JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 437–442 (1992)

POTENTIOMETRIC EVALUATION OF THE ION-SELECTIVE CHARACTERISTICS OF 2-BORONO-1,3-XYLYL CROWN ETHERS

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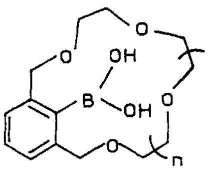
Poly(vinyl chloride) (PVC) membranes impregnated with 2-borono-1,3-xylyl crown ethers were evaluated in ion-selective electrodes. The response pattern obtained with these crown ethers appears to be essentially independent of ring size but there is a linear correlation between selectivity and hydration enthalpy of the cation which is similar to that obtained for electrodes prepared only with the lipophilic anionic site KTClPB. The similarities in correlation and mechanism between these two types of electrodes has been attributed to the presence of anionic sites in both cases dominating the observed selectivity. For the four ionophores considered the pH-dependent ionization of the boronate group to the boronate anion is proposed to be responsible for the domination of anionic sites on the properties of the ionophores. The ionophores proved to be good K^+ neutral carriers, showing responses to this ion in the range 10^{-1}–10^{-4} M. The compounds tested showed a fast response to changes in K^+ concentration which was stable to within $<0{\cdot}2\ mV\,h^{-1}$.

INTRODUCTION

Ionophore impregnated polymeric membranes [(typically plasticized poly(vinyl chloride) (PVC)] have played an important role in the development of ion-selective electrodes (ISEs) and ion-selective field-effect transistors (ISFETs) for applications in analytical chemistry.[1–5] Our interest is in the synthesis and characterization of 1,3-xylyl crown ethers, of which the properties of macrocyclic polyethers[6,7] and polythioethers[8,9] have been investigated. The 2-position located near the site of complexation points into the hole of the ring and affects the binding properties of alkali metal ions[6] either by altering the cavity size, ion–dipole interactions or the disposition of ethereal oxygens or by acting cooperatively as an additional binding site. Studies on 1,3-xylyl crown ethers and 2-bromo-1,3-xylyl crown ethers in PVC membranes as ion-selective electrodes[10] have indicated that the relative responses of these crown ethers for ions is independent of the ring size and that substitution of a bromo group in the 2-position produces small effects on the specificity of detection of Na^+, Li^+, Ca^{2+} and Mg^{2+}, indicating that the xylyl ring is sufficiently flexible to prevent the bromo group from interferring with binding.



1. n = 1
2. n = 2
3. n = 3
4. n = 4

Figure 1. Neutral carriers

To investigate further the effects of the substitution of the 2-position on selectivity, we prepared four 1,3-xylyl crown ethers substituted with a borono residue (see Figure 1) and studied the responses and selectivities of these ionophores in PVC membranes to alkali and alkaline earth metal cations. The 2-borono group of 1,3-xylyl crown ethers have been shown by infrared spectrometry to be hydrogen bonded to the ethereal oxygen of the macrocyclic ring[11] and could therefore be expected to affect binding and selectivity by controlling ring size or rigidity or acting as an additional binding site for ions.

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0894-3230/92/080437-06$08.00

Received 18 November 1991
Revised 8 April 1992

RESULTS AND DISCUSSION

The selectivities determined for a given ionophore are dependent on the membrane composition and the nature of solutions (e.g. ionic strength, pH) to which the membranes are exposed.[12] To obtain relative responses due to the ionophores, all electrodes, unless stated otherwise, were tested under identical conditions using the same PVC membranes, plasticizer and lipophilic anionic site [e.g. potassium tetrakis(*p*-chlorophenyl)borate (KTClPB)]. The typical resistances of ionophore membranes, measured *in situ* using a Keithley 617 electrometer in the ohmmeter mode, was found to vary between 0·5 and 3·5 MΩ.

A comparison was made of the responses obtained for ionophores 1–4 due to a sequential increase in ring size from 4 to 7 oxygen atoms. All electrodes exhibited a marked selectivity for alkali metal (monovalent) over alkaline earth metal (divalent) cations (see Figure 2). The response pattern (see Figure 2) observed for ionophores 1–4 with KTClPB and different cations decreased in the following general order: $Cs^+ \geqslant K^+ > NH_4^+ > Na^+ > Ca^{2+} > Li^+ > Mg^{2+}$. This behaviour appeared to be essentially independent of the ring size, which varied in this study from about 1·5 Å for ionophore 1 to 4·0 Å for ionophore 4, indicating that the 'optimal spatial fit concept' (circular recognition)[13] did not hold for these ionophores when tested under these conditions. A study undertaken on membranes prepared without an ionophore but with KTClPB as the cation exchanger showed a similar response pattern: $Cs^+ > K^+ > NH_4^+ > Na^+ > Ca^{2+}$.

The slopes and detection limits for ionophores 1–4 with KTClPB and membranes prepared with KTClPB alone for the determination of alkali and alkaline earth metal cations according to Analytical Commission rules[14] from response curves as shown in Figure 2 are given in Tables 1 and 2. The slopes for the electrodes prepared with ionophores 1–4 with KTClPB ranged from 53 to 10 mV per decade with detection limits varying from $2{\cdot}5 \times 10^{-4}$ to 2×10^{-2} M depending on the nature of the cation and ionophore. Near-Nernstian responses were observed for Cs^+ and K^+ with some ionophores, e.g. 3, but not for Na^+, NH_4^+, Li^+, Ca^{2+}, and Mg^{2+}. Membranes prepared with KTClPB alone

Table 1. Performance characteristics of electrodes based on ionophores 1–4 with KTClPB and KTClPB alone

	Slope (mV per decade)				
Ionophore	K^+	Cs^+	NH_4^+	Na^+	Ca^{2+}
1	42	41	34	18	10
2	53	48	38	21	11
3	53	53	28	21	13
4	43	41	18		
KTClPB[a]	44	53	43	33	10

[a] Without ionophore.

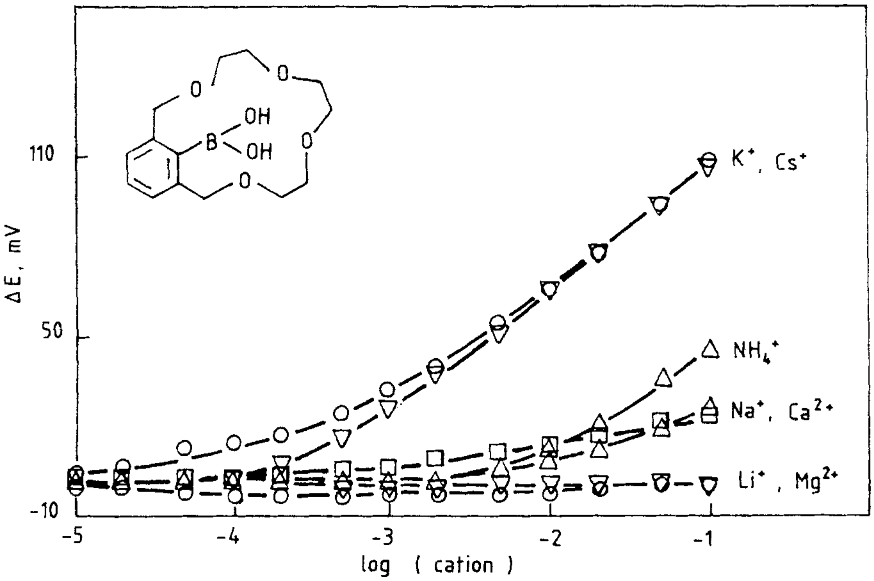


Figure 2. Cation selectivity of an electrode based on ionophore 1 in 0·1 M Tris–HCl (pH 7·5). The electrode was exposed to the salts of (▽) caesium, (○) potassium, (△) ammonium, (△) sodium, (□) calcium, (○) magnesium and (▽) lithium

Table 2. Detection limits (M) with electrodes based on ionophores 1–4 with KTClPB and KTClPB alone

Ionophore	K^+	Cs^+	NH_4^+	Na^+	Ca^{2+}
1	6×10^{-4}	3×10^{-4}	5×10^{-3}	5×10^{-3}	6×10^{-4}
2	6×10^{-4}	4×10^{-4}	5×10^{-3}	2×10^{-2}	4×10^{-4}
3	6×10^{-4}	6×10^{-4}	4×10^{-3}	1×10^{-2}	2.5×10^{-4}
4	8×10^{-4}	7×10^{-4}	7×10^{-3}	3×10^{-3}	
KTClPB[a]	6×10^{-5}	4×10^{-5}	2×10^{-4}	2×10^{-3}	

[a] Without ionophore.

Table 3. Detection limits (M) with electrodes based on ionophores 1–4 without KTClPB

Ionophore	K^+	Cs^+	NH_4^+	Na^+
1	6×10^{-5}	1×10^{-5}	3×10^{-4}	1×10^{-3}
2	6×10^{-5}	1×10^{-5}	4×10^{-4}	3×10^{-3}
3	6×10^{-5}	1×10^{-4}	2×10^{-4}	2×10^{-3}
4	8×10^{-5}	3×10^{-4}	1×10^{-4}	8×10^{-4}

Table 4. Performance characteristics of electrodes based on ionophores 1–4 without added KTClPB

	Slope (mV per decade)				
Ionophore	K^+	Cs^+	NH_4^+	Na^+	Ca^{2+}
1	44	30	29	30	10
2	44	27	26	23	7
3	44	33	33	33	10
4	44	33	34	33	8

exhibited a near-Nernstian response for Cs^+ and tenfold lower detection limits for cations such as K^+, Cs^+, and NH_4^+ (see Table 2) than in the presence of inophores 1–4 with added KTClPB. However, measurements made at the same time on electrodes prepared with ionophores 1–4 but without added KTClPB showed similar detection limits for these ions (see Table 3). This difference in detection limits may reflect problems associated with comparison studies undertaken on two different occasions or may reflect real differences as a consequence of complex interactions between the ionophores and KTClPB in the membrane. The corresponding slopes for electrodes prepared from ionophores 1–4 without added KTClPB are given in Table 4 and are similar to those obtained for electrodes prepared with KTClPB alone (compare Tables 1 and 4), except for Cs^+ and NH_4^+, where a higher response was observed for KTClPB electrodes.

Selectivity coefficients for K^+ with respect to alkali-metal and alkaline- earth-metal cations are summarized in Figure 3; they were obtained using the fixed interference method[14] as this represents one of the conditions under which these electrodes could be used. The selectivity observed for ionophores 1–4 with KTClPB were found to be independent of ring size for all the cations tested (see Figure 3). The result may indicate an

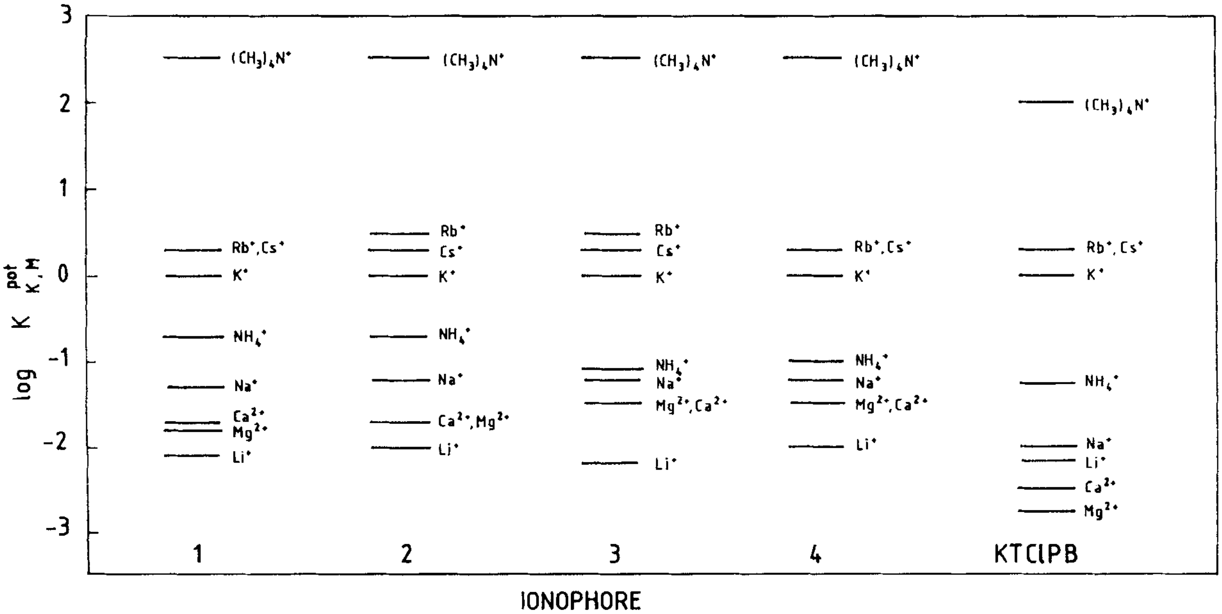


Figure 3. Selectivity coefficient for K^+ in electrodes with ionophores 1–4 + KTClPB and KTClPB alone

involvement of the borono group in complexation, as studies on 1,3-xylyl and 2-bromo crown ethers[10] showed that the selectivity for lithium, calcium and magnesium decreased with increasing ring size, consistent with the preference of these cations to be hexacoordinated to oxygen ligands.[15,16] Another possible explanation is that the observed selectivity may be due primarily to the presence of KTClPB added to the membrane, as this electrode exhibits some similarities in selectivity to membranes prepared with ionophores 1–4 and KTClPB except for the difference in the relative position of Li^+ with respect to the other ions. The observed selectivites for monovalent cations (see Figure 3) plotted against their hydration enthalpies are shown in Figure 4(a) for ionophore 1. A linear correlation between selectivity coefficient and hydration enthalpy with a correlation coefficient $R = 0{\cdot}95$ was observed for ionophores1–4:

$$\log K^{pot}_{K,M} = 0{\cdot}012\,\Delta H^0 + 3{\cdot}7$$

This correlation indicates that the contribution of solvation energy in the membrane is small compared with the hydration energy[17] and tends to support an enthalpically controlled mechanism of molecular complexation for monovalent cations in membranes. A similar relationship was reported for potassium tetrakis(phenyl)borate (KTPB)[18] and was observed here

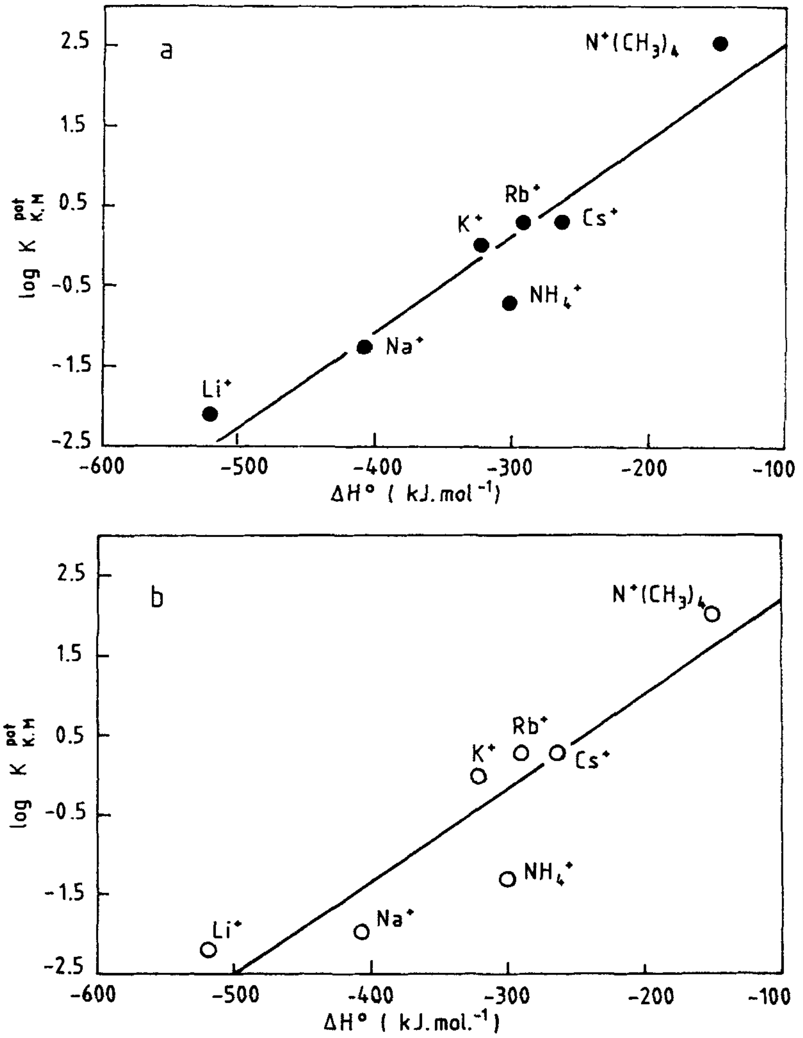
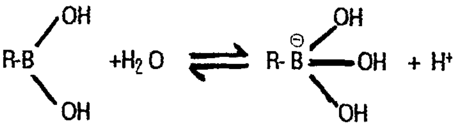


Figure 4. Dependence on selectivity of log K^{pot}_{KM}, for (a) ionophore 1 + KTClPB with monovalent cations and (b) KTClPB alone with monovalent cations versus enthalpy of hydration, ΔH^0 (kJ mol^{-1}

[see Figure 4(b)] for membranes prepared with KTClPB alone:

$$\log K^{\text{pot}}_{\text{K,M}} = 0{\cdot}012\,\Delta H^{0} + 2{\cdot}8 \quad (R = 0{\cdot}9)$$

The similarities in correlation observed between $\log K^{\text{pot}}_{\text{K,M}}$ and ΔH^{0} for both types of electrodes indicate that similar mechanisms contribute to the overall selectivity of both types of electrodes. This suggests that it is the KTClPB added to both types of electrodes that is responsible for the observed selectivity. However, if we consider the properties of the 2-borono group of ionophores 1–4, an alternative explanation can be proposed for the apparent similarities in selectivity of these two types of electrodes. At pH 7·5 the boronate group in these ionophores may exist partially as the boronate anion[19] according to the following pH-dependent equilibrium:



Assuming that the pK_a value of the 2-borono group of ionophores 1–4 is not significantly different from that of phenylboronic acid, pK_a = 8·86,[20] then from the Henderson–Hasselbalch equation at least 6·9% of this group will exist in the anionic form at pH 7·5, which corresponds to 0·6 μM of anionic sites in the membrane based on the concentration of ionophore used. This value is similar to the concentration of anionic sites (0·8 μM) added in the form of KTClPB. If the presence of these anionic sites dominate the properties of ionophores 1–4, this would account for the similarities between the selectivities of these electrodes and that of the cation exchanger KTClPB and the absence of an effect of ring size on selectivity.

Typical responses of PVC membranes to a tenfold increase in K^+ concentration for ionophores 1–4 were 2·2, 1·6, 1·3 and 2·9 s, respectively. Stability measurements on these electrodes in an unstirred thermostated beaker of 1×10^{-3} M KCl solution at 25 °C showed them to have a stability of <0·2 mV h^{-1} over a period of 18 h, However, the long-term stability of these electrodes in comparison with 1,3-xylyl crown ethers[10] was poor, probably as a result of easier leaching of the more polar ionophore from the membrane.

During the processing of this paper, Reetz *et al.*[21] reported the complexation characteristics of ionophore 3 with a range of potassium salts in dichloromethane. Their results showed that both homotropic and heterotropic complexes are formed, depending on the nature of the potassium salt. However, competition experiments showed exclusive formation of the heterotropic complex in which the boronate group exists in the form of an anion. This result is consistent with our explanation that the complexation characteristics of these ionophores is dominated by the ionization properties of the 2-borono group.

In conclusion, it has been shown that 2-borono-1,3-xylyl crown ethers are reasonable potassium-selective ionophores exhibiting response characteristics similar to those of KTClPB.

EXPERIMENTAL

Materials. The following materials were used as received: poly(vinyl chloride) and lithium chloride (BDH, Speke, Liverpool) and caesium fluoride, sodium chloride, rubidium chloride and tetramethylammonium bromide (Aldrich Chemical, Gillingham, Dorset). Potassium tetrakis(*p*-chlorophenyl)borate (KTClPB) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka (Glossop, Derbyshire). Tetrahydrofuran (THF) was obtained from Rathburn Chemicals (Walkerburn, Scotland) and was dried over sodium before being redistilled. Tris [tris(hydroxymethyl)aminomethane], magnesium chloride, ammonium chloride, calcium chloride and potassium chloride were purchased from Sigma Chemical (Poole, Dorset). All standard solutions and buffers were prepared using deionized water.

Syntheses of ionophores. Ionophores 1–4 are shown in Figure 1 and were prepared by the condensation of the methyl derivative of 2-borono-1,3-bis(bromomethyl) benzene with the appropriate polyethylene glycol according to the method of Tuladhar and D'Silva.[11]

Membranes and electrode fabrication. The polymeric membranes were prepared as follows: PVC (31·2 mg), NPOE (66 mg), KTClPB (0·4 mg) and the appropriate ionophore (8·6 μM) were dissolved in 1 ml of THF. The solution was poured into a flat glass ring (17 mm i.d.), and the solvent evaporated at room temperature overnight[10] to yield an elastic, translucent membrane of thickness 0·14–0·18 mm. The resulting polymeric membranes were conditioned for 24 h in 1×10^{-3} M KCl solution, then deposited on the end of a 5·5 mm i.d. glass tube containing an internal reference solution (1×10^{-3} M KCl) and chloridized silver wire as an internal reference electrode.[22] All potentiometric measurements were performed with the use of the following cell:

$$\text{Hg, Hg}_2\text{Cl}_2\text{, KCl(sat.)} \,\|\, \text{sample solution} \,\|\, \text{membrane} \,|\, \text{Tris-HCl } (1 \times 10^{-3}\ \text{M}) \,|\, \text{AgCl, Ag}$$

E.m.f. measurements. The response of the electrodes were measured with a Thurlby Model 1503 digital multimeter and a Keithley 617 electrometer and time-dependent responses were recorded with a Siemens

Model X-T C1012 chart recorder. All measurements were performed in a temperature-controlled room at 25 °C relative to a Radiometer porous pin-junction calomel reference electrode. Electrodes were stored in 1×10^{-3} M KCl when not in use. The electrodes were calibrated by syringing 5 ml aliquots of known concentrations of different electrolyte standard solutions into a stirred beaker containing 20·0 ml of 0·1 M Tris–HCl buffer (pH 7·5) (Tris does not cause any interferences[10]) with KCl of various concentrations. To obtain the calibration graph for the ISEs, ΔE values (i.e. the increase in potential with respect to the baseline) were plotted versus the logarithm of the concentration of cation present in the buffered solution.

Selectivity coefficients (K_{KM}^{Pot}). Selectivity coefficients were determined by the fixed interference method.[14] The background concentration of the interference ions employed were 0·1 M for LiCl, NH_4Cl, $CaCl_2$, $MgCl_2$ and NaCl, 0·01 M for CsF and RbCl and 0·001 and 1×10^{-5} M for $(CH_3)_4NBr$.

ACKNOWLEDGEMENTS

C.D. thanks GEC and the Fellowship of Engineering for the award of a Senior Fellowship in Molecular and Biomolecular Electronics and the SERC for support under Grant GR/F 16424. The authors acknowledge the gift of a Keithley 617 electrometer and microcomputer to C.D. by the Fellowship of Engineering and GEC.

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