.

Based on previous X-ray structural analyses of dipyrrolylquinoxalines [13], we expect that the actual binding sites formed in the case of the monomer A are formed from the cooperation of free electron pairs of pyrrolic nitrogens and benzopyrazine nitrogens, while in the case of C the corresponding binding site is formed by a combination of thiophene sulfur and benzopyrazine nitrogen atoms.

As a general rule, for the electrodes containing the monomeric nitroquinoxalines A and C, the potentiometric response toward alkali metal cations are characterized by slopes of ca. 44–50 mV decade⁻¹, with the actual detection limits varying with the lipophilicity of the cation. Compared to the control membrane electrode based on a tetraphenylborate, the presence of quinoxaline ionophores A and C within the PVC-matrix stabilizes the potentiometric signal, expands the working concentration range by one order of magnitude and brings the sensitivity close

Table 1 Potentiometric characteristics (sensitivity in mV decade⁻¹ and linear concentration working range in mol L⁻¹) of electrodes based on the monomeric and polymeric forms of receptors A and C

Cation	Receptor A		Receptor C		
	Monomer/ o-NPOE	Polymer	Monomer/ o-NPOE	Monomer/ DOP	Polymer
Na ⁺	– ^a	– ^a	– ^a	– ^a	– ^a
K ⁺	44.8 (10 ⁻³ –10 ⁻¹)	– ^a	45.0 (10 ⁻³ –10 ⁻¹)	– ^a	– ^a
Rb ⁺	44.7 (10 ⁻⁴ –10 ⁻¹)	– ^a	47.5 (10 ⁻⁴ –10 ⁻¹)	– ^a	– ^a
Cs ⁺	47.3 (10 ⁻⁴ –10 ⁻¹)	– ^a	50.8 (10 ⁻⁴ –10 ⁻¹)	– ^a	– ^a
Ca ²⁺	– ^a	– ^a	– ^a	– ^a	– ^a
Mg ²⁺	– ^a	– ^a	21.1 (10 ⁻⁵ –10 ⁻¹)	– ^a	– ^a
Zn ²⁺	33.0 (10 ⁻⁴ –10 ⁻¹)	51.7 (10 ⁻³ –10 ⁻²)	– ^a	29.3 (10 ⁻⁵ –10 ⁻²)	30.7 (10 ⁻³ –10 ⁻²)
Cu ²⁺	27.9 (10 ⁻⁴ –10 ⁻¹)	38.2 (10 ⁻⁴ –10 ⁻¹)	– ^a	24.3 (10 ⁻⁵ –10 ⁻²)	36.6 (10 ⁻³ –10 ⁻¹)
Co ²⁺	30.6 (10 ⁻⁴ –10 ⁻²)	26.9 (10 ⁻⁵ –10 ⁻³)	35.6 (10 ⁻³ –10 ⁻²)	– ^a	– ^a
Pb ²⁺	29.9 (10 ⁻⁵ –10 ⁻¹)	– ^a	– ^a	22.6 (10 ⁻⁶ –10 ⁻²)	– ^a
Hg ²⁺	17.7 (10 ⁻⁵ –10 ⁻²)	– ^a	82.5 (10 ⁻⁶ –10 ⁻³)	37.4 (10 ⁻⁶ –10 ⁻³)	39.7 (10 ⁻⁶ –10 ⁻⁴)
Ag ⁺	56.4 (10 ⁻⁵ –10 ⁻²)	65.9 (10 ⁻⁵ –10 ⁻²)	45.9 (10 ⁻⁵ –10 ⁻²)	– ^a	56.7 (10 ⁻⁵ –10 ⁻²)

^aWeak or no response

Table 2 Selectivity coefficients $\log K_{Ag^+/j}^{Pot.}$ recorded for ion-selective electrodes derived from the monomeric and polymeric forms of receptors A and C (o-NPOE plasticized)

Interfering ions (j)		Mg ²⁺	Cu ²⁺	Co ²⁺	Zn ²⁺	Hg ²⁺	Pb ²⁺	Na ⁺	K ⁺
A	Monomer	-3.7	-3.2	-3.1	-2.9	-2.2	-3.0	-2.2	-2.2
	Polymer	-3.4	-3.6	-3.4	-3.4	-	-3.4	-2.0	-2.0
C	Monomer	-3.7	-2.9	-3.1	-2.8	-2.5	-2.9	-2.2	-2.2
	Polymer	-3.7	-3.7	-3.7	-3.7	-	-3.6	-2.1	-1.8

to the theoretical values. The affinity of the membrane electrodes based on quinoxaline to alkali cations was found to depend on the lipophilicity of the analyte as well as the specific nature of the tetraphenylborate-containing membrane electrode. Both ionophores A and C demonstrate an analogous attraction to Ag⁺ ions, with the detection limits, c_{min} , reaching $7.9 \times 10^{-6} \text{ mol L}^{-1}$. On the other hand, receptor A shows a selectivity for divalent cations such as Pb²⁺ ($c_{min} = 5.0 \times 10^{-6} \text{ mol L}^{-1}$), Zn²⁺, Cu²⁺ ($c_{min} = 6.3 \times 10^{-5} \text{ mol L}^{-1}$) and Co²⁺ ($c_{min} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$), whereas electrodes based on its thienyl analog C exhibit no response towards these divalent cations, with the exception of Co²⁺.

The availability of PVC-membranes containing di-thienylquinoxaline derivatives (system C) allowed the effect of the plasticizer to be studied. Whereas the use of a more polar plasticizer (o-NPOE) was found to increase the discrimination for monovalent cations over divalent cations, the converse proved true in the case of the less polar membrane plasticizer, DOP. In fact, the use of the latter plasticizer, engenders selectivity for the divalent cationic species Cu²⁺, Zn²⁺, Hg²⁺, and Pb²⁺ with responses $22.6\text{--}37.4 \text{ mV decade}^{-1}$ and detection limits 6.3×10^{-6} to $6.3 \times 10^{-7} \text{ mol L}^{-1}$. However, it does so at the price of Ag⁺ selectivity, as can be appreciated by reference to the data presented in Table 1.

To put the present study on a more quantitative footing, the potentiometric selectivity coefficients ($\log K_{Ag^+/j}^{Pot.}$) of the PVC-membranes derived from A and C were evaluated (Table 2). For both monomers, the selectivity sequence is: Mg²⁺ < Cu²⁺, Co²⁺, Pb²⁺, Zn²⁺ < Hg²⁺, Na⁺, K⁺ < Ag⁺, an ordering that makes it clear that electrodes containing both monomers A and C (o-NPOE) display high Ag⁺ selectivity. Among the cations tested, the selectivity toward Ag⁺, as compared to Mg²⁺, Cu²⁺, Co²⁺, Pb²⁺ and Zn²⁺, is the highest ($\log K_{Ag^+/j}^{Pot.} \approx -2.8$) and is nearly identical for both monomers A and C. In the presence of Hg²⁺ and alkali cations, the selectivity coefficients ($\log K_{Ag^+/j}^{Pot.}$) observed for these membranes range between -2.5 and -2.2 .

A study of the cell potentials vs. pH was carried out (Fig. 3) in an effort to correlate the degree of membrane protonation with the observed response efficacy and affinity. This study was carried out by exposing PVC membranes containing systems A and C, to aqueous solutions of varying pH. From the figure it can be clearly seen that the potential of electrodes is dependent on pH and in the

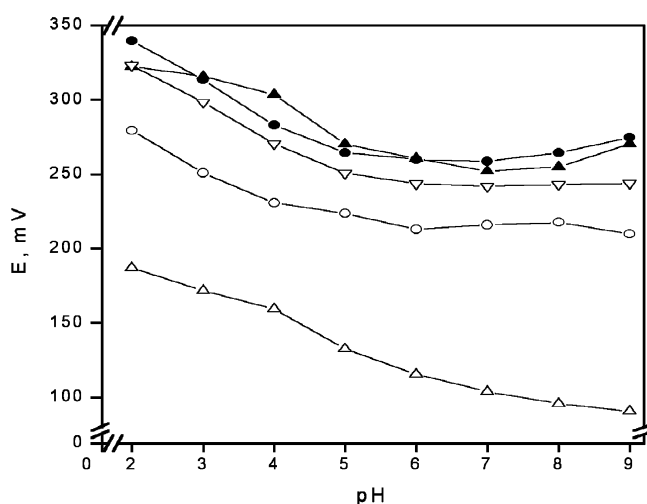


Fig. 3 Dependence on pH of potential of polymeric and monomer-containing membrane electrodes of disubstituted 5-nitroquinoxaline derivatives bearing pyrrolyl A (open circle, membrane with o-NPOE; closed circle, polymer) and thienyl C (open inverted triangle, membrane with DOP; filled triangle, polymer) substituents in the 2 and 3 positions. As appropriate, the pH was adjusted by adding dilute nitric acid or sodium hydroxide

case of PVC/o-NPOE vs. PVC/DOP the curves have significantly different shape. The protonation could induce conformational changes and could alter the response of the given receptor for cationic species. Many transition metal cations show a tendency to form very stable complexes either as a result of accepting π -electrons from unsaturated organic molecules or via coordination to the donor atom of the heterocycle [14]. In the case of system C, cation complexation presumably involves not only the thiophene sulfur atom(s) but also one or more nitrogen atoms of the pyrazine ring, as implied above. To the extent this is true, protonation of one of the pyrazine ring nitrogens should serve to “kill”, or at least substantially reduce, the cation binding efficacy. In fact, for the o-NPOE/PVC-membrane containing receptor C, we observed a selectivity towards monovalent cations. On the other hand, for the corresponding DOP/PVC-membrane containing receptor C a selectivity towards divalent cations was observed.

Complicating interpretation of protonation effects are issues involving receptor conformation. Such effects are important because the orientation of the dihedral angle be-

tween the quinoxaline core and the appended heterocycle could serve to establish whether or not the pyrazine nitrogen and, e.g., the thiophene sulfur atom(s) act in a cooperative fashion. This angle, and indeed the overall receptor conformation is expected to be influenced by the degree of protonation. It can also be influenced by the plasticizer since, depending on its polarity, the latter may or may not interact with more open conformations of the receptor. In fact, we propose that these latter kinds of effects explain the loss of the selectivity toward heavy metal ions observed for the PVC/o-NPOE –membranes. Specifically, we propose that the improved selectivity for Ag⁺ ions observed when o-NPOE (Table 2) is used as a plasticizer reflects the fact that the thiophene sulfur atoms are “bound”, at least in part, by this polar medium, thereby reducing their ability to “cooperate” with the pyrazine nitrogen atom(s) so as to bind a competing divalent cation. To the extent such an interpretation is true, our data provide support for the logical notion that both the pyrazine nitrogen and thiophene sulfur atoms act in concert to effect complexation of most cationic analytes.

Based on our experimental findings, we believe that there are three main factors affecting the complexation ability of the monomeric quinoxaline derivatives contained within the PVC-membranes, namely the nature of the heterocyclic substituent, the extent of protonation, and the polarity of the medium determining the conformation of the receptor. While the interplay between these factors can lead to an overall binding mechanism that is quite complex, it is also expected that they will dominate the behavior of polymerized electrodes containing receptors A and C, thus potentially simplifying interpretations of these latter systems, as discussed below.

Electropolymerized electrodes

The second step in this two-part study involved generating electropolymerized films from receptors A and C and comparing their potentiometric behavior with that of the corresponding monomer-containing electrodes. After preparation in accord with the protocol outlined in the experimental section, it was found that the best potentiometric properties with the polymer derived from pyrrolyl-substituted quinoxaline A were obtained for Ag⁺ (66 mV decade⁻¹, $c_{\min}=5.6 \times 10^{-6}$ mol L⁻¹), Cu²⁺ (38 mV decade⁻¹, $c_{\min}=5 \times 10^{-5}$ mol L⁻¹), Co²⁺ (27 mV decade⁻¹, $c_{\min}=5 \times 10^{-6}$ mol L⁻¹); this parallels what was seen for the PVC electrodes derived from the corresponding monomer (Table 1). In the case of the thienyl-substituted quinoxaline C, both the monomeric (o-NPOE) and polymeric electrodes were found to display a high affinity toward Ag⁺ ions.

However, compared to the monomeric system, the potentiometric selectivity for Ag⁺ ions versus Zn²⁺, Cu²⁺, Co²⁺, Pb²⁺ ($\log K_{\text{Ag}^+/\text{j}}^{\text{Pot.}} \gg -3.7$) is improved in the case of the polymerized receptor C (Table 2). On the other hand, a significant poisoning effect from Hg²⁺ ion is observed for polymer as compared to the monomer, presumably, this simply reflects the fact that the mercury(II) interferent is

used at ca. 100-fold higher concentration in the case of the polymerized system as compared to what was employed in the case of the monomer electrode (ca. 10⁻³ vs. 10⁻⁵ mol L⁻¹). In spite of the above singular anomaly it is important to appreciate that as a general rule (i.e., for both systems A and C), the selectivity sequences for the polymers were found to be similar to those of the corresponding monomeric electrodes (Table 2).

Similarity in the potentiometric behavior seen for the monomeric and polymeric quinoxaline electrode systems supports the contention that similar binding modes are operative in both cases. However, it was also found that prolonged soaking of the polymeric electrodes in solutions of Ag⁺ leads to a stabilization of, and simultaneously improvement in their potentiometric characteristics, including such critical parameters as sensitivity and detection limits in contrast to what was seen for the membrane electrodes. This leads us to suggest that the polymerized forms of the quinoxaline-based electrodes could make them the systems of choice for use in various “real world” applications.

Conclusion

In summary, the potentiometric response and selectivities for electropolymerized electrodes based on 5-nitroquinoxaline derivatives substituted in the 2 and 3 positions by 2-pyrrolyl (A) and 2-thienyl (C) heterocyclic subunits toward various cationic species were determined and found to parallel closely those seen for the corresponding PVC-membrane-supported, monomeric electrode systems. Indeed, the similarity in the potentiometric behavior of the monomeric and polymeric forms of A and C leads us to suggest that the main binding modes effective in the monomeric forms are operative in the polymeric structures as well. Within the context of this general conclusion, it was found that the response characteristics are dependent on the conditions of electrode preparation and the specifics of the measurement. For instance, in the case of the dithienylquinoxaline monomer C, the plasticizer polarity and the extent of protonation were found to influence the discrimination between mono- and divalent cations, an observation leading us to the conclusion that both the quinoxaline nitrogen and thiophene sulfur atoms, acting in concert, are needed to create a binding site that recognizes divalent cations well.

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