

# Sulfonamides as Ionophores for Ion-Selective Electrodes. II. Macrocyclic Ligands Containing Two Sulfonamide Groups as Ionophores

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(Received: 7 December 1987; In final form: 7 March 1988)

**Abstract.** Ten macrocyclic compounds (1–10), each containing two sulfonamide groups have been incorporated into PVC membrane electrodes as ionophores. Their selectivity towards alkali and alkaline earth metal cations has been studied and compared to selectivities found in cation transport experiments.

**Key words.** Macrocyclic compounds, sulfonamides, ionophores, ion-selective electrodes.

## 1. Introduction

It is well known that both crown compounds and compounds containing amide or ester carbonyl groups are effective chelating agents for the alkali and alkaline earth cations. These types of ligands are capable of the selective transport of those cations across membranes and have been used in PVC membrane electrodes [2–5].

We have reported a study of PVC membrane electrodes using ligands with sulfonamide groups, such as *N,N,N',N'*-tetrasubstituted amides of *o*-sulfobenzoic acid, *o*-benzenedisulfonic acid and (2'-sulfo-4'-*t*-butylphenoxy) acetic acid. It was found that these compounds showed a preference towards large monovalent cations, such as  $K^+$ . Changing the substituents on the nitrogen atoms modified the ionophoric properties, probably due to the conformational changes in the ligand [6].

Inserting two sulfonamide groups into a macrocyclic compound would give a large ring where sulfonyl groups and ether oxygen atoms act as electron donors. These materials should have interesting ionophoric properties. We have reported the synthesis of a variety of the macrocyclic ligands containing two sulfonamide groups (see Figure 1) [7–9]. Some of these compounds are effective in transporting the alkali metal cations from a source phase of high pH through a methylene chloride bulk membrane into a water receiving phase [9]. This study reports the ionophoric properties of the ten *bis*-sulfonamido-crowns (Figure 1) in ion-selective PVC-membrane electrodes and compares the ionophoric properties and selectivity coefficients with the membrane transport results [10, 11] for these ligands.

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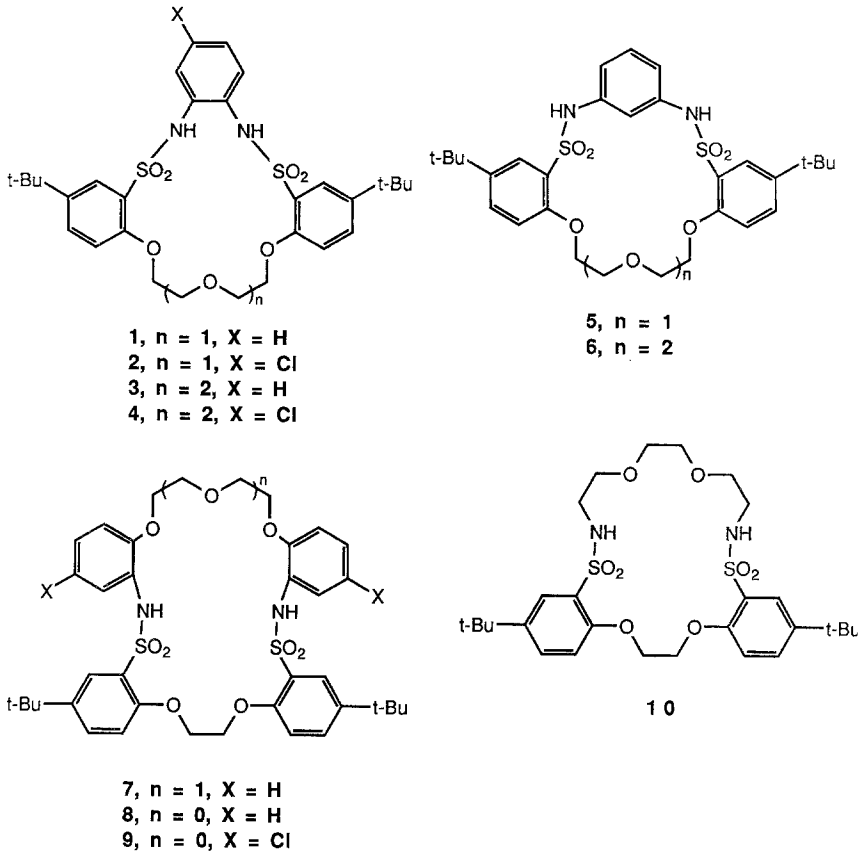


Fig. 1. Macrocyclic sulfonamides used as ionophores.

## 2. Experimental

The ionophores **1–10** were synthesized as described previously [7–9]. Analytical grade metal chlorides were used in all experiments.

### 2.1. ELECTRODE SYSTEM

The poly(vinyl chloride) (PVC) membranes were prepared conventionally, as described [6], with di-*n*-butylphthalate as plasticizer. The PVC membranes were incorporated into Ag/AgCl electrode bodies, with 0.01 M KCl as the internal electrolyte. Before measurements, the electrodes were kept in 0.1 M KCl for 24 hours. A double-junction reference electrode of the Radelkis OP0820P type was used with 0.1 M tetramethylammonium nitrate in the bridge cell.

### 2.2. E.M.F. MEASUREMENTS

All potentials were measured at  $20 \pm 1^\circ C$  using a N517 MERA ELWRO pH-meter equipped with a V541 digital voltmeter, which allowed a reading accuracy up to

$\pm 0.1$  mV. The electrodes respond to changing concentration within a few seconds. Selectivity coefficients were ( $\log K_{K^+/M^+}^{pot}$ ) obtained by the mixed solution method [2, 12]. The amount of interfering ion ( $M^+$  = alkaline and alkaline earth metal cations) was constant ( $0.01$  M/dm<sup>3</sup>) and the amount of  $K^+$  ion was varied in the range  $10^{-7}$ – $10^{-1}$  M/dm<sup>3</sup>.

### 3. Results and Discussion

In Table I are presented the characteristics of the electrodes containing ligands **1–10** and, for comparison, the electrode containing no ligand. All of the synthesized *bis*-sulfonamido-crowns behaved as ionophores in the ion-selective electrodes. The potentiometrically determined ion-selectivities are shown in Figure 2. All of the compounds, which include crowns with 17-, 18-, 20-, 21- and 23-ring atoms, showed a preference for the large monovalent ions such as  $K^+$ ,  $Rb^+$ ,  $Cs^+$ , however, the electrode selectivities for potassium over sodium are not as good as that of the standard valinomycin electrode [12]. There were no significant differences in the selectivity coefficients caused by differences in the ring size or by having an electron withdrawing chlorine atom in the system. This latter effect is shown by comparing electrodes 8 and 9, (containing ligands **8** and **9**), where there appears to be a favorable effect on selectivity by the chlorine substituent on **9**. These effects seem to be opposite when electrodes 3 and 4 are compared.

The most important factor responsible for cation inclusion seems to be the confirmation of the ligand molecule and mutual interaction of both sulfonamide groups. Most of the investigated crowns have rather rigid conformations. For the analogous compounds **7** and **8**, the more selective electrode is the one which contains the larger (23-atoms) and therefore less rigid ring, **7**. The comparison of the X-ray structures of compounds **7** and **8** confirms this reasoning. Compound **7**, with the longer polyether chain has a conformation in which two sulfur atoms are close to each other and therefore the effective size of the ring is smaller [8].

An important characteristic of the sulfonamido crowns is that they possess ionizable protons. However, no significant changes in potential measurements of the electrodes

Table I. Slopes and linear response towards  $K^+$  ion of the electrodes with ligands **1–10**.

Electrode & Ionophore	Characteristics of the Electrodes	
	The slope [mV]	Linear range $-\log [K^+]$
1	57	4.25–1
2	54	4.5 –1
3	53	4.5 –1
4	54	4.25–1
5	53	4.5 –1
6	52	4.5 –1
7	55	4.25–1
8	59	4.25–1
9	54	4.25–1
10	53	4.0 –1
11(Blank)	45	3.25–1

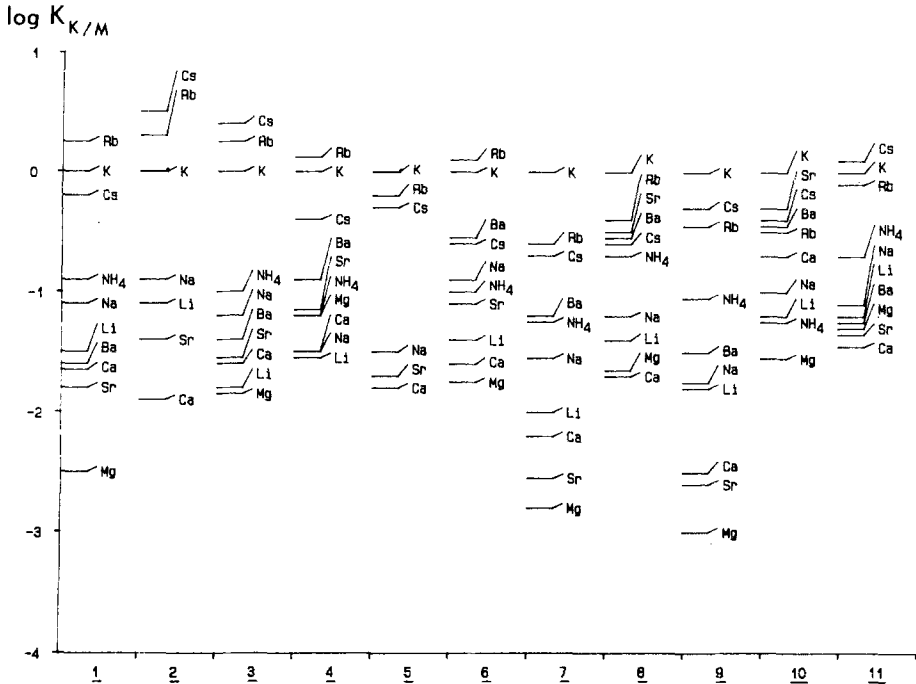


Fig. 2. The selectivity coefficients ( $\log K_{K/M}^{\text{pot}}$ ) for electrodes 1–11 (11 has a blank membrane).

were observed at pH values in the range of 1–13. Thus, the selectivity coefficients ( $\log K_{K^+/M^+}^{\text{pot}}$ ) for the electrodes 7 and 8 measured in 0.1 M NaOH solution and in 0.1 M NaCl were nearly identical.

The source compounds, at high pH values, are very active transport agents [9–11]. The transport of the alkali metal ions by these ligands gave the selectivity patterns shown in Table II.

Table II. Cation selectivity in the transport of alkali metal ions through a  $\text{CH}_2\text{Cl}_2$  bulk membrane.<sup>a</sup>

Ligand	pH	Ions of Preference
1	13.5	Cs > Na > K > Rb > Li
2	13	Very low transport
3	13	Na > Li > K > Rb > Cs
4	13	Rb > K > Na > Li > Cs
5	14	Very low transport
6	13.5	Rb > K > Na > Li
7	13	K > Rb > Cs > Na > Li
8	13.5	Rb > K > Na > Cs > Li
9	13	Rb > K > Cs > Na > Li
10	up to 14	No transport

<sup>a</sup> Data from Refs. [10 and 11]. The preference was taken at receiving phase = pH 7.

Comparing transport results using these ligands with the behavior of these ligands in ion-selective electrodes, one observes the following correlations. First, compounds **4** and **9** are the best alkali metal ion carriers at pH 13 [10, 11]. The electrode with **9** showed the highest selectivity towards  $K^+$  (Figure 2) but **9** transported  $Rb^+$  the best [11]. Ligand **4**, on the other hand, showed the highest selectivity and transport for  $Rb^+$ . Second, ligands **7** and **8** were selective for  $K^+$  both in ion-selective electrodes and in transport at a source phase pH of 13. Third, ligands **5**, **6**, **8** and **10** exhibited only marginal selectivity in ion-selective electrodes and they were poor transport agents [10, 11].

Macrocyclic **10** with aliphatic carbon atoms attached to the amide nitrogen atoms was washed from the membrane due to its low lipophilicity and, therefore, electrode **10** lost its ionophoric ability after only a few days. Probably the same factor caused the lack of transport effectiveness by ligand **10** through the liquid membrane (Table II). All other electrodes were in use for about 3 months and were still functional.

As described above, the selectivity patterns in liquid membrane transport and in ion-selective electrodes are generally parallel. This suggests that the active species in the electrodes and membranes are the respective ligand anions. This also suggests that ion selectivity data from ion-selective electrodes might be useful for the prediction of thermodynamically controlled transport selectivities.

## Acknowledgement

We appreciate the help of Elżbieta Chudzińska for technical assistance. Financial support of this work by CPBP 01.15 project (Poland) and U.S. Department of Energy, Office of Basic Energy Sciences Grant No. DE-FG-02-86ER13463 is gratefully acknowledged.

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