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Dedicated to Professor Valer Fărcăşan at his 85th anniversary

NEW MACROCYCLES INCLUDING SPIRO-1,3-DIOXANE UNITS AS IONOPHORES FOR CATION SELECTIVE ELECTRODES

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ABSTRACT. The paper is concerned with preliminary studies on new macrocycles-"monomers and dimers"-containing spiro-1,3-dioxane units as ionophores for poly(vinyl chloride) membranes for potentiometric sensing of sodium, potassium, calcium and magnesium ions. The best macrocycles were evaluated for each cation.

The optimum membrane composition and the appropriate preparation procedure for obtaining the electrodes with good electrochemical characteristics were closely followed.

INTRODUCTION

A large and diverse range of ligands[1] (hosts for metal ions and neutral molecules) has been prepared, exhibiting both remarkable selectivity and useful reactivity properties. The crown ethers are among the simplest and most appealing macrocyclic (large ring) ligands.

The interplay of complex stability and cation exchange kinetics is very important in the uses of supramolecular cation hosts. On the basis of their behaviour, we may distinguish between cation receptors (slow kinetics, large stability constants) and cation carriers (fast kinetics, lower stability). The crown ethers[2] are among the important ionophores for ion-selective electrodes.

This type of electrodes is widely used for blood-electrolyte analysis[3].

Some papers[4] has indicated that the hospitals would carry out 50-200 analyses of cations on each working day.

In view of medical applications or environmental analysis the development of cheap and small Na^+, K^+, Ca^{2+}, Mg^{2+}- sensors[5] are of interest.

Many authors[6-8] achieve low detection limits for determination of these cations.

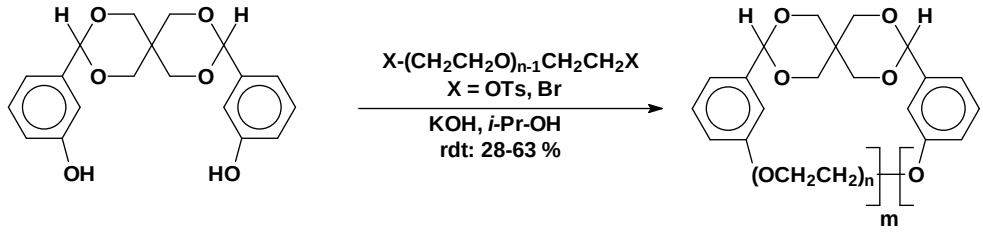
Our paper is concerned with preliminary studies on new synthesized ligands as ionophores for potentiometric sensing of cations (sodium, potassium, calcium and magnesium).

EXPERIMENTAL

Materials:

The reagent and materials used were obtained from: potassium tetrakis(4-chlorophenyl)borate and 2-nitrophenyl octyl ether (NPOE)- Fluka, Switzerland; sodium chloride p.a., potassium chloride p.a., calcium nitrate p.a., magnesium nitrate p.a., poly(vinylchloride) (PVC-high molecular weight), ionophores - Romania, tetrahydrofuran (THF) p.a.- Carlo Erba, Italy. The THF was distilled before use for removing 2,6-di-*tert*-butyl-*p*-cresol.

The ionophores were synthesized as described previously[9] (Figure 1). The monomeric and dimeric macrocycles **2b**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a** and **7a** were used in our experiments as ligands for cations[10].



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n = 1, m = 2 **2b**
n = 2, m = 2 **3b**
n = 3, m = 1 **4a**; m = 2 **4b**
n = 4, m = 2 **5a**; m = 2 **5b**
n = 5, m = 2 **6a**; m = 2 **6b**
n = 6, m = 2 **7a**; m = 2 **7b**

Figure 1

Preparation of membranes:

PVC membranes were prepared by a standard procedure using the following compositions as presented in Table 1.

Table 1

PVC membranes compositions

Composition	Cation			
	Sodium	Potassium	Calcium	Magnesium
Ionofor (%)	6,50	1,00	1,00	1,40
2-Nitrophenyl octyl ether (%)	66,70	67,00	65,60	64,50
PVC (%)	26,80	31,70	32,80	33,10
Potasiumtetrakis(4-chlorophenyl)borate (%)	-	0,30	0,60	1,00

The membrane components were dissolved in THF and the resulting solution poured into a teflon mould. Upon evaporation (24 h), homogeneous, transparent PVC membranes with a thickness of about 0.2 mm were obtained. Disks of the appropriate diameter are cut out with a punch. For each membrane composition two electrodes were prepared. The membranes were glued on teflon electrod body.

Cell potentials were measured relative to a double junction calomel reference electrode (with internal reference solution 0.1M calcium nitrate for sodium, potassium and magnesium ion determination and 0.1M potassium chloride for calcium ion determination) with an ionometer DXC-91 (Datronix Computer). All potentiometric measurements were carried out at 20±0.5^{0}C.

Calibrated solutions were prepared by serial dilution of 0.1 M XCl (X= Na^+, K^+) and 0.1 M $X(NO_3)_2$ (X= Ca^{2+}, Mg^{2+}) stock solutions to 10^{-6} M, with deionizer water.

Before the experiment to be performed and between the experiments, membranes were conditioned and stored in the same stock solutions.

RESULTS AND DISCUSSION

Membranes were evaluated by studying their behavior in various test solutions. The calibration functions are represented in Figure 2 and their slopes/ linear calibration ranges are presented in Table 2.

Table 2

The slopes and the linear response range for ion-selective membranes

Membrane	S [mV/pE]/ linear response range			
	Cation			
	Na	K	Ca	Mg
2b (dimer)	40 10^{-3}-10^{-1}	62 10^{-4}-10^{-1}	25 10^{-6}-10^{-1}	20 10^{-4}-10^{-1}
3b (dimer)	14 10^{-2}-10^{-1}	67 10^{-5}-10^{-1}	20 10^{-5}-10^{-1}	29 10^{-3}-10^{-1}
4a (monomer)	28 10^{-4}-10^{-1}	74 10^{-5}-10^{-1}	23 10^{-5}-10^{-1}	41 10^{-5}-10^{-1}
4b (dimer)	47 10^{-3}-10^{-1}	69 10^{-5}-10^{-1}	39 10^{-5}-10^{-1}	26 10^{-3}-10^{-1}
5a (monomer)	47 10^{-4}-10^{-1}	72 10^{-5}-10^{-1}	19 10^{-5}-10^{-1}	24 10^{-5}-10^{-1}
5b (dimer)	34 10^{-3}-10^{-1}	66 10^{-5}-10^{-1}	34 10^{-4}-10^{-1}	15 10^{-5}-10^{-1}
6a (monomer)	55 10^{-3}-10^{-1}	72 10^{-5}-10^{-1}	24 10^{-5}-10^{-1}	27 10^{-4}-10^{-1}
7a (monomer)	51 10^{-3}-10^{-1}	57 10^{-5}-10^{-1}	24 10^{-5}-10^{-1}	23 10^{-5}-10^{-1}

In order to asses the membranes lifetime the slope over the above range was measured each week over a period of 3 months, while the electrode was in continual use.

The membranes continued to function in a reproducible manner for approximately three months, after a small decline in slope. The initial potential is changed between two sets of measurements. The process governing the lifetime of cation selective electrodes include the loss of the active site, of the additives and of the plasticizer, particularly by diffusion into the sample solution.

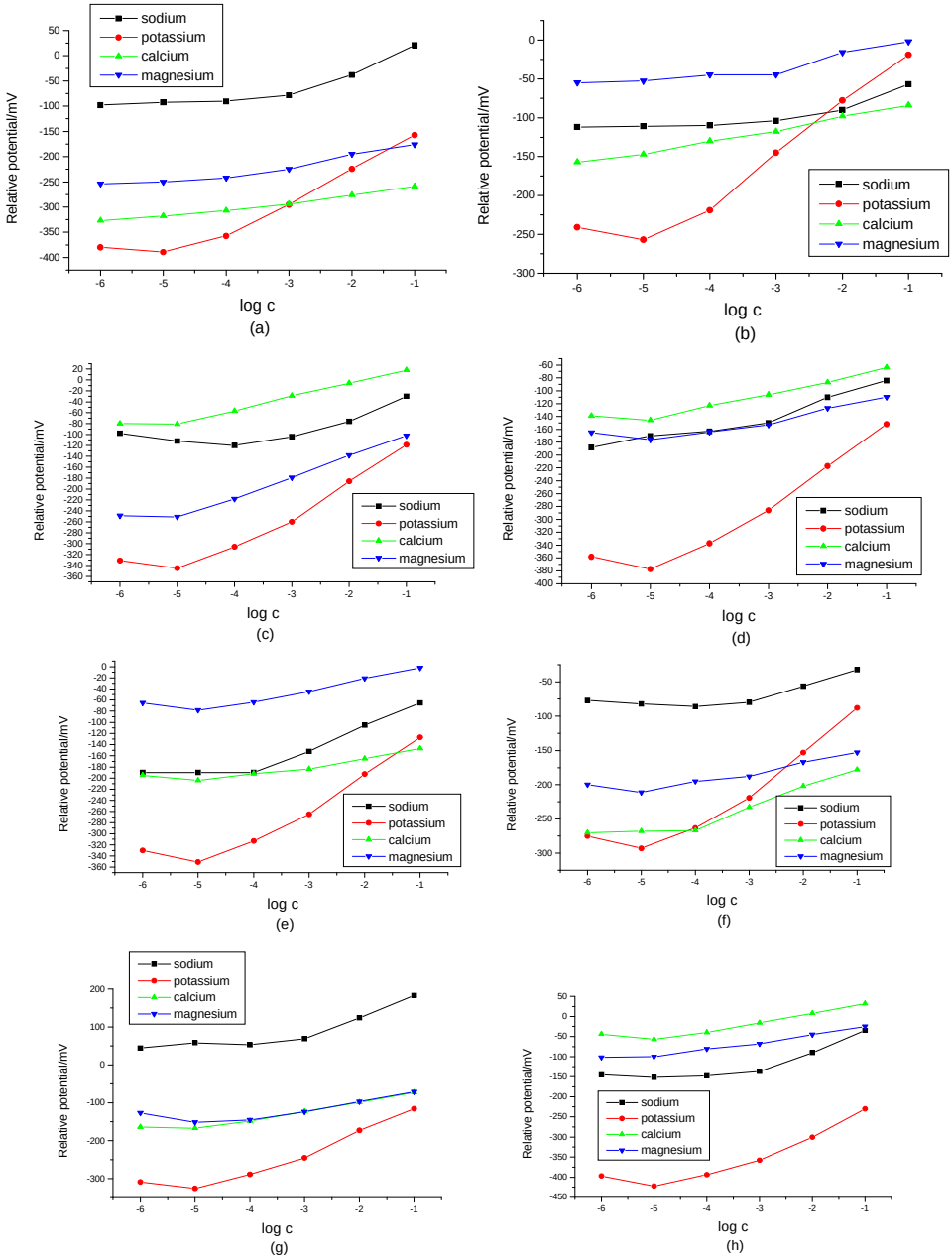

Figure 2. The calibration functions for cations. Membrane:(a) 2b; (b) 3b; (c) 4a; (d) 4b; (e) 5a; (f) 5b; (g) 6a; (h) 7a

The results of cations determination are presented in Table 3.

Table 3

The ion-selective membranes electrochemical response

electrochem respons	Membranes							
	2b d	**3b** d	**4a** m	**4b** d	**5a** m	**5b** d	**6a** m	**7a** m
excellent	**Ca**	**K** **Mg**	**K** **Mg**	**K** **Ca**	**K**	**K** **Ca**	**K** **Na** **Mg**	**K**
good	**K**			**Mg**	**Mg**		**Ca**	**Na** **Ca**
poor	**Mg**		**Ca**		**Na**			**Mg**
very poor		**Na** **Ca**	**Na**		**Ca**	**Mg**		

The response of membranes is rapid (<10 sec).

The metal binding ability of such ligands is effective by virtue of the chelate and macrocyclic effects. The selectivity for cations is very much improved for macrocyclic cavities, more rigid and restricted so that they are unable to constrict sufficiently to bind cations that are too small for the cavity; they cannot expand to accommodate cations with radii greater than the optimum size fit. A successful host exhibits a strong affinity for one particular guest and a much lower affinity for other cations. The selectivity is governed by an enormous number of factors: size match between cation and host cavity, electrostatic charge, coordinating ability, cation binding kinetics, chelate ring size, etc. That is why to designate a particular ligand to be highly selective for a given cation is very complicated.

In our case we can conclude that all ligands are selective for K^+ having very good electrochemical response but only 6a and 7a monomers have good electrochemical response for Na^+. The monomers have a good electrochemical response for calcium ion while the dimers have a good electrochemical response for magnesium ion.

The solid-state molecular structure was determined for some monomers[9]. The structures revealed different orientation of the aromatic rings and the collapse of the middle part of the macrocycle. This suggests that these compounds may be able to coordinate as a ditopic “host” molecule.

The selectivity of ligands also depend on the ability of the large, flexible parts (the length of the polyethoxylated chain) of macrocycles to “wrap” around the metal cation, effectively enclosing it almost entirely within an organic sheath.

We conclude that there is no rule concerning the electrochemical response of the ligands for these cations.

The research will be continued with studies on selectivity and improving the detection limit of the best ligands as ionophores.

CONCLUSIONS

The new series of ligands was used as ionophores for polymeric membranes for Na^+, K^+ , Ca^{2+},Mg^{2+} determination having good electrochemical characteristics.

These membranes could be used in clinical determination of cations where the concentration in human blood plasma is between: 135-145 mmol/l for Na^+, 3.5-5 mmol/l for K^+, 1-1.3 mmol/l for Ca^{2+} and 0.6-0.9 mmol/l for Mg^{2+}

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