# Comparative Studies on 1,3-Xylyl and 2-Bromo-1,3-xylyl Crown Ethers as Ion-Selective Electrodes

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1,3-Xylyl and 2-bromo-1,3-xylyl crown ethers have been tested as ion-selective electrodes in poly(vinyl chloride) (PVC) membranes. The pattern of selectivity appears to be essentially independent of ring size and probably reflects the ease with which substitution of water molecules from the inner hydration sphere of the ion can be effected. The ionophores have proved to be good K<sup>+</sup> neutral carriers showing near-Nernstian responses to this ion, in the range  $10^{-1}-10^{-4}$  M. The fixed-interference method was used to determine relative selectivity coefficients for all the electrodes. The highest selectivity for potassium relative to sodium, lithium, calcium, and magnesium was obtained with 1,3-xylyl-15-crown-5 ether using NPOE plasticizer. The compounds tested exhibited a fast Nernstian response to changes in K<sup>+</sup> concentration, which was stable to within <100  $\mu$ V/h.

# INTRODUCTION

Ion-selective electrodes (ISE's) based on ionophore-impregnated polymer membranes (typically, plasticized poly-(vinyl chloride) (PVC)) are now commonly used in a variety of analyses (1-4). Considerable effort has been given to the syntheses and characterization of ionophores in order to improve selectivity and detection limits. The synthesis and properties of macrocyclic polyethers (5,6) and polythioethers (7,8) incorporating 1,3-xylyl units have been recently investigated. It has been shown that the 5-position of the aryl group although remote from the complexation site, has a considerable effect on the properties of the crown, which has been interpreted as evidence that the  $\pi$  system acts as a binding site (6). The 2-position located near the site of complexation points inward into the hole of the cycle and effects the binding properties of alkali-metal ions (5) either by altering the cavity size, ion-dipole interactions, or the disposition of ethereal oxygens or acting cooperatively as an additional binding site.

The X-ray crystallographic structure of 2-bromo-1,3-xylyl-18-crown-5 has recently been reported (9). The results show the C-Br distance to be a normal value of 1.90 Å and the bromo group too large to fit in the macrocycle cavity. This causes the xylyl ring to be tilted out of the mean macrocyclic plane by an angle of 54° with the bromo group protruding under the cavity. The bromo group is hydrophobic in character and may alter the environment of the cavity and its complexation properties. To investigate this effect, we have prepared a series of 1,3-xylyl crown ethers substituted at the 2-position with a bromo residue and have studied the response and selectivities of these ionophores, in comparison with unsubstituted 1,3-xylyl crown ethers (see Figure 1), in PVC membranes to alkali- and alkaline-earth-metal cations.

### EXPERIMENTAL SECTION

**Reagents.** The following reagents were used as received: poly(vinyl chloride), strontium chloride, barium chloride, lithium chloride, and calcium chloride (BDH, Speke, Liverpool) and cesium fluoride, 1,3-bis(bromomethyl)benzene, triethylene glycol, tetraethylene glycol, pentaethylene glycol, and hexaethylene glycol, N-bromosuccinimide (NBS), and sodium hydride (Aldrich Chemical Co., Gillingham, Dorset). Potassium tetrakis(pchlorophenyl)borate (KTpClPB) and 2-nitrophenyl octyl ether (NPOE) were purchased from Fluka (Glossop, Derbyshire). 2,2'-Azobis(2-methylpropionitrile) or azoisobutyronitrile (AIBN) was obtained from Ventron GmBH, W. Germany. Tetrahydrofuran (THF) was obtained from Rathburn Chemicals (Walkerburn, Scotland) and was dried over sodium. Tris(hydroxymethyl)aminomethane (Tris) and potassium chloride were from Sigma Chemical Co. (Poole, Dorset). All standard solutions and buffers were prepared by using deionized water. Neutral carriers were prepared in our laboratory as described below.

Apparatus. Voltages were monitored with a Thurlby (Model 1503) digital multimeter or on a in-house built differential digital pH/mV meter (10) and recorded on a Siemens (Model X-T C1012) chart recorder. A radiometer saturated calomel electrode was used as a reference.

Syntheses of Ionophores. Ionophores 1-8 are shown in Figure 1 and were prepared by the condensation of 1,3-bis(bromomethyl)benzene (compounds 1, 3, 5, and 7) or 2-bromo-1,3-bis-(bromomethyl)benzene (compounds 2, 4, 6, and 8) with the appropriate polyethylene glycol according to the methods of Cram or Reinhoudt (5, 9, 11). 2-Bromo-1,3-bis(bromomethyl)benzene was prepared according to literature procedures (5) except AIBN replaced benzoyl peroxide as the radical initiator.

General Procedures for the Preparation of Crown Ethers 1-8. To a stirred refluxing mixture of sodium hydride (12 mmol) in dry THF (400 mL) was added dropwise a solution of 1,3-bis-(bromomethyl)benzene (compounds 1, 3, 5, and 7) (4 mmol) or 2-bromo-1,3-bis(bromomethyl)benzene (compounds 2, 4, 6, and 8) (4 mmol) and the appropriate polyethylene glycol (n = 1, 2,3, or 4) (4 mmol) in dry THF (100 mL) during 6 h. After complete addition, reflux was continued for 20 h and excess THF recovered by distillation. The residue was hydrolyzed with water, evaporated under reduced pressure, then dissolved in CHCl<sub>3</sub> (100 mL), washed with water, dried (MgSO<sub>4</sub>), and evaporated. Flash chromatography of the residue using ethyl acetate afforded either a colorless oil or solid.

**1,3-Xylyl-15-crown-4 ether (1)** (11, 12): yield 47% (oil); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.68, 3.70 (s, 12 H, OCH<sub>2</sub>), 4.64 (s, 4 H, ArCH<sub>2</sub>), 7.05, 7.22 (m, 3 H, ArH), 7.98 (s, 1 H, ArH).

**2-Bromo-1,3-xylyl-15-crown-4 ether (2)** (9, 12): yield 77% (oil solidified on standing), mp 35–37 °C (lit. (9) mp 43–47 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.28–3.75 (m, 12 h, OCH<sub>2</sub>), 4.30, 5.12 (AB q,  $J_{AB} = 15$  Hz, 4 H, ArCH<sub>2</sub>), 7.25–7.31 (m, 3 H, ArH).

**1,3-Xylyl-18-crown-5 ether (3)** (5, 11): yield 75% (oil solidified on standing), mp 44-46 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.58, 3.64 (m, 16 H, OCH<sub>2</sub>), 4.55 (s, 4 H, ArCH<sub>2</sub>), 7.06, 7.21 (m, 3 H, ArH), 7.66 (s, 1 H, ArH).

**2-Bromo-1,3-xylyl-18-crown-5 ether (4)** (5, 9): yield 74% (oil); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.57, 3.65 (m, 16 H, OCH<sub>2</sub>), 4.73 (s, 4 H, ArCH<sub>2</sub>), 7.24–7.37 (m, 3 H, ArH).

**1,3-Xylyl-21-crown-6 ether (5)** (11): yield 58% (oil); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.65–3.77 (m, 20 H, OCH<sub>2</sub>), 7.63 (s, 4 H, ArCH<sub>2</sub>), 7.21–7.35 (m, 3 H, ArH), 7.48 (s, 1 H, ArH).

**2-Bromo-1,3-xylyl-21-crown-6 ether (6)** (9): yield 50% (oil); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.59, 3.70 (m, 20 H, OCH<sub>2</sub>), 4.70 (s, 4 H, ArCH<sub>2</sub>), 7.26-7.42 (m, 3 H, ArH).

**1,3-Xylyl-24-crown-7 ether (7)** (11): yield 76% (oil); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.59–3.74 (m, 24 H, OCH<sub>2</sub>), 4.62 (s, 4 H, ArCH<sub>2</sub>), 7.20–7.35 (m, 3 H, ArH), 7.48 (s, 1 H, ArH).





**2-Bromo-1,3-xylyl-24-crown-7 ether** (8) (9): yield 54% (oil solidified on standing), mp 48–51 °C (lit. mp 55–58 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.61, 3.75 (m, 24 H, OCH<sub>2</sub>), 4.72 (s, 4 H, ArCH<sub>2</sub>), 7.41, 7.52 (m, 3 H, ArH).

Membranes and Electrode Fabrication. The polymeric membranes used in this study were prepared as follows: PVC (31.2 mg), NPOE (66 mg), KTpClPB (0.4 mg) and appropriate ionophore (8.6  $\mu$ M) 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 (13) to yield an elastic, translucent membrane of 0.2–0.3-mm thickness. The resulting polymeric membranes were conditioned for 24 h in 1 × 10<sup>-3</sup> M KCl and then deposited onto the end of a glass tube 5.5 mm i.d. containing an internal reference solution (1 × 10<sup>-3</sup> M) and chloridized silver wire as an internal reference electrode (14). The fabricated electrodes were further conditioned for 24 h in 1 × 10<sup>-3</sup> M KCl before use. All potentiometric measurements were performed by the use of the following cell:

Hg, Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd)||sample solution | membrane|AgCl, Ag

**Emf Measurements.** The responses of the electrodes were measured with a digital multimeter and time-dependent responses recorded with a differential pH/mV meter connected to a X-t chart recorder. All measurements were performed in a temperature-controlled room at 21 °C relative to a radiometer porous pin-junction calomel reference electrode. Electrodes were stored in  $1 \times 10^{-8}$  M KCl when not in use. The calibration of electrodes were carried out by preparing solutions containing known concentrations of electrolyte in the range  $1 \times 10^{-6} - 1 \times 10^{-1}$  M in 0.1 M Tris-HCl, pH 7.5 buffer (Tris does not present an interference (13)). To obtain the calibration curve of the ISE's the data were plotted as  $\Delta E$  (i.e., the increase in potential with respect to the base line) vs the logarithm of the concentration of cation present in the buffered solution.

Selectivity Coefficients  $K_{E,M}^{ex}$ . Selectivity coefficients were determined by the fixed interference method (15). The background concentrations of the interference ions employed were 0.1 M for LiCl, NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> and 0.14 M for NaCl, which was approximately equal to the concentration found in blood serum (16).

### **RESULTS AND DISCUSSION**

The selectivities reported for a given ionophore vary depending on membrane composition and the nature of solutions (e.g. ionic strength, pH) to which the membranes are exposed (17). For comparison purposes we have prepared all ionophores using the same PVC membranes, plasticizer, and lipophillic anionic site (e.g., potassium tetrakis(p-chlorophenyl)borate (KTpClPB)) to obtain relative response due to the ionophores. The typical resistances of membranes prepared, measured in situ with a Kiethley 617 electrometer in the ohmmeter mode was found to be in the range 1-1.5 M for all the ionophore membranes tested. All compounds



Figure 2. Cation selectivity of an electrode based on ionophore 3 in 0.1 M Tris-HCI, pH 7.5. The electrode was exposed to the saits of cesium (1), rubidium (2), potassium (3), ammonium (4), barium (5), sodium (6), lithium (7), strontium (8), magnesium (9), and calcium (10).



Figure 3. Cation selectivity of an electrode based on ionophore 4 in 0.1 M Tris-HCI, pH 7.5. The electrode was exposed to the saits of cesium (1), rubidium (2), potassium (3), ammonium (4), barium (5), sodium (6), lithium (7), strontium (8), magnesium (9), and calcium (10).

 
 Table I. Relative Cation Responses of Electrodes Based on Ionophores 1-8

ionophore

1

 $Cs^+ > Rb^+ = K^+ > NH_4^+ > Ba^{2+} = Na^+ > Li^+ > Sr^{2+}$ 

relative cation response

- >  $Mg^{2+} > Ca^{2+}$ 2  $Cs^+ > Rb^+ > K^+ > NH_4^+ > Li^+ > Na^+ > Ca^{2+} >$
- $\begin{array}{ccc} Mg^{2+} \\ 3 & Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Li^+ > Na^+ > Sr^{2+} \\ & > Mg^{2+} > Ca^{2+} \end{array}$
- 4  $K^+ > Ca^+ > Rb^+ > NH_4^+ > Na^+ > Ba^{2+} > Sr^{2+} > Li^+$  $> Mg^{2+} > Ca^{2+}$
- 5  $Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > Ba^{2+} > Sr^{2+}$ >  $Mg^{2+} > Ca^{2+}$
- 6  $Rb^+ \ge K^+ = Cs^+ > NH_4^+ > Na^+ > Li^+ > Ba^{2+} > Sr^{2+} > Mg^{2+} > Ca^{2+}$
- 7  $Cs^+ > Rb^+ > K^+ > NH_4^+ \ge Li^+ > Na^+ > Ba^{2+} = Ca^{2+}$ >  $Sr^{2+} > Mg^{2+}$
- 8  $Cs^+ > K^+ > Rb^+ > NH_4^+ > Na^+ > Li^+ > Ba^{2+} > Ca^{2+}$ >  $Sr^{2+} > Mg^{2+}$

evaluated in this study provided functionally active ion-selective electrodes with a wide variety of electrochemical responses.

A comparison of the slectivity obtained due to a sequential series of modification in which the ring size of the macrocycle was varied from four to seven oxygen atoms for ionophores 1-8 were undertaken. All neutral carrier electrodes exhibited a marked selectivity for alkali-metal (monovalent) over alkaline-earth-metal (divalent) cations (see Figures 2 and 3). The selectivity patterns obtained from figures such as Figures 2 and 3 for the different ionophores are tabulated in Table I. The pattern observed for ionophores 1, 3, 5, and 7 with different quest ions decreased in the following general order:

 Table II. Performance Characteristics of Electrodes Based

 on Ionophores 1-8

ionophore	slope, mV/decade							
	Cs <sup>+</sup>	Rb <sup>+</sup>	K+	NH4+	Na <sup>+</sup>	Li <sup>+</sup>		
1	55	45	50	46	40	35		
2	53	55	54	52	28	32		
3	58	56	55	61	31	35		
4	46	44	56	40	45	32		
5	46	53	47	44	37	35		
6	52	52	49	52	51	20		
7	58	53	54	43	38	43		
8	52	48	52	49	43	49		

 $Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > Ba^{2+} > Sr^{2+} > Mg^{2+}$ =  $Ca^{2+}$ . This pattern appeared to be essentially independent of ring size, which varied in this study from about 1.5 Å for 1 to 4.0 Å for 7, indicating that the "optimal spatial fit concept" (circular recognition) (18) did not hold for these ionophores under these conditions of measurement. The values of association constant (6) for ionophore 3 in chloroform with different quest cations were reported by Moore et al. too decrease in the following order:  $NH_4^+ = K^+ > Rb^+ > Cs^+ >$  $Na^+ > Li^+$ . The deviation in the observed order of cations in this work is probably caused by solvent differences (CDCl<sub>3</sub> vs  $H_2O$  and the composition of membranes. In chloroform ions are poorly solvated while in water effective solvation increases the effective diameter of the ion (19) in comparison to the unsolvated state. The selectivities displayed by ionophores 1, 3, 5, and 7 for alkali-metal cations probably reflect the ease with which substitution of water molecules from the inner hydration sphere of the ion is most readily effected by the ionophore, which is easiest for the largest diameter ion,  $Cs^+$  (3.3 Å), than for the smallest,  $Li^+$  (1.56 Å). Another possible contribution toward this pattern of selectivity is the potassium tetrakis(p-chlorophenyl)borate (KTpClPB), which is added to membranes to improve response characteristics and membrane resistance (20); however, the exchanger may reduce monovalent vs divalent cation selectivity (21) and can generally favor large cations (22).

Substitution of a bromo residue in the 2-position in ionophores 2, 4, 6, 8 in general changed only the order of selectively for the Na<sup>+</sup>, Li<sup>+</sup>, Ba<sup>2+</sup>, and Sr<sup>2+</sup> ions (see Table I). This effect was most noticeable in the detection of Na<sup>+</sup> and Li<sup>+</sup> due to the higher responses and detection limits than for Ba<sup>2+</sup> and Sr<sup>2+</sup> whose detection limits could not be accurately determined due to a lower response.

The responses, slopes, and detection limits for the various ionophores 1–8 with alkli-metal cations determined according to analytical commission rules (15) are shown respectively in Tables II and III. The slopes of the electrodes ranged from 61 to 20 mV/decade with lower detection limits varying from  $7 \times 10^{-5}$  to  $1 \times 10^{-2}$  M depending on the nature of the cation and ionophore. Near-Nernstian responses were observed for the cations Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> with most ionophores, e.g. 3, but not for Na<sup>+</sup> and Li<sup>+</sup>. This result prevents the use



IONOPHORE

Figure 4. Selectivity coefficient for K<sup>+</sup> in electrodes with ionophores 1-8.

of these ionophores in the determination of  $K^+$  in samples containing high concentrations of the other three cations (Cs<sup>+</sup>, Rb<sup>+</sup>, NH<sub>4</sub><sup>+</sup>). This is not a problem in medical applications of these electrodes, as they are rarely present in significant concentrations.

Selectivity coefficients for K<sup>+</sup> with respect to other alkaline-earth cations are summarized in Figure 4 and were obtained by using the fixed interference method (15), as this represents one of the conditions under which these electrodes could be used. The selectivity observed for sodium relative to potassium was found to be independent of ring size, while for lithium, calcium, and magnesium the selectivity decreased with increasing ring size. The latter observation is consistent with the preference of these cations to be hexacoordinated to oxygen ligands (16, 23). The optimum selectivity for sodium (-2.1), lithium (-3.7), calcium (-2.8), and magnesium (-3.0)was observed with 1,3-xylyl-15-crown-5 ether. Comparison of the selectivities of the 1,3-xylyl crown ethers with their 2-bromo-substituted counterparts indicates that the bromo group does not significantly alter the selectivity pattern of these ionophores. However, small differences in selectivity were observed for lithium, ionophore 3 vs 4, calcium, and magnesium, ionophore 5 vs 6. This result indicates that the xylyl ring is sufficiently flexible to prevent the bromo group from interferring with binding, by protruding into the cavity.

A typical response of a PVC membrane to a stepwise change in K<sup>+</sup> concentration is illustrated in Figure 5 for ionophore 2. The trace shows a fast Nernstian response to a 10-fold increase in K<sup>+</sup> concentration (59 mV) that is essentially complete within a few seconds. Stability measurements in an open unstirred thermostated beaker of  $10^{-3}$  M KCl at 25 °C showed the electrode to have a stability of  $<0.1 \mu$ V/h.

In conclusion it has been shown that 1,3-xylyl crown ethers are good potassium-selection ionophores and that substitution of a bromo group in the 2-position has minimal effects on the



ionophore	lower detection limit, M								
	Cs <sup>+</sup>	Rb <sup>+</sup>	K+	NH4 <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>			
1	$1 \times 10^{-4}$	$1.3 \times 10^{-4}$	3 × 10-4	$1 \times 10^{-3}$	$6 \times 10^{-3}$	$1 \times 10^{-2}$			
2	$1 \times 10^{-4}$	$2 \times 10^{-4}$	$4 \times 10^{-4}$	6 × 10 <sup>-4</sup>	$3.3 \times 10^{-3}$	$8 \times 10^{-3}$			
3	1.3 × 10 <sup>-4</sup>	1.3 × 10 <sup>-4</sup>	3 × 10⁴	$8 \times 10^{-4}$	$1 \times 10^{-3}$	$7 \times 10^{-8}$			
4	$8 \times 10^{-6}$	$7 \times 10^{-5}$	$1.3 \times 10^{-4}$	$4 \times 10^{-4}$	5 × 10 <sup>-4</sup>	$1 \times 10^{-2}$			
5	$2 \times 10^{-4}$	$2 \times 10^{-4}$	$2 \times 10^{-4}$	$1 \times 10^{-3}$	$2 \times 10^{-3}$	$5 \times 10^{-3}$			
6	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$2 \times 10^{-4}$	4 × 10 <sup>-4</sup>	8 × 10⁴	$1 \times 10^{-4}$			
7	$2 \times 10^{-4}$	$2 \times 10^{-4}$	6 × 10 <sup>-4</sup>	9 × 10 <sup>-4</sup>	$3 \times 10^{-3}$	$1 \times 10^{-3}$			
8	$1 \times 10^{-4}$	$1.7 \times 10^{-4}$	$1.6 \times 10^{-4}$	9 × 10-4	$1.7 \times 10^{-3}$	$1.2 \times 10^{-3}$			



Figure 5. Response curve for a PVC membrane based on ionophore 2 to a change in concentration of KCI from 1  $\times$  10<sup>-3</sup> to 1  $\times$  10<sup>-2</sup> M.

selectivity pattern with alkali-metal and alkaline-earth-metal cations.

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# Selectivity-Modifying Influence of Anionic Sites in Neutral-Carrier-Based Membrane Electrodes

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The potentiometric ion selectivity of liquid membrane electrodes is largely dependent on the amount of anionic sites incorporated into the membrane phase. Selectivities were measured for membrane electrodes containing a given amount of neutral carrier and varying amounts of the additive potassium tetrakis(p-chlorophenyl)borate. The measured data are compared to an earlier published model for which the basic assumptions, a general solution, as well as a table with the optimum anionic site:neutral carrier ratios for some cases of practical relevance are given. The pronounced selectivity changes and the selectivity maxima agreed with the theoretical model. Both theory and experiment confirmed that a well-defined optimum ratio exists if the primary ion either has a higher charge or/and if it is complexed by fewer ligand molecules as compared to the interfering ions.

# INTRODUCTION

Originally, neutral-carrier-based liquid membrane electrodes with incorporated anionic sites, e.g. tetraphenylborate ions, were introduced in order to reduce interference by lipid-soluble sample anions (1, 2). The presence of mobile cation-exchange sites in cation-selective membranes based on neutral carriers has also proved to be beneficial in many other respects. The additive lowers the electrical membrane resistance as well as the activation barrier for the cation-exchange reaction at the membrane/solution interface, reduces the time response after an activity step, and gives rise to significant changes in selectivity (3-6).

The concentration of anionic membrane components affects the ion selectivity, primarily by controlling the concentration of exchangeable cations and, in addition, by influencing the concentration of free carriers available for complexation of cations. A theoretical analysis of the selectivity-modifying influence of charged components in neutral-carrier-based membrane electrodes is presented in ref 3. The theoretical model may be used to evaluate the optimum composition of neutral carrier membranes yielding the highest possible carrier-induced selectivity for the respective primary ion. In this paper we report on the basic assumptions as well as the derivation of a general formula for the calculation of optimum anionic site:carrier ratios. The results show that these optimum ratios are only a function of ion charges and ion:ligand complex stoichiometries but are virtually independent of ionic

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