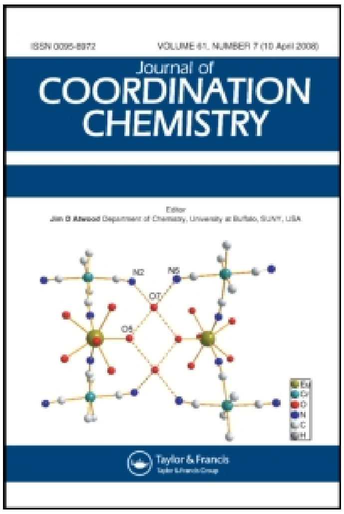

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SULFONAMIDES AS IONOPHORES FOR ISE. III. GUANIDINIUM ION-SELECTIVE ELECTRODES BASED ON LIPOPHILIC BIS-SULFONAMIDE PODANDS

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PVC membrane ion-selective electrodes based on bis-sulfonamide podands and DOS (Bis(2-ethylhexyl)-sebacate) as plasticizer are described. They were found to behave as guanidinium ion sensors, exhibiting high selectivity for guanidinium ions over potassium ions.

Keywords: Sulfonamides, podands, ionophores, ion-selective electrodes, guanidinium ion

1. INTRODUCTION

Macrocyclic ligands containing two proton-ionizable sulfonamide groups were found to be effective transport agents for alkali metal cations.[1] Their ionophoric properties in ISE were also studied.[2] It was found that all macrocycles studied, the crowns with 17-, 18-, 20-, 21- and 23-ring atoms show preference for large monovalent ions such as K, Rb, Cs. Transport[3] of these cations requires high pH values of the source aqueous phase. The electrodes studies were carried out at neutral pH but nevertheless it was possible to find some correlation of the results.[2]

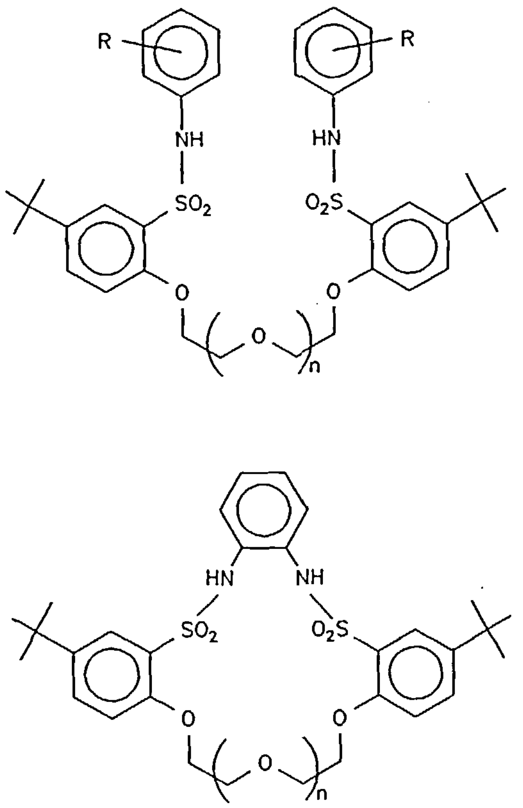
The synthesis of the open chain ligands of the bis-sulfonamido type (see Figure 1) and their interaction with metal cations, investigated by solvent extraction was reported.[4,5] High extractability of Na^+ and K^+ by bis-sulfonamido podands was observed. It was also found that in the presence of tetramethylammonium hydroxide in the water phase both metal cation and organic tetramethylammonium ions are extracted into the organic phase.

There is a growing interest in finding suitable hosts for complexing organic ions and molecules.[6–8] The importance of guanidine derivatives in biological and medical fields explains the need for search for ligands forming stable complexes with the guanidinium ion. The optimal arrangement of hydrogen bonds [NH...O or NH...N] and a suitable size of the macroring cavity is responsible for the formation of stable complexes with guanidinium ions.[9–11] Guanidinium ion-selective electrodes reported up to date were based on dibenzo-27-crown-9.[12,13]

Here we report the ionophoric properties of the bis-sulfonamido podands in ion-selective PVC membrane electrodes. The results are compared with the solvent extraction data. The presented electrodes behave also as excellent guanidinium ion sensors, exhibiting high selectivity for guanidinium over potassium ions.

2. EXPERIMENTAL

The synthesis of ionophores 1–9 was described in reference 4. In all experiments analytical grade metal chlorides were used.



1 n = 0 R = p–NO$_2$
2 n = 1 R = p–NO$_2$
3 n = 2 R = p–NO$_2$
4 n = 0 R = o–OCH$_3$
5 n = 1 R = o–OCH$_3$
6 n = 2 R = o–OCH$_3$
7 n = 2 R = p–OCH$_3$
8 n = 1 R = o–CH$_3$
9 n = 2 R = p–CH$_3$

n = 1
n = 2

FIGURE 1 Compounds used in this study.

The electrode system: poly(vinyl chloride) (PVC) membranes were prepared conventionally[2,14,15] as described in our earlier publications using lipophilic plasticizer DOS (dioctyl sebacate). The PVC membranes were incorporated into Ag/AgCl electrode bodies with 0.01 M KCl as internal electrolyte. A double junction reference electrode (OP 0820P, Radelkis) was used with a 0.1 M CH_3COOLi solution in the bridge cell.

EMF measurements: all potentials were measured at 20°C using a N517 MERA ELWRO pH-meter equipped with a V541 digital voltmeter, allowing a reading accuracy up to 0.1 mV. The electrodes responded to changing concentration within a few seconds. The selectivity coefficients, which are presented in Figure 2 were obtained by the separate solution method (SSM) but in the case of guanidinium/potassium selectivity they were also obtained by the fixed interference method (FIM), with 0.01 M KCl as the background electrolyte and 10 μmoles–100 mmoles of guanidinium hydrochloride. The results obtained by both methods are similar. Some examples are presented in Table II.

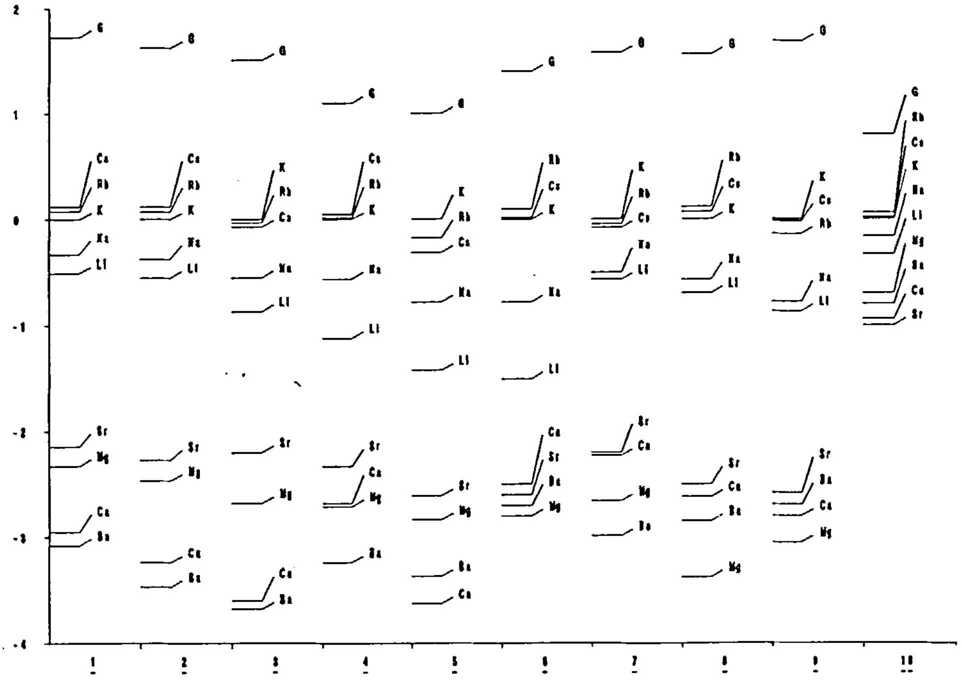


FIGURE 2 Selectivity coefficients for investigated electrodes.

TABLE I
Properties of the electrodes with ionophores 1-9 and DOS as plasticizer.

Electrode and ionophore	K^+ slope [mV]	Linear range $-\log[K^+]$	Guianidinium slope [mV]	Linear range $-\log[G^+]$	Selectivity coefficient $\log K_{K,G}$
1	56	4.0–1	59	5.5–1	1.6
2	56	4.0–1	56	5.3–1	1.65
3	56	5.1–1	60	5.5–1	1.55
4	57	4.5–1	57	5.8–1	1.5
5	57	5.0–1	59	6.0–1	1.2
6	56	4.0–1	58	5.5–1	1.4
7	54	4.0–1	58	5.5–1	1.5
8	57	5.0–1	57	5.5–1	1.3
9	56	4.5–1	59	6.0–1	1.6
10	25	4.0–1	37	4.2–1	—

3. RESULTS AND DISCUSSION

The characteristics of the electrodes containing ligands **1–9** and an electrode with a blank membrane for comparison are presented in Table I. All of the bis-sulfonamido podands presented in Figure 1 behave as ionophores in membrane ion-selective

TABLE II
Properties of guanidinium-selective electrodes.

Electrode	Ionophore	Slope [mV]	Linear range	Selectivity $\log K_{G,K}$
1	1	59	5.5–1	−1.6,[a] −1.73[b]
9	9	59	6.0–1	−1.6,[a] −1.69[b]
ref. 12	DB-27-C-9	50	4.0–1	−1.0[a]
ref. 13	DB-27-C-9	55	4.0–1	−0.55[b]
ref. 13	DB-27-C-9/GTPB	60	4.5–1	−1.5[b]

[a] FIM, [b] SSM.

electrodes. They showed, like analogous crown ethers (see Figure 1), a preference for the large monovalent ions such as K^+, Rb^+, Cs^+.[2] It was also found that bis-sulfonamido podands are good complexing agents for organic amines, as for example tetramethylammonium cations[4] and guanidinium ions and their derivatives, such as creatinine.[16] The presented electrodes behave as excellent guanidinium sensors, superior to those described so far[12,13] (see Table II). All compounds studied show good ionophoric behaviour for guanidinium ions however those with the longest polyether chain (4 ether oxygen atoms), ligands **3**, **6**, **7**, **9** or those with nitro groups (ligands **1**, **2**, **3**) in the amide phenyl ring are the best. These suggest that the ligand molecule wraps around the guanidinium ion, which interacts with sulfonamide groups and also with nitro groups. The more flexible the molecule, the better the interaction.

All studied compounds differ in the length of the polyether chain and in the substituents in the amide phenyl ring but their lipophilicity (log P) does not differ significantly, which is probably the reason for similar ionophoric behaviour. The lipophilicities of compounds **1–9** are rather high (log P is within the 8.5–10.4 range, as calculated according to the method of Hansch[17]) and they meet the requirements for good electrode sensors.

The selectivity for K^+ over Na^+ is generally not very high for all reported compounds. The selectivity coefficients are presented in Figure 2.

ACKNOWLEDGEMENTS

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