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POTASSIUM-SELECTIVE ELECTRODE BASED ON A CALIX[6]ARENIC ESTER (C6Es6)

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ABSTRACT. An ion-selective electrode (ISE) was elaborated based on a calyx[6]arenic ester (C6Es6) as ionophore and PVC as polymer matrix. Potentiometric measurements were performed in standard solutions of Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ and Li^+. The best response was observed for K^+: slope 52 mV/ΔpK; linear range from 0.1 mM up to 0.1 M; detection limit of 0.02 mM; potentiometric selectivity coefficients of 0.06 and 0.16 for Na^+ and NH_4^+, respectively.

Keywords: *calyx[6]arenic ester, PVC-based ISE, potassium ISE*

INTRODUCTION

Ion-selective electrodes (ISE) are of great importance due to their wide applications mainly in clinical, food and environmental chemistry [1]. For example, it was estimated that, all over the world, over a billion of clinical analyses are performed annually using ISE [2].

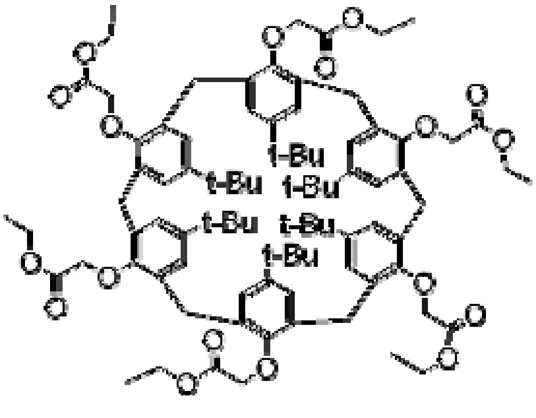

Figure 1. The structure of C6Es6 ester

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The ion selective membrane of an ISE is usually made of a polymer matrix (such as PVC) incorporating an ionophore. Most often, ionophores are macrocyclic compounds, which selectively bind different ions by entrapping them in their cavity. Consequently, the selectivity of the membrane strongly depends on the size match between the ion and the host cavity, but also on the ion charge. Many calixarenic compounds have been successfully used as ionophores [3- 10].

The aim of this paper was to evaluate the ionophore abilities of a calyx[6]arenic ester synthesized at ICCRR (Cluj-Napoca) using a new chemical route. The structure of this compound, named 4-tert-butylcalix [6]arene-hexaacetic acid hexaethyl ester (C6Es6), is shown in Figure 1. The study was focused on the determination of the main analytical parameters (sensitivity, detection limit, selectivity) of C6Es6-based ISE for various alkaline and alkaline-earth cations.

RESULTS AND DISCUSSION

I. Calibration curves for Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ *and* Li^+

As the ionophore properties of the C6Es6, synthesized using a new chemical route, were unpredictable, our study started with the evaluation of the sensitivity (S) and detection limit (DL) towards several cations of biotechnological and medical interest: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ and Li^+. All measurements were performed in "batch", using the known addition method for the preparation of standard solutions. Figure 2 shows the calibration curves obtained in presence of K^+ and Na^+, at variable ionic strength. The calculated values of the corresponding S and DL parameters are presented in Table 1. All values represent the average of two successive measurements, carried out with four electrodes, under the same experimental conditions.

The best S values were obtained for Na^+, K^+ and NH_4^+, being quasi-nernstian in the limit of experimental errors. For all other investigated cations the S values were significantly under-nernstian. A low interelectrode reproducibility was observed for S value calculated in the presence of Ca^{2+}.

DL values around 10^{-5} M were observed for K^+ and NH_4^+. All other DL values were at least 10 times higher than for K^+ and NH_4^+.

Table 1. Values of S and DL for C6Es6-based ISE in presence of different cations

Ion	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**NH_4^+**	**Li^+**
S (mV/Δp_i)	14-26	12	55	52	56	5
DL (mM)	$2.2*10^{-3}$	$5.4*10^{-4}$	$1.4*10^{-4}$	$2.0*10^{-5}$	$8.6*10^{-5}$	$1.1*10^{-3}$

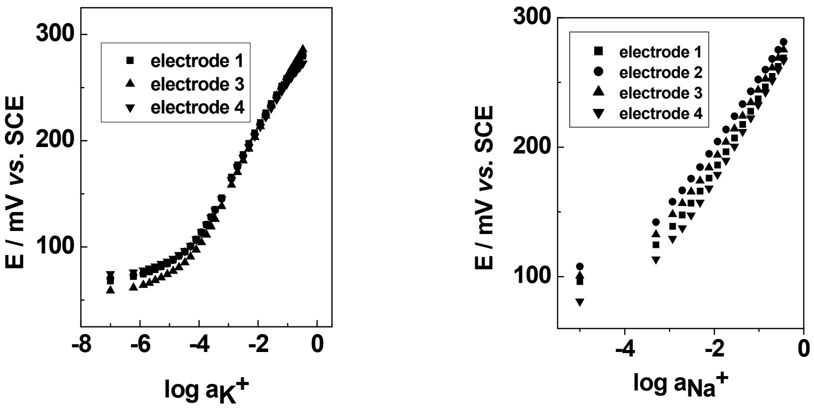

Figure 2. Calibration curves recorded for C6Es6-based ISE in presence of K^+ and Na^+

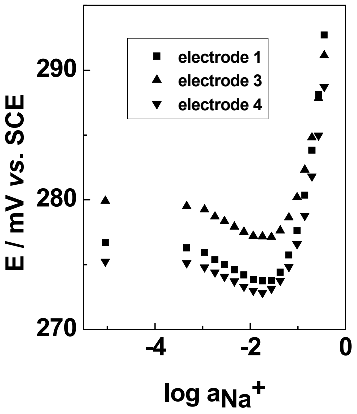

Figure 3. Potentiometric response recorded at C6Es6-based ISE in presence of constant concentration of K^+ and variable concentrations of Na^+

II. Study of the ionic interference

Based on the calibration curves obtained for the investigated cations, K^+ was chosen as primary ion (best S and DL values). During the whole interference study the K^+ concentration was kept at 10^{-2} M for two main reasons: (i) this value corresponds to the middle of the linear range on the K^+ calibration curve; (ii) the K^+ concentration in common biologic fluids (blood, plasma) is close to this value. A rigorous evaluation of the potentio-metric selectivity coefficients requi-res a quasi-nernstian response for the interfering cations, too. For this reason the selectivity study was restricted only to Na^+ and NH_4^+ ions.

Figure 3 presents an example of potentiometric response obtained from the interference study carried out in presence of variable Na^+ concentration. The average values of the potentiometric selectivity coefficients estimated for Na^+ and NH_4^+ were 0.06 and 0.16, respectively.

Obviously, the selectivity study can be extended for different concentrations of the primary ion. Taking into account that the selectivity coefficients are a complex function on the primary and interfering ion concentration, the level of the primary ion concentration should be established in direct correlation with the specific application of the investigated ISE.

III. Study of repeatability

Based on experimental results obtained from calibration curves recorded in presence of Na^+ and K^+, studies of inter-measurement and inter-electrode repeatability were also performed.

As can be seen from Figure 4, an excellent repeatability was observed both between two successive measurements and between four similar electrodes. The data dispersion observed in the domain of low concentrations could be due to the absence of the supporting electrolyte.

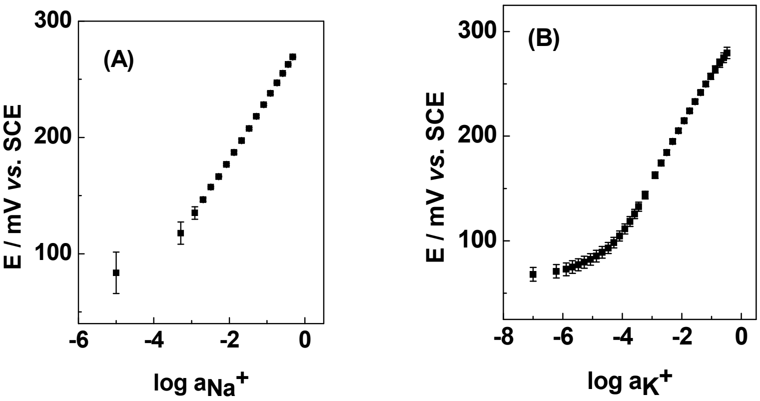

Figure 4. Mean values and standard deviations for: (A) two measurements performed successively, using the same electrode for Na^+ ion; (B) measurements performed in parallel, using four electrodes for K^+ ion

CONCLUSIONS

The aim of the present study was to evaluate the main analytical parameters of ISE based on a PVC membrane containing the ionophore C6Es6, synthesized by a new chemical route. Measurements were performed in separate solutions of Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ and Li^+. Quasi-nernstian slopes were obtained for K^+ (52 mV), Na^+ (55 mV) and NH_4^+ (56 mV).). For all the other ions, the sensor showed undernernstian sensitivities. The lowest detection limit was obtained in the case of K^+ ($2.0*10^{-5}$ M). A very good repeatability was observed both for inter-measurement and inter-electrode tests.

Based on these main electroanalytical parameters, it can be concluded that the newly prepared calix[6]arenic ester may be used as an ionophore for obtaining K^+-selective electrodes, good enough to replace the consecrated but expensive valinomycin. Further studies are in progress in order to optimize the PVC membrane composition.

EXPERIMENTAL SECTION

I. Materials

The C6Es6 ionophore was provided by dr. Elisabeth-Jeanne Popovici from "Raluca Ripan" Chemistry Research Institute, Cluj-Napoca (Romania).

All reagents used were of analytical grade. Calcium chloride, lithium acetate, lithium chloride, ammonium chloride, 2-nitrophenyloctylether (NPOE), high molecular weight polyvinyl chloride (PVC) and tetrahydrofurane (THF) 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).

II. Membrane preparation

The ISE membrane was prepared from 1% (w/w) ionophore (C6Es6), 33% (w/w) polymer matrix (PVC), and 66% (w/w) plasticizer (NPOE); the mixture had a total weight of 0.3 g. The components were successively dissolved in THF, under stirring, in the following order: ionophore, polymeric matrix, and plasticizer. After complete dissolution, the mixture was poured into a glass cylinder and covered by a glass recipient, under which a THF-impregnated paper was placed, in order to avoid pores formation. When dried, the membrane was placed for one day in a dark place, in open air.

III. Experimental setup

All the measurements were performed using a PC-controlled setup [11]; its scheme is presented in Figure 5. This device is composed of: the electrochemical cell; a personal computer; two interfaces for communication between the computer and other components; an unit for controlling the solution stirring; a magnetic stirrer; a peristaltic pump allowing automatic exponential additions of standard solution.

The system control as well as data acquisition were performed using the LabView 5.1 software. Data processing was done by using the Origin 5.0 software.

EIS 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. Four similar electrodes were tested in parallel, and each measurement was repeated three times under same experimental conditions. A double-junction saturated calomel electrode was used as external reference. The external liquid junction was filled with CH_3COOLi 0.1 M.

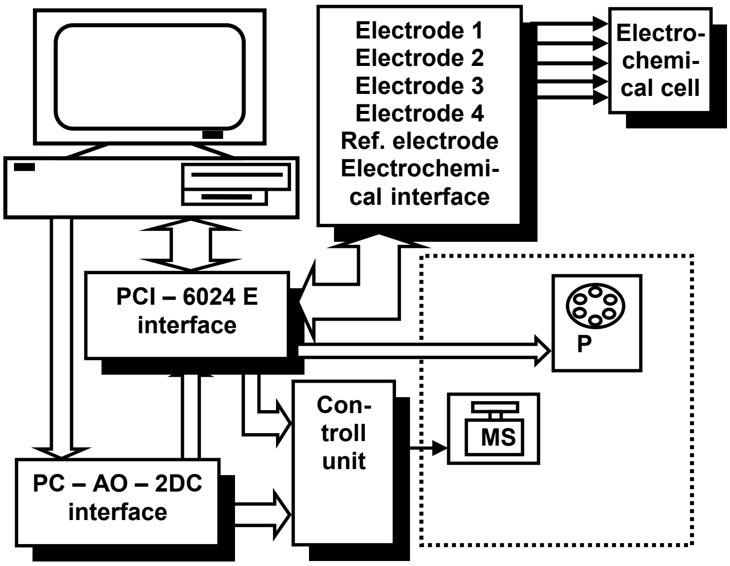

Figure 5. The scheme of the computer-controlled device used for the ISE potentiometric measurements; MS – magnetic stirrer; P – peristaltic pump

IV. Experimental procedure

Before use, all electrodes were conditioned for at least 24 hours in the solution containing the cation to be determined.

The experimental procedure consisted in two main parts: in the first one, the potentiometric response of the prepared membranes was recorded for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+} and Li^{+} using separate solutions, and the corresponding calibration curves were recorded. In the second part, the ionic interference between K^{+} and different common cations was examined. All 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 fixed primary ion concentration was used: the primary ion concentration was kept constant, while the concentrations of the interfering ions were increased.

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