

# The Effect of Substituents in Macrocyclic Polyethers Containing Aromatic Rings on Ion-Selective Electrode Properties

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**Abstract.** Ion-selective electrodes, containing derivatives of crown ethers with aromatic rings, have been investigated. The electrodes were characterized by determining their detection limits and selectivity coefficients. The *t*-butyl derivative of naphtho-15-crown-5 was found to exhibit the best properties ( $L_d = 1 \times 10^{-5}$ ,  $K_{Na/K} = 6 \times 10^{-4}$ ).

**Key words.** Crowns, ion-selective electrodes, potassium.

## 1. Introduction

Macrocyclic polyethers have been thoroughly investigated since their discovery in 1967 [1]. Their application in ion-selective electrodes, especially for potassium ions, has aroused great interest. A few papers have been devoted to ion-selective electrodes with mono crown ethers as the electroactive substance [2-7]. Their properties, except for naphtho-15-crown-5 [8], were found to be of no special interest. It has been reported that derivatives of benzo-15-crown-5 form 2 : 1 sandwich complexes with potassium ions [9]. This property led to the synthesis of numerous bis-crown ethers with two crown ether rings linked by a flexible chain. The selectivity of these compounds for potassium was greatly increased in relation to benzo-15-crown-5. The use of bis-crown ethers in ion-selective electrodes led to detectors with properties comparable to those of the valinomycin electrode [10].

We have investigated the properties of ion-selective electrodes based on the derivatives of aromatic mono crown ethers with 5 and 6 oxygen atoms in the macrocyclic ring.

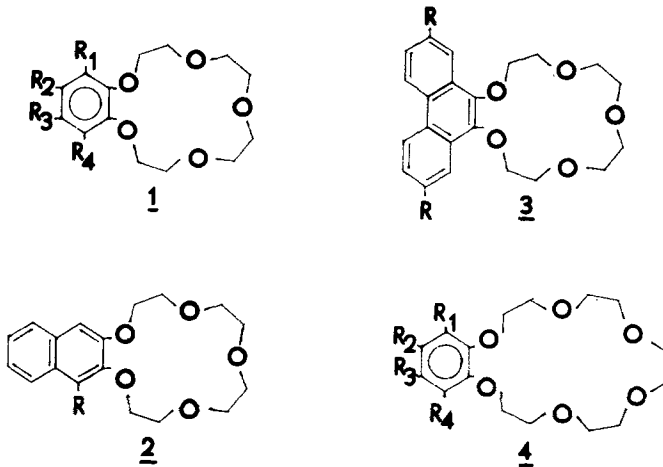
We have found that incorporation of a lipophilic substituent in the aromatic ring of a crown ether causes a considerable improvement in the electrode properties of ion-selective electrodes based on the above compounds. The investigated compounds are shown in Figure 1.

## 2. Experimental

The syntheses of all new compounds will be described elsewhere.

Poly(vinyl chloride) membranes were prepared conventionally [11]. For example: 50 mg of PVC, 10 mg of benzo-15-crown-5 and 100  $\mu$ L of *o*-nitrophenyloctyl ether were dissolved in 1 mL of THF. The solution was poured into a glass ring and left to evaporate for 24 hours. The discs obtained were incorporated into Ag/AgCl electrode bodies, with

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1	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	3	R
a	H	H	H	H	a	H
b	H	CHO	H	H	b	<i>t</i> -butyl
c	H	CH <sub>3</sub> CO	H	H		
d	H	CH <sub>2</sub> OH	H	H	4	R <sub>1</sub>
e	H	<i>t</i> -butyl	H	H		R <sub>2</sub>
f	H	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub>	H	H		R <sub>3</sub>
g	H	Cl	H	H	a	H
h	H	Br	H	H	b	<i>n</i> -butyryl
i	H	NO <sub>2</sub>	H	H	c	<i>n</i> -butyl
j	H	CH <sub>3</sub>	CH <sub>3</sub>	H	d	<i>iso</i> -butyl
k	H	<i>s</i> -butyl	<i>s</i> -butyl	H	e	<i>t</i> -butyl
l	H	Br	Br	H	f	CH <sub>3</sub> CO
m	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	g	C <sub>2</sub> H <sub>5</sub>
n	Cl	Cl	Cl	Cl	h	Cl
o	Cl	Br	Br	Cl	i	NO <sub>2</sub>
					j	CH <sub>3</sub>
2		R				
a		H				
b		<i>t</i> -butyl				

Fig. 1. Compounds used in this study.

10<sup>-2</sup> M KCl as the internal electrolyte. Other crowns were used in such amounts so that their molar concentration in the membrane was the same as in the case of benzo-15-crown-5.

An identical procedure was used in the preparation of benzo-18-crown-6 derivatives, but di-*n*-butyl phthalate was used as the plasticizer in this case.

A RADELKIS OP-08020P (Ag/AgCl, KCl) double-junction reference electrode with tetraethylammonium nitrate in the bridge was used. All potentials were measured at 25°C using a N517 (MERA ELWRO) pH-meter equipped with a V-541 digital voltmeter, allowing readings to ±0.1 mV.

The detection limits of the electrodes for potassium were evaluated as recommended by Camman [12]. Selectivity coefficients,  $K_{X/K}^{pot}$  (interfering ion/measured ion) were evaluated by the standard mixed solution method [13] from potential measurements in solutions

containing a fixed concentration ( $10^{-1}$  M) of interfering cation and a varying amount of potassium cation ( $10^{-6}$ – $10^{-1}$  M).

### 3. Results and Discussion

The logarithms of the selectivity coefficients of ion-selective electrodes based on the examined compounds, derivatives of 15-crown-5, are collected in Figure 2. The slopes of the electrodes vary from 53 to 60 mV. The detection limits are in the range from  $7 \times 10^{-6}$  to  $5 \times 10^{-5}$ .

It is known that benzo-15-crown-5 forms 2 : 1 sandwich complexes with potassium ions, whereas it only forms 1 : 1 complexes with sodium. This property led to the synthesis of numerous bis-crown ethers, in which the formation of the sandwich-like complex was greatly facilitated. These bis-crowns were applied in ion-selective electrodes. The best electrodes, based on these compounds, had  $K_{Na/K}$  selectivity coefficients of about  $2 \times 10^{-4}$ . The synthesis of bis-crown ethers is quite complicated and requires rare and expensive substrates. The application of simpler compounds, obtained from more common substrates, in ion-selective electrodes is thus justified.

A strong substituent effect on the properties of ion-selective electrodes, based on simple derivatives of 15-crown-5 ethers with aromatic rings, was observed.

We suspected a strong electronic effect of substituents causing an increase in the electronic density on oxygen atoms attached to the aromatic rings. The above assumption was not confirmed by MNDO calculations. For example, the electronic density on oxygen

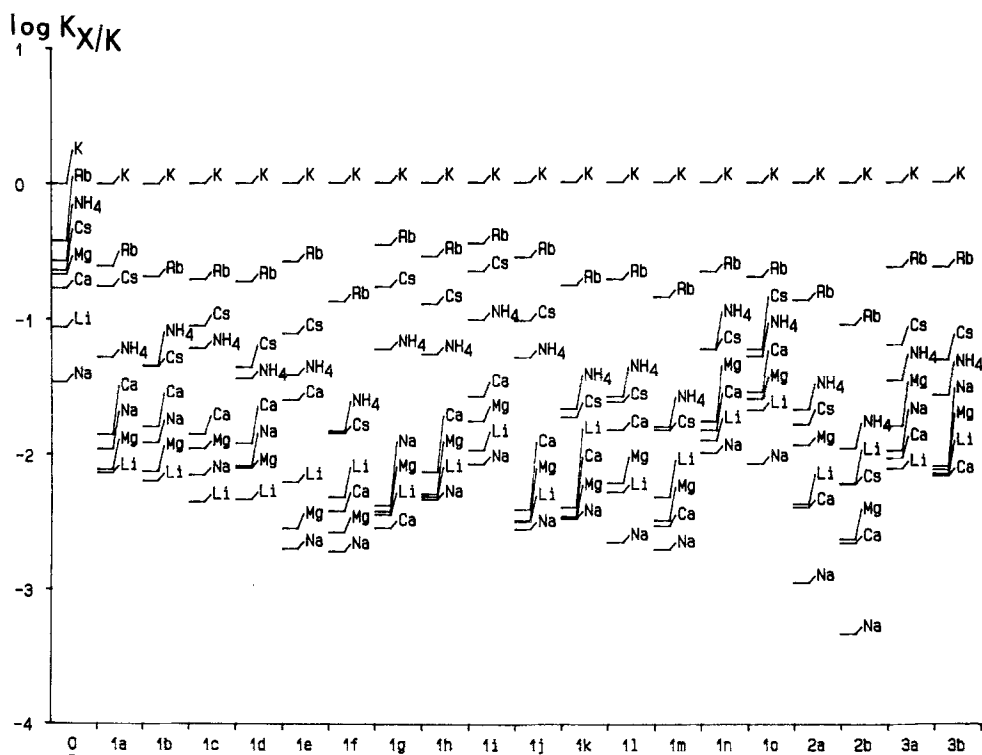


Fig. 2. The selectivity coefficients of electrodes based on aromatic derivatives of 15-crown-5.

atoms next to the aromatic ring in compounds **1a** and **1j** differs by less than 0.001 electron [14] and is thus insignificant.

Lipophilic substituents significantly increased the selectivity of potassium-selective electrodes. The effect was especially visible in the case of bulky *t*-butyl substituents. The determined properties of the best electrodes based on substituted 15-crown-5 ethers are comparable to the properties of electrodes based on bis-crowns. The lipophilicity of the compounds is substantially increased by the substituents. The plot of  $\log P$  values, calculated according to Hansch *et al.* [15, 16], in relation to  $\log K_{\text{Na/K}}$  values for the described 15-crown-5 derivatives is shown in Figure 3. A linear relation is observed. The correlation coefficient for the above relation for all compounds excluding **1n**, **1o**, **2a**, **2b**, **3a** and **3b** is equal to 0.798 (0.899 if compound **1k** is also left out).

As already mentioned, 15-crown-5 derivatives form 2 : 1 complexes with potassium. The cation is completely encapsulated by the two ligands. Complexation by crown ethers with lipophilic substituents would thus result in a strong increase of the lipophilicity of a 2 : 1 complex. The lipophilicity of a 1 : 1 complex with sodium will increase insignificantly because the sodium cation is still exposed to interaction with water molecules above and below the macrocyclic ring plane. This assumption has been confirmed by X-ray crystallographic structure determinations of benzo-15-crown-5 complexes with sodium and potassium [17, 18, 19].

The substituents in positions 3 and 6 of the benzene ring in compounds **1n** and **1o** strongly interact with the hydrogen atoms of carbon atoms of the macrocyclic ring connected directly to the oxygen atoms next to the aromatic ring. The above interaction probably causes a deformation of the macrocyclic ring hindering the complexation of cations. The same is true for compounds **3a** and **3b**. In this case the interaction probably

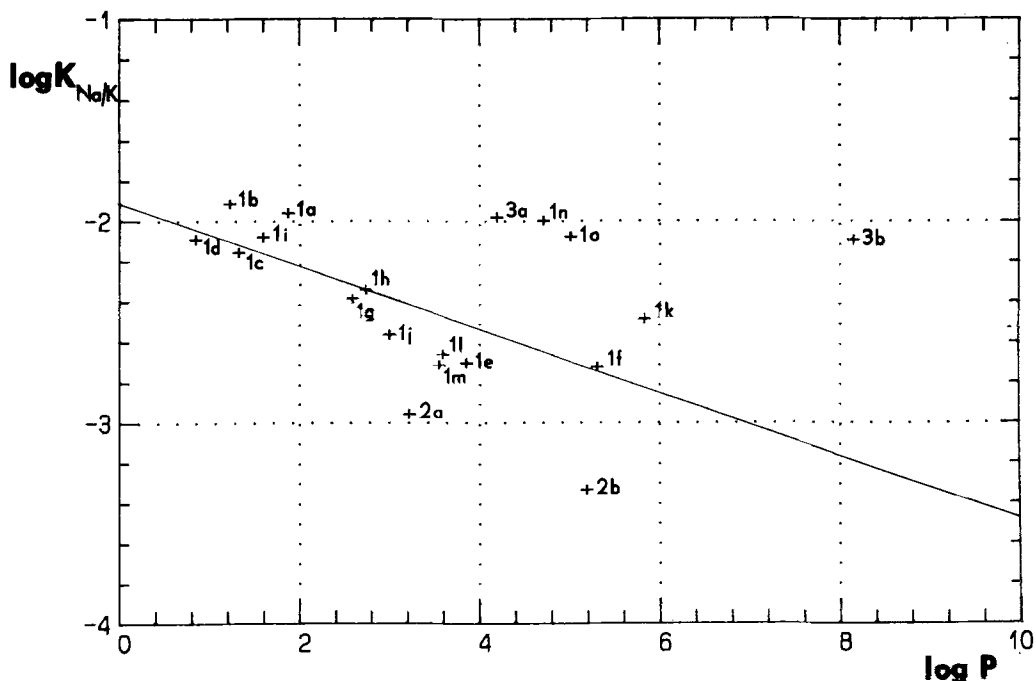


Fig. 3. The plot of  $\log P$  vs  $\log K_{\text{Na/K}}$  for 15-crown-5 derivatives.

occurs between hydrogen atoms of the same macrocyclic ring carbon atoms and the hydrogen atoms of carbon atoms 1 and 8 of the phenanthrene residue. The deformation of the macrocyclic ring explains the low selectivity coefficients, in spite of the high calculated lipophilicities, of compounds **1n**, **1o**, **3a** and **3b**.

Unusually high selectivity coefficients are observed for the naphtho derivatives in relation to their lipophilicities. This phenomenon is at the moment difficult to explain. It is probable that the greater length of the bond between carbon atoms 2 and 3 of the naphthalene group in naphtho-15-crown-5 (1.415 Å [20]) due to the less aromatic character, in comparison to benzene where the C—C bond length is equal to 1.39 Å, is responsible for a higher conformational flexibility of the macrocyclic ring, facilitating better complexation.

The results of measurements for some electrodes with benzo-18-crown-6 derivatives are gathered in Table I.

No dependence in relation to lipophilicity is observed in this case. It is probable that this is caused by a very small tendency for benzo-18-crown-6 to form 2 : 1 complexes even with larger alkali cations.

The synthesis of substituted compounds given in Figure 1 is very simple and the substrates are quite common and inexpensive, justifying their application in ion-selective electrodes.

Table I. The properties of electrodes based on derivatives of benzo-18-crown-6.

Membrane with compound	Selectivity coefficient	Detection limit [mol/dm <sup>3</sup> ]	Slope [mV/decade]
<i>K<sub>Na/K</sub></i>			
4a	$1.6 \times 10^{-2}$	$6 \times 10^{-5}$	54
4b	$1.3 \times 10^{-2}$	$4 \times 10^{-5}$	61
4c	$1.1 \times 10^{-2}$	$7 \times 10^{-5}$	50
4d	$1.3 \times 10^{-2}$	$3 \times 10^{-5}$	53
4e	$7.0 \times 10^{-3}$	$5 \times 10^{-5}$	62
4f	$1.4 \times 10^{-2}$	$2 \times 10^{-5}$	42
4g	$1.8 \times 10^{-2}$	$3 \times 10^{-5}$	50
4h	$8.0 \times 10^{-3}$	$3 \times 10^{-5}$	54
4i	$1.4 \times 10^{-2}$	$2 \times 10^{-5}$	57
4j	$8.0 \times 10^{-3}$	$7 \times 10^{-6}$	50
<i>K<sub>Na/Cs</sub></i>			
4a	$1.8 \times 10^{-2}$	$2 \times 10^{-4}$	60
4b	$4.0 \times 10^{-2}$	$9 \times 10^{-5}$	55
4c	$2.8 \times 10^{-2}$	$2 \times 10^{-4}$	56
4j	$4.0 \times 10^{-2}$	$1 \times 10^{-4}$	54
<i>K<sub>K/Rb</sub></i>			
4a	$5.0 \times 10^{-1}$	$8 \times 10^{-5}$	62
4c	$5.4 \times 10^{-1}$	$1 \times 10^{-4}$	47
4e	$1.7 \times 10^{-1}$	$1 \times 10^{-5}$	60
4h	$2.5 \times 10^{-1}$	$4 \times 10^{-6}$	51

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