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In memoriam prof. dr. Liviu Oniciu

NEW [4.4.4.4]CYCLOPHANE AS IONOPHORE FOR ION-SELECTIVE ELECTRODES

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ABSTRACT. A new cyclophane derivative (M7F2) was tested as ionophore for ion-selective electrodes (ISE), based on PVC membrane. Two types of ISE membranes were prepared and compared: one with, and one without potassium tetrakis(4-clorophenyl)borate as ionic additive. Potentiometric tests were performed in calcium, magnesium, sodium and potassium standard solutions. The best response was obtained for calcium, i.e., lowest detection limit, highest linear range and a quasi-nernstian slope. The investigated cyclophane ISE showed comparable analytical performances.

Keywords: *cyclophane, PVC-based ISE, calcium ISE*

INTRODUCTION

Ion-selective electrodes (ISE) are well-known for their wide applications in important fields such as clinical, food and environmental chemistry [1]. For example, it is estimated that over a billion clinical analyses are performed annually in laboratories all over the world using ISE [2].

ISE are usually made of a polymer matrix incorporating an ionophore. Macrocyclic compounds are the most frequently used ionophores; they selectively bind different ions by entrapping them in their cavity. The selectivity of the membrane is thus strongly influenced by the size match between the ion and the host cavity. Many cyclophane derivatives are successfully used as ionophores [3, 4].

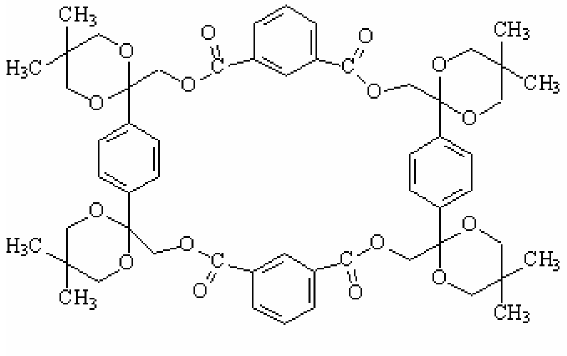

Figure 1. The structure of M7F2 ionophore

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This paper aims at testing a newly synthesized [4.4.4.4]cyclophane as ionophore for cation-selective membranes. Its name, 5,5,10,10,22,22,27,27-tetrakis[3',3'-dimethyl-1',5'-dioxapentan-1',5'-diyl]-2, 13,19,30-tetraoxo-3,12,20,29-tetraoxapenta-cyclo[29.3.$2^{6,9}$.$2^{23,26}$.$1^{14,18}$.$1^{1,31}$]tetracontan-1^{40},6,8,14,16,18^{37},23^{38}, 24,26^{39},31,33-dodecaene is abbreviated as M7F2. The structure of the ionophore is shown in Figure 1.

RESULTS AND DISCUSSION

I. Calibration curves for Ca^{2+}, Mg^{2+}, Na^+, K^+

An example of calibration curves obtained for both types of prepared membranes, in presence of different concentrations of calcium ion, is shown in Figure 2. The calculated values of the corresponding slopes and detection limits (DL) are presented in Table 1. All values represent the average of three measurements, performed successively with three electrodes, in the same working conditions.

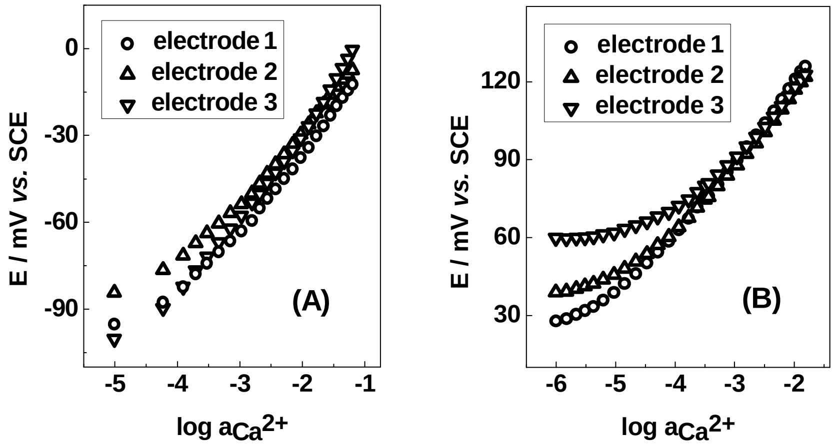

Figure 2. Calibration curves obtained in presence of Ca^{2+} solution for the membrane with (A) and without ionic additive (B)

Table 1.

Values of slope and DL for the membranes with and without ionic additive

Ion / Membrane type	Slope (mV/Δp$_{ion}$)				DL (mM)			
	Ca^{2+}	Mg^{2+}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	K^+
With ionic additive	26.8 ± 1.1	32.6 ± 5.2	39.8 ± 5.4	39.3 ± 4.9	1.92* *10^{-2}	5.42	8.62	1.23* *10^{-1}
Without ionic additive	29.0 ± 2.0	5.2 ± 0.4	57.7 ± 7.0	37.0 ± 5.1	2.22* *10^{-2}	-	3.02* 10^{-1}	4.00

From Table 1 it can be noticed that both prepared membranes presented potentiometric response to the tested cations. For calcium, both membranes present a nernstian slope (S) of about 28 mV/decade, the lowest DL (≈ $2*10^{-5}$ M) and a large linear range (≈ 4 decades). For all other tested ions, significantly higher DL were obtained. In presence of K^+, both membranes presented undernernstian response. A nernstian response was also obtained for Mg^{2+} and Na^+ using the membrane with, and without ionic additive, respectively.

II. Study of the ionic interference

Based on DL and sensitivity results, calcium was chosen as primary ion. Concentrations of interfering ion (Mg^{2+}, Na^+, and K^+) varied up to 0.5 M, while calcium was kept at a constant concentration of 5 mM.

Figure 3 shows an example of calibration curve obtained during the interference study carried out in presence of variable sodium concentration. Table 2 lists the average values of the potentiometric selectivity coefficients.

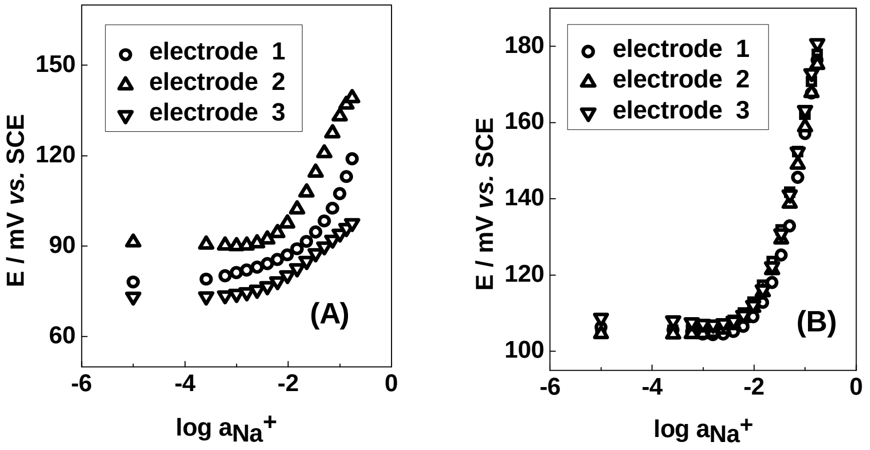

Figure 3. Calibration curves obtained for Na^+ in presence of constant Ca^{2+} concentration (5 mM), for the membrane with (A) and without ionic additive (B)

Table 2.
Values of selectivity coefficients for the two membranes, with Ca^{2+} as primary ion (5 mM) and Mg^{2+}, Na^+, K^+ as interfering ions

Interferent **Membrane type**	$\log K^{pot}_{A,B}$		
	Mg^{2+}	Na^+	K^+
With ionic additive	-0.38 ± 0.05	2.23 ± 0.24	4.64 ± 0.48
Without ionic additive	-0.32 ± 0.14	1. 43 ± 0.04	1.34 ± 0.02

The lowest interference with respect to Ca^{2+} is observed in the case of Mg^{2+}, which is a remarkable fact, taking into account the usually high interference between the two ions [8]. For the ionic additive-free membrane, $\log K^{pot}_{Ca,Mg}$ was -0.32, and for the other one it was -0.38.

The positive values of $\log K^{pot}_{Ca,Na}$ and $\log K^{pot}_{Ca,K}$ suggest a high sensitivity towards Na^+ and K^+ at the chosen concentration of Ca^{2+}. In the case of the membrane with ionic additive, the high value $\log K^{pot}_{Ca,K}$ can be due to the high amount of potassium ions introduced in the membrane through the ionic additive. In order to improve the estimated selectivity, additional tests should be performed at different concentrations of primary and/or interfering ions, depending on the prospective applications of the ISE. For example, in some mineral waters where sodium and magnesium are ten times less concentrated than calcium, the concentration of the last one can be successfully measured using ISE based on the M7F2 compound.

III. Study of repeatability

Both the inter-electrode and inter-measurements repeatability were estimated and two examples of representative results are presented in Figure 4. The first case shows the mean values of the response recorded with the same electrode (based on ionic additive-free membrane) during three successive tests performed for Ca^{2+} in the same working conditions. The second figure shows the mean value of the responses for three similar electrodes (with additive-free membrane), recorded simultaneously in Na^+ solutions. In both cases, a good repeatability was obtained, in spite of a relatively high dispersion observed at low concentrations. This dispersion is due to the high level of the electric noise caused by the absence of supporting electrolyte.

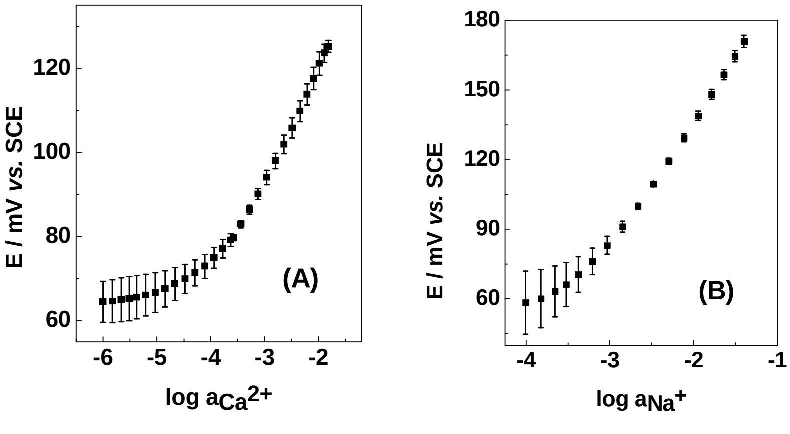

Figure 4. Mean value and standard deviation of three measurements successively performed in Ca^{2+} solution with the same electrode (based on the additive-free membrane) and in the same working conditions (A), and for simultaneous measurements performed with three similar electrodes in Na^+ solution (B)

CONCLUSIONS

This study aimed at characterizing the M7F2 cyclophane as ionophore for ISE based on two types of PVC membranes prepared with and without an ionic additive, respectively. A good detection limit (≈ $2*10^{-5}$ M), a wide linear range (about four decades) and a quasi-nernstian slope (≈ 28 mV/decade) were obtained for Ca^{2+} in the case of both types of investigated membranes. The electrodes also showed potentiometric response to other ions (Mg^{2+}, Na^{+}, K^{+}) but their analytical parameters were poorer than those obtained for calcium.

It is worth to mention that the best selectivity against Ca^{2+} was obtained for Mg^{2+}, the values of the logarithm of the selectivity coefficient being -0.38 and -0.32 for the membrane with, and without ionic additive, respectively.

A good repeatability was obtained both for inter-measurements and inter-electrode tests.

EXPERIMENTAL SECTION

Materials

The M7F2 ionophore was synthesized [5, 6] in the research team of prof. Ion Grosu from the OCD of our faculty. All reagents used were of analytical grade. Calcium chloride, lithium acetate, 2-nitrophenyloctylether (NPOE), high molecular weight polyvinyl chloride (PVC), tetrahydrofurane (THF) and potassium tetrakis(4-clorophenyl)borate (KTkClPB) were purchased from Fluka (Darmstadt, Germany). Potassium chloride was from Riedel-deHaën (Darmstadt, Germany), magnesium chloride was purchased from Chimopar (Bucharest, Romania) and sodium chloride was from Merck (Darmstadt, Germany).

Membrane preparation

Two types of membranes were investigated: (i) the first contained 0.7% (w/w) M7F2 as ionophore, 0.3% (w/w) KTkClPB as ionic additive, 33% (w/w) PVC as polymer matrix and 66% (w/w) NPOE as plasticizer; (ii) the second membrane had the same composition excepting that it was prepared without ionic additive and the percent of ionophore was 1% (w/w). Each membrane weighted 0.3 g.

Membranes were prepared according to the following procedure. The ionophore, ionic additive, plasticizer and polymer matrix were successively dissolved in THF, under stirring. After dissolution, the mixture was poured into a glass cylinder, in THF atmosphere, in order to avoid pores formation. The membranes were dried and stored in dark. Before use they were conditioned for at least 24 hours in the solution containing the cation to be determined.

Experimental setup

Measurements were performed using a PC-controlled setup [7]. The system control, as well as data acquisition were performed using LabView 5.1. Data treatment was done by using the Origin 5.0 software.

Two lots of three electrodes (based on the two types of investigated membranes) were prepared by fixing an 8 mm diameter disc membrane at the bottom end of a plastic syringe body. As internal reference, a Ag/AgCl system was used. The inner electrolytes contained the same ion as the test solution, at a concentration of 5 mM. The similar electrodes were tested simultaneously, and each measurement was repeated three times in the same working conditions. A double-junction saturated calomel electrode was used as external reference. The external liquid junction was filled with CH_3COOLi 0.1 M.

Experimental procedure

The experimental consisted in two main parts: in the first one, the potentiometric response of the two types of the prepared membranes was recorded for Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} using separate solutions, and the corresponding calibration curves were drawn. In the second part, the ionic interference between Ca^{2+} and different common cations was examined.

Potentiometric measurements were performed in batch mode, using the standard addition method for the preparation of standard solutions. For the interference study, the method of constant primary ion concentration was used: the primary ion concentration was constant, while increasing concentrations of the interfering ion were added.

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