



Potentiometric sensors arrays based on perfluorinated membranes and silica nanoparticles with surface modified by proton-acceptor groups, for the determination of aspartic and glutamic amino acids anions and potassium cations

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ABSTRACT

Hybrid materials based on perfluorosulfonic cation-exchange membranes and silica nanoparticles with surface modified by nitrogen-containing groups have been obtained. The influence of concentration, size and proton acceptor ability of modifying groups on the oxide surface onto the response stability and sensitivity of potentiometric sensors in aspartic and glutamic acid solutions with pH 4–9 has been investigated. A correlation between sensor cross-sensitivity to cations and anions in test solutions and membrane diffusion permeability is revealed. Optimal membrane compositions for arrays of cross-sensitive sensors have been chosen. Proposed sensors allow to carry out a simultaneous determination of potassium cations and amino acid anions in test solutions with concentrations ranged from $1.0 \cdot 10^{-4}$ to $1.0 \cdot 10^{-2}$ M, with an error < 14%.

1. Introduction

Dicarboxylic acid salts (aspartic and glutamic) of alkali and alkali earth metals are widely used as flavor enhancers in foods and as pharmaceuticals for the treatment of central nervous system disorders, cardiovascular diseases etc. [1,2]. Alkaline hydrolysis is one of the stages in the production of amino acids. Technological solutions, obtained at different stages of amino acid separation and purification by electrochemical methods, contain amino acid ions, alkali metal ions and products of water dissociation. The necessity to control the quality of nutrition and pharmaceutical products as well as the efficiency of their production processes creates a demand for methods of qualitative and quantitative determination of aspartate and glutamate ions in the presence of alkali metal cations at variable pH values.

Presently, chromatographic methods [3], capillary electrophoresis [4,5] and electrochemical methods [6] are widely used for the determination of amino acids. Some articles are devoted to the development of chemical [6–11] and biological [12–14] sensors for determination of amino acids, in particular aspartic and glutamic acids [15–17]. Despite the growing number of publications on the subject, insufficient attention is paid to the problem of pH influence on the

analytical signal. But change of pH has a considerable influence on the ratio of amino acid ionic forms in solution [18]. Since the composition of the investigated media is complex, it appears promising to create multisensory systems with response processing using multivariate mathematical methods. This approach makes it possible to analyze the ionic composition of a solution and at the same time to take into account its influence on the analytical response of sensors to the analyzed amino acid. Utilization of such arrays for simultaneous determination of several components in a solution becomes possible if each sensor demonstrates high sensitivities for several analytes and a correlation between their responses is not significant [19,20]. Multisensory analysis has a widespread use in evaluating of the integral characteristics in various complex media [21–23]. At the same time markedly fewer studies are devoted to determination of their individual components [24–26]. It is in part associated with a limited number of materials used in potentiometric multisensory arrays (mostly polyvinylchloride membranes with ionophores and glass membranes of different compositions [19,20,27]). Experience gained in the development of selective sensors indicates that creation of hybrid materials, based on commercially available ion-exchange membranes, which number is limited, is an attractive possibility to find novel sensor materials and ways to improve

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their properties [28–30].

Silica is an excellent matrix for the biomolecules immobilization. Thus, composites based on silica exhibit sorption properties to some amino acids (for example, enantiomers of tryptophan [31], N-carbamate protected alanine, leucine, phenylalanine, proline [32]). This property is used in chromatography. Composite materials with silica are also widely used in the development of biosensors [31–40]. Voltammetric and potentiometric biosensors based on silica nanoparticles and glucose oxidase are used for the glucose determination [33,34]. Silica nanoparticles modified with an organometallic cobalt complex and amino groups are utilized in biosensors to determine DNA molecules [35,36]. Polyamide membranes doped by silica modified with dibromofluorescein luminescent molecules are used for determination of the human immunoglobulin [37]. The data on the use of mesoporous silicate materials and hybrid materials based on them in electrochemical biosensors are summarized in the review [38]. Chemical voltammetric sensors based on mesoporous silica, for example, for the determination of the bisphenol hormone are known also [39].

Among the promising materials for electrochemical sensors the membranes of Nafion® type membranes can be mentioned [40–42]. Nanostructuring processes, taking place in such membranes due to simultaneous presence of hydrophilic sulfo groups and hydrophobic perfluorinated chains, lead to the formation of a system of pores ($\approx 3\text{--}5\text{ nm}$ in size) and interconnecting channels [43]. The incorporation of dopant nanoparticles into the pores of perfluorinated ion-exchange membranes results in the change of their sorption, ion-exchange and sensory properties that affect the characteristics of electrochemical sensors [44–48]. In particular, sensors based on Nafion films and silica are known. There are a number of studies devoted to use glassy carbon electrodes coated with composites based on Nafion films and Tris (2,2'-bipyridyl) ruthenium (II) complex immobilized on silica for determination of methamphetamine, tetracyclines, melamine in pharmaceuticals and food [49–54]. In such sensors the detection principle is electrogenerated chemiluminescence. In addition, the possibility of modification of the silica surface by functional groups (amino groups, thiol, carboxyl groups, etc.) provides high performance for the determination of organic and inorganic ions. Glassy carbon electrodes coated with composites based on Nafion and thiol-functionalized mesoporous silica have been developed to determine heavy metal ions (Cd^{2+} , Pb^{2+} , Cu^{2+}) in natural waters and urine [55].

It was shown earlier, that an increase in the selectivity of perfluorinated cation exchange membranes (Nafion and its Russian analogue MF-4SC) allows to decrease the sensitivity of potentiometric DP-sensors (the Donnan potential is an analytical signal) to hydroxonium ions, which interfere to the determination of organic cations at $\text{pH} < 7$ (on the example of solutions of novocain and lidocaine [56] and glycine and alanine [57]). This was achieved by varying the concentration of zirconia and silica incorporated into the membranes and proton acceptor properties of their surface [56,57]. The use of membranes with silica modified with hydrophobic fragments (dodecyl- and 1H,1H,2H,2H-perfluorodecyl-) results in the increase in the sensitivity of DP-sensors to cations of hydrophobic amino acids (in the example of solution of phenylalanine and valine) and decrease in the sensitivity to interfering hydroxonium ions at $\text{pH} < 7$ [58]. This was achieved by the increase in the sorption of cations and zwitterions of amino acids due to a simultaneous decrease in the hydration level of the membrane and an increase in the pore size, as well as due to an affinity of the dopant groups and the hydrophobic amino acid radical.

Nafion and MF-4SC membranes doped by zirconia and silica were used in DP-sensors to determine the anions of taurine and pyruvic acid in alkaline solutions [59]. Additionally, the acid properties of the oxides were varied by modifying their surface with $-\text{SO}_3\text{H}$ containing fragments. The influence of the concentration and acid properties of the dopant, as well as influence of the diffusion permeability of membranes on the sensitivity of DP-sensors to the anions of drugs at $\text{pH} > 7$, was described in [60]. The incorporation of the nanoparticles of hydrated

silica with a surface modified by proton acceptor groups into the MF-4SC membrane matrix leads to a significant change in the water uptake and the rate of ion transport through the membranes. This fact, as well as the possibility of incorporation into the membrane matrix groups that are oppositely charged than the functional groups of the polymer, makes the use of such materials in DP-sensors promising for the determination of different ionic forms of amino acids.

The aim of the present work was to develop arrays of cross-sensitive DP-sensors for determination of amino acid ions, having two negatively charged carboxylic groups and a positively charged amino group (aspartic and glutamic acids), at different values of pH solution. To this end, we used hybrid perfluorosulfonic cation-exchange MF-4SC membranes (Russian analogue of Nafion®) contained silica nanoparticles with the surface modified by amine-containing groups.

2. Theoretical part

The distance between the reference solution and the test solution corresponds to a membrane thickness in the classical potentiometric membrane electrodes with an internal reference solution. The analytical signal of such sensors is a membrane potential, including a diffusion potential in membrane phase and two Donnan potentials at the membrane/internal reference solution and the membrane/test solution boundaries. The problem of such sensors is the influence of diffusion and migration on their response in polyionic solutions [61,62]. The traditional approach, which makes it possible to achieve a high sensitivity and selectivity of potentiometric sensor, is the use of ionophores that selectively interact with analyte ions [61–67]. The distance between the reference and test solutions in DP-sensors corresponds to a membrane length [60]. It makes it possible to minimize the ion flow from the reference solution to the test solution and to eliminate the diffusion potential across the membrane [68]. The Donnan potential at the membrane/test solution boundary makes the main contribution into the circuit voltage used for determination of sensor response [68]. Due to this, the stability and sensitivity of sensor response in polyionic solutions are increased. The multisensory approach described in [19,20] was used to analyze multicomponent solutions thus a high selectivity of DP-sensors to analyte ions was not achieved. The sensory arrays having a high sensitivity simultaneously to several analytes of the test solution, high response stability and a low correlation between their responses were selected. A variation of DP-sensors characteristics was achieved by modifying one end of membrane with dopant nanoparticles. The changes in the pore size, the charges distribution in them and composition of inner membrane solution as a result of modification result in the changes in the DP-sensors sensitivity to amino acids and inorganic ions. The same factors influence on the transport properties of membranes. Therefore, the dependence of DP-sensors sensitivity to amino acids and inorganic ions on the transport properties of hybrid membranes was studied to optimize the membranes compositions for DP-sensors.

3. Material and methods

3.1. Reagents and materials

Solution of perfluorosulfonic polymer in the H^+ -form in isopropyl alcohol (MF-4SC, LTD “Plastpolymer”, 10.0 wt% solution, ion-exchange capacity (IEC) $\sim 0.95\text{ mg-eq/g}$, equivalent weight 1100), tetraethoxysilane (Fluka, 98%), (3-aminopropyl)trimethoxysilane (Fluka, 98%), 3-(2-imidazoline-1-yl)propyltriethoxysilane (Fluka, 98%), aqueous ammonia (chemically pure, Chimmed), hydrochloric acid (chemically pure, Chimmed), sodium chloride (chemically pure, Chimmed), sodium hydroxide (standard reference solution, LTD “Ecohim”), potassium hydroxide (standard reference solution, LTD “Ecohim”), glutamic acid (Sigma-Aldrich, 99%), aspartic acid (Sigma-Aldrich, 99%), deionized water (resistance 18.2 M Ω).

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