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Novel Carbon paste selective material for potassium detection

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Potassium ion plays a crucial role for the organisms life. Its detection is performed usually by potassium selective electrodes (PSE) having membranes made of a polymer matrix (such as PVC) incorporating macrocyclic compounds as ionophore. We propose a novel potassium selective material (PSM) based on a new synthesized crown-ether ionophore incorporated in carbon paste conductive matrix (PSM-CP). Electrochemical measurements proved the affinity of PSM-CP for the potassium cation, which is selectively bound by entrapping in the crown-ether cavity. The results are comparable with those obtained by using a PSE based on PVC-ionophore membrane.

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1. Introduction

Among various alkaline and alkaline-earth-metal ions the potassium ion plays a critical role as regulator of water retention at the cell membrane, muscle contraction and chlorophyll photosynthesis [1]. Macrocyclic systems such as crown ethers, cryptands, calixarenes, and porphyrines proved to be active hosts for different cations generating strong complexes through electrostatic interaction. [2].

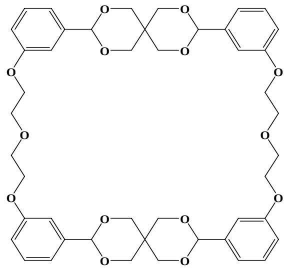
Crown ethers have gained considerable attention in the last decade due to a wide range of applications in different areas such as medicine [3], chemical sensors [4] and separation of metals by extraction [5]. Chemically modified electrodes for the determination of organic molecules and various metal ions are based on macrocyclic compounds [6,7]. The potassium selective electrode (PSE) is usually made of a polymer matrix membrane (such as PVC) [8,9], incorporating macrocyclic compounds as ionophore species [2,10]. Chemically modified carbon paste electrodes are used because they have low background currents, have a large potential domain, are low cost as well as are easy to prepare and regenerate [11,12].

We propose here a novel carbon paste potassium selective material (PSM) based on a new synthesized crown-ether ionophore [13], incorporated in carbon paste conductive matrix (PSM-CP). It is a simple and versatile manufactured material, exhibiting renewable surface, suitable for rapid and efficient potassium detection in aqueous solutions and can be used to build wireless system detection in complex matrix media.

2. Experimental details

2.1 Chemicals

Graphite powder and paraffin oil were purchased from Fluka. Potassium trifluoromethanesulfonate (K(CF3SO3)), potassium chloride (KCl), tetraethylammonium chloride (TEAC), lithium perchlorate ($LiClO_4$), cadmium acetate ($Cd(CH_3COO)_2$), dipotassium phosphate dihydrated ($K_2HPO_4 \cdot 2H_2O$) and potassium phosphate monobasic hydrated ($KH_2PO_4 \cdot H_2O$) were purchased from Merck. Crown-ether Bis(3,9-dibenzo-2,4,8,10-tetraoxo[5.5] undecan)-40-crown-6, denoted BDBTU40C6, has been synthesized accordingly to the protocol previously described [13] and used as ionophore (see Scheme 1).



Scheme 1. Bis(3,9-dibenzo-2,4,8,10-tetraoxo[5.5]undecan)-40-crown-6, (BDBTU40C6).

All other reagents were of analytical grade and used as received. The supporting electrolyte was a 0.1 M phosphate buffer solution. The pH was adjusted to 6.8 using appropriate phosphoric acid (H_3PO_4) or sodium hydroxyde (NaOH) solutions.

2.2 Electrode preparation

Equal amounts of BDBTU40C6 and graphite powder were thoroughly grounded in a mortar and then mixed with paraffin oil, in order to obtain the modified carbon paste material (PSM-CP). The final composition was 30:30:40 (w/w) of ionophore, graphite powder and paraffin oil. Plain (unmodified) carbon paste electrode (CPE) was prepared in a similar manner, with a 60:40 (w/w) composition of graphite powder and oil without any modifying agent.

The preparation of PSM-CP was reproducible when the experimental conditions and variables were maintained constant during the preparation. The potential response of the electrodes did not change significantly by storing them in air for several months.

The potassium selective material was constructed using also PVC –bases membranes, as reported previously [14]

2.3 Solution preparation

Stock solutions of BDBTU40C6 (1 mM) and potassium trifluoromethanesulfonate, denoted K triflate (1mM), were prepared by dissolving the appropriate amounts into 1,4-dioxane. Then, aliquot parts were used to prepare solutions of 10^{-4} and 10^{-5} M necessary for UV-Vis and fluorescence investigations.

2.4 Instrumentation

Cyclic voltammetry (CV) and potentiometric experiments were performed on a PC-controlled electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, The Netherlands). Electrochemical experiments (CV) were carried out using a typical three-electrode electrochemical cell. The modified and unmodified carbon paste electrodes were used as working electrodes, a platinum ring as counter electrode and Ag|AgCl/KCl_{3M} as reference electrode. The experimental results are the average of at least 3 identically prepared materials, if not otherwise mentioned. Potentiometric measurements were performed using an Ag|AgCl/KCl_{3M} reference electrode with double junction.

The UV-Vis absorption spectra were recorded on a Jasco V550 UV-Vis spectrophotometer in the 190-900 nm wavelengths range with a 2 nm resolution and 200nm/min, using 10 mm length two-window quartz cells.

The fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer in the 190-900 nm wavelengths range. The general setting was resolution 2 nm, response 0.5 sec, band widths 5 nm (excitation) and 5 nm (emission), using 10 mm length four-window quartz cells with a volume of 4 ml.

All measurements were performed at room temperature.

3. Results and discussion

In practice, the behavior of an ionophore is evaluated after its incorporation into the sensor. For example, membrane-based techniques have been used to evaluate the binding properties of the ionophore with cations or anions according to the sensor response [15]. Preliminary complexing investigations by spectroscopic methods were performed in order to validate the process.

3.1 UV-VIS study

UV spectrum of ionophore BDBTU40C6 displays three maxima at 232 nm, 274 nm si 281 nm. This molecule contains two cromophore types: the benzene nucleus and oxygen atoms of the polyethyleneglycol chain. Absorption maxima at 274 nm and 281 nm can be attributed to the benzene nuclei contribution, in which there is a specific aromatic state conjugation as evidenced by characteristic bands K (conjugated) and B (benzenoidic) due to the $\pi \rightarrow \pi^*$ transitions. In this case it generates intense bands because electronic transition occurs simultaneously with the vibratory transition of C-H bonds of the molecule and causes a diminishing in specific symmetry of benzene molecule.

The oxygen atom (attractive effect + E) directly linked to the benzene nucleus favors by its lone pair electrons conjugation with π electrons of the benzene nucleus and causes red shift absorption peaks.

Titration of BDBTU40C6 solution by addition of well defined amounts of potassium salt (K triflate) was highlighted by the systematic decrease of peak absorbance, which can be explained by the interaction of potassium ion with crown ether followed by its complexation (see Fig. 1).

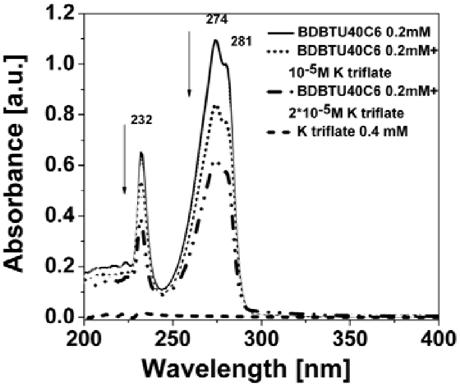


Fig. 1. Decreased absorbances of BDBTU40C6 in 1,4-dioxane solution (0.2 mM) in the presence of potassium triflate concentration range of 0-0.2 mM.

3.2 Fluorescence study

Binding of potassium cation to the BDBTU40C6 molecule was also investigated using fluorescence spectroscopic technique. Thus, to a volume of macrocyclic compound solution (0.01 mM) was added an equal volume of potassium triflate solution (0.37 mM), distributed into well defined portions. For the sake of clarity we present here only a few spectra recorded after each titration. The systematic decrease of fluorescence intensity comes to support the UV investigations and can be attributed to potassium ion complexing by the crown ether derivative BDBTU40C6.

In Fig. 2 are presented fluorescence spectra recorded for BDBTU40C6 (0.01 mM), solvent 1,4-dioxane and potassium triflate (0.37 mM) at excitation wavelength of 274 nm and emission wavelength of 600 nm.

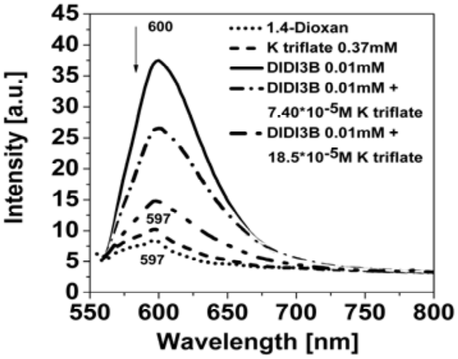


Fig. 2. Decreased intensities of BDBTU40C6 in 1,4-dioxane solution (0.01 mM) in the presence of potassium triflate in the concentration range of 0.02-0.185 mM, λ_{ex} = 274 nm, λ_{em} = 600 nm.

3.3 Complexation study by electrochemical methods

Electrochemical behavior of the crown-ether-modified carbon paste material was investigated by cyclic voltammetry recorded at different potential scan rates (Fig. 3).

In order to validate the liniar dependence of the peak current on $v^{1/2}$ (redox species in solution) or on v (adsorbed redox species) was represented log I_p *vs.* log v (results not shown).

For the adsorbed redox species the dependence of the current peak (I_p) on the potential scan rate (v) is described by A. J. Bard [16].

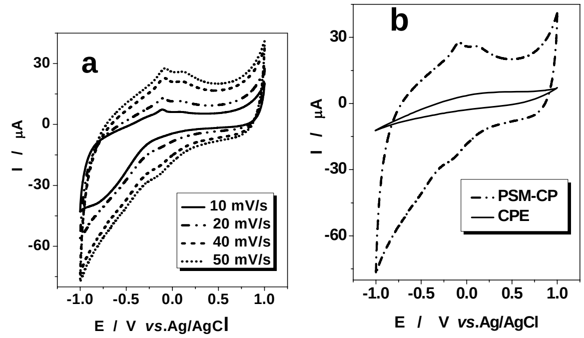


Fig. 3. Cyclic voltammograms for carbon paste electrode embedding crown ether derivative (PSM-CP) at different potential scan rates (a) and PSM-CP with unmodified carbon paste electrode (CPE) recorded at 50 mV/ s (b); Experimental conditions: starting potential, -1V vs. Ag|AgCl/KCl$_{3M}$; potential scan rate, 10-400 mV s^{-1}; supporting electrolyte, 0.1 M potassium phosphate buffer, pH 6.8.

The slope of the log- log linear regression, corresponding to the current peak dependence on the potential scan rate for PSM-CP, is ~0.85 (see Table 1).

The values close to the unit of the slope suggest a partial adsorption of the species involved in complex formation on the electrode surface.

Table 1. Parameters of the log- log linear regresion corresponding to the peak current dependence on the potential scan rate for PSM-CP.

	Slope	
	Reduction	Oxidation
	0.80± 0.002	0.86± 0.009
R/n	0.9999/ 10	0.9994/ 10

Taking into account that BDBTU40C6, used as ionophore, is embedded in the carbon paste, it is supposed that the interaction of crown ether derivative with K^+ takes place after adsorption on the electrode surface. On the other hand, the electrode is immersed in solution containing potassium ions and the cations migration to the macrocyclic species adsorbed on graphite is controlled by a diffusion process, which occurs at the interface between solution and the modified electrode. Therefore, in the range of scanning rates studied it can be assumed that the redox electrode process is a mixed one, controlled both by diffusion and surface processes, as expected for an adsorbed system.

3.4 Potentiometric study

Simple potentiometric titration of the macrocyclic ligand, embedded in carbon paste, with a solution of the potassium salt can be used in case of K^+ detection. First, the plain (unmodified) carbon paste electrode (CPE) was investigated in order to establish its behavior as blank for the modified one.

The carbon paste modified electrode was tested in KCl solutions of different concentrations. Due to the presence of potassium chloride in the reference cell, which can change the sensor response to potassium ion, a double junction was used. The second junction electrolyte has not to contain ionic species which can interact with the ionophore, its role being only to ensure the electric contact between the reference electrode and sample solution. Therefore, several electrolytes were investigated to optimize the electrode sensitivity. The results presented in Table 2 indicate cadmium acetate ($Cd(CH_3COO)_2$) as the most suitable electrolyte from those tested. Consequently, all measurements were performed using this second junction electrolyte.

Table 2. Comparison of the electrodes performance in potassium response.

Electrode type	Electrolyte	Slope (mV/decade)	R/N
PSM-CP	TEAC	14.79±0.26	0.995/29
	$LiClO_4$	11.05±1.04	0.986/5
	$Cd(CH_3COO)_2$	19.95±0.40	0.999/5
PSM-PVC	$Cd(CH_3COO)_2$	19.38±2.01	0.989/5
CPE	$Cd(CH_3COO)_2$	6.94±0.23	0.998/5

The modified carbon paste electrodes response to potassium ion was compared with that of a classical one (PVC membrane). Identical conditions were used, except the matrix for the ionophore dispersion. Thus, the sensibility of PSM-CP to potassium is comparable with that of the PSM-PVC, even the slope is not a nernstian one (Fig. 4).

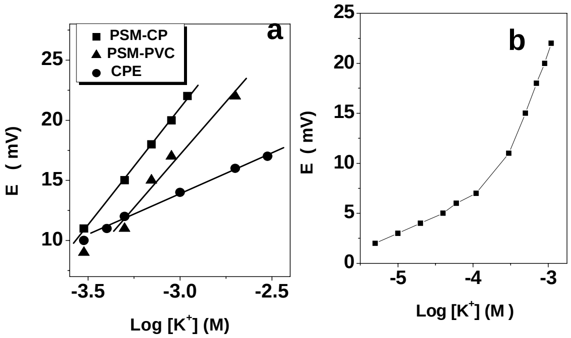


Fig. 4. Linear dependence of the potential on potassium ions concentration for PSM-CP, CPE and PSM-PVC electrodes (a); calibration graph for PSM - CP in KCl solutions (b).

It should be noted that conjugation n-π between electrons of oxygen and benzene nuclei reduces the donicity of the oxygen atoms in the ring and hence the cation–crown ether interaction is diminished.

The unmodified carbon paste electrode (CPE) displays an insignificant response to the potassium ion presence (Table 2).

4. Conclusions

The new designed carbon paste material based on crown-ether derivative exhibits renewable surface being suitable for rapid and efficient potassium detection in aqueous media.

The detection efficiency of this carbon paste selective device for potassium is comparable to that of a classic electrode based on PVC membrane in conditions of the same ionophore usage.

The novel potassium sensitive material is simple, versatile and rapid manufactured, solid and less expensive than PSM-PVC.

Acknowledgments

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