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ELECTROACTIVE PROPERTIES OF SUPRAMOLECULAR COMPLEXE OF ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDES AND POLYOXOMOLIBDATE

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ABSTRACT

Electroactive supramolecular complexes based on alkylbenzyldimethylammonium chloride and polyoxometalates have been obtained. To study the electroactive properties of supramolecular complexes, plasticized polyvinyl chloride membranes were obtained. Anions of 12-molybdophosphate heteropolyacid were used as polyoxometalates. The electroactive characteristics of the resulting membranes (angle of inclination, linearity of the electrode function, minimum detectable concentration) were studied depending on the content of supramolecular complexes in it, the nature of the solvent-plasticizer of the membrane, and the pH of the solution under study. Rational conditions for obtaining membranes based on supramolecular complexes have been established. The resulting membranes can be used to develop potentiometric sensors for the determination of benzalkonium chloride salts in industrial products and environmental objects.

Keywords: alkylbenzyldimethylammonium chloride, benzalkonium chloride, catamine AB, electroactive substance, membrane, 12-molybdophosphate acid, polyoxometalates, supramolecular complexes.

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1. INTRODUCTION

Benzalkonium chloride (alkyldimethylbenzylammonium chloride or catamine AB) is a quaternary ammonium chloride, a representative of cationic surface-active substance, which has three main uses: preservative, cationic surface-active resin, phase transfer agent [1]. Alkyldimethylbenzylammonium chloride (fig.1) is a mixture of various benzalkonium chlorides, which have a benzene aromatic ring and a wide range of C_8-C_{18}, with the greatest bactericidal power from C_{14} [2].

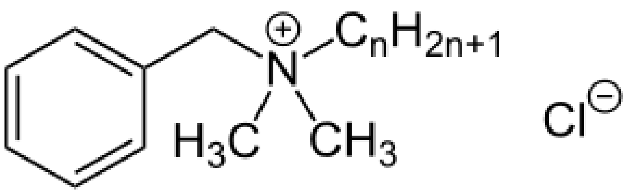

Figure-1. The structural formula of benzalkonium chloride.

Benzalkonium chloride is a cationic antiseptic that exhibits spermicidal, antibacterial, antiprotozoal, and antifungal activity [3-5]. Due to its antimicrobial activity, benzalkonium chloride is used as an antimicrobial component in composition [6-8]:

- pharmaceutical products (active ingredient of drops for eyes, ears, nose; disinfectants for skin, means for washing wounds, means for throat and oral cavity, spermicidal creams or as a preservative);
- personal hygiene products (hand products, wet wipes, shampoos, soaps, deodorants);
- cleaning agents for floors and hard surfaces;
- algicides for cleaning algae, moss, lichens of pools, etc.

The antimicrobial effect of cationic antiseptics significantly depends on the structure of their molecules, which usually contain one or two hydrophilic groups and a large lipophilic fragment [9]. Catamine AB, like other cationic antiseptics, breaks the permeability barrier of microbial cells, affecting the cell wall and cytoplasmic membrane; they are also capable of inhibiting the activity of the adenosine triphosphatase enzyme in bacterial membranes and causing the loss of important cytoplasmic components (potassium ions, inorganic phosphorus, sugars, purines and pyrimidines, nucleic acids). At high concentrations, cationic antiseptics penetrate the cytoplasm and precipitate nucleic acids and proteins, which negatively affects the vital activity of microorganisms. A positive aspect of the use of cationic antiseptics, in particular benzalkonium chloride, is that under their influence the absorption of antibiotics by bacterial cells increases, and the effectiveness of antibiotics increases, even against resistant strains of bacteria [10-12].

This paper presents the results of the electroactivity study of the obtained supramolecular complexes of catamine AB with polyoxometalates of molybdenum (POM), which can be widely used in various industries. The results of our previous studies in the field

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of supramolecular complexes based on organic substances and polyoxometalates testify to the prospect of obtaining such inorganic-organic hybrid compounds for the subsequent development of sensors based on them, for example, potentiometric ones, for the determination of these organic substances in environmental objects and industrial production [13-26].

2. MATERIALS AND METHODS

2.1 Materials Used in the Work

The following reagents are used in the work:

- 12-molybdophosphate acid, $H_3PMo12O_{40}x26H_2O$ (analytical grade);
- alkylbenzyldimethilammonaum chloride (pure grande);
- chloride acid (analytical grade);
- sodium hydroxide (analytical grade);
- polyvinyl chloride (PVC), brand C-70 (pure grade);
- cyclohexanone (CH), (analytical grade);
- dibutyl phthalate (DBP), (pure grade);
- dioctyl phthalate (DOP), (pure grade).

2.2 Devices Used in the Work

An electrochemical cell was used for direct potentiometric studies:

The galvanic cell included a film potentiometric sensor (with an internal solution $1.0{\cdot}10^{-4}$ M solution of the test substance and an internal electrode - Ag/AgCl wire in $KCl_{sat.}$) and silver chloride reference electrode EBL-1M31 with KCl saturated solution, was consisted. Measurement of EMF is carried out with the ionomer I-130. To determine the pH the electrode with brand ESK-10601/4 was used.

2.3 Method for the Synthesis of a Supramolecular Electroactive Substance

10.0 ml of an aqueous solution of benzalkonium chloride with a pH of 6.0 and a concentration of $1.0{\cdot}10^{-2}$ mol/l is added to a 50 ml beaker; slowly add 30.0 ml of a solution of 12-molybdophosphate heteropolyacid with a concentration of $1.0{\cdot}10^{-2}$ mol/l. A white precipitate is formed. The sediment is left for a day to solidify, after which it is centrifuged, the liquid above the sediment is removed and the sediment is dried.

2.4 Method for the Synthesis of a Plasticized Membrane

Plasticized polyvinyl chloride membranes were synthesized according to the following procedure: 0.45 g of polyvinyl chloride was dissolved in 4.5 ml of cyclohexanone with weak heating (does not exceed 60°C) with constant stirring up to complete dissolution. Separately, we prepared a solution of a sample of 0.001, 0.010 or 0.050 g of the supramolecular complexes in 1.1 ml of a plasticizer solvent (dibutyl phthalate or dioctyl phthalate). The solutions were mixed and transferred to Petri dishes with a diameter of 50-60 mm in the form of a transparent homogeneous liquid mixture. A transparent elastic film of a plasticized PVC membrane was obtained from the mixture after complete evaporation of cyclohexanone in 3-4 days.

3. RESULTS AND DISCUSSIONS

Results of studies of the influence of various factors (type plasticizer solvent, the percentage of supramolecular complex in the composition of the membrane, pH of the investigated solution) on the electrode function of the membrane based on the supramolecular complex of benzalkonium chloride with 12-molybdophosphate heteropolyacid (Figures 2-7). For this purpose, standard solutions of benzalkonium chloride (BAC) were used with concentrations in the range of $1.0{\cdot}10^{-7}$ - $1.0{\cdot}10^{-2}$ mol/l.

Figures 2-3 present the results of studying the influence of the quantitative content of the electroactive substance (EAS) - a supramolecular complex of catamine AB with 12-molybdophosphate heteropolyacid, depending on the type of solvent-plasticizer and the pH of the solution under study, on the linearity of the electrode function of the polymer polyvinyl chloride membrane.

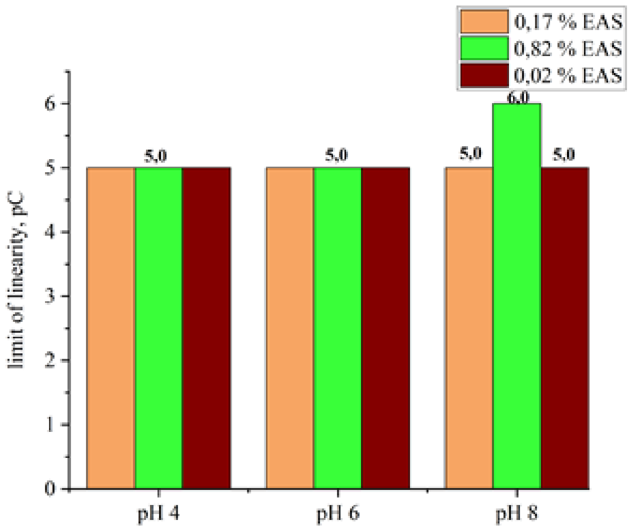

Figure-2. Influence of various factors on the lower limit of linearity of the graphical dependence E - pC of a polymer membrane (solvent - DBP).

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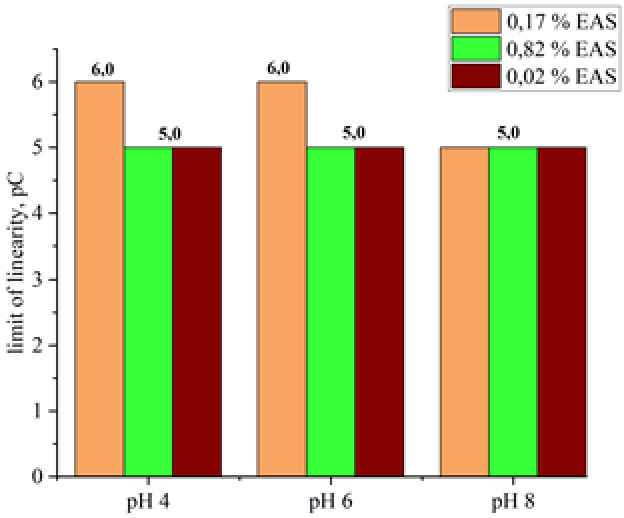

Figure-3. Influence of various factors on the lower limit of linearity of the graphical dependence E - pC of a polymer membrane (solvent - DOP).

From the presented data it is clear that the linearity of the electrode function does not significantly depend on the composition of the membrane and is quite high (10^{-5} mol/l), however, the best results are achieved when the content of the supramolecular complex in the membrane is 0.17% when used as a solvent-plasticizer - dioctyl phthalate and the pH of the test solutions are 4.0 and 6.0, as well as when the content of the electroactive substance is 0.82%, the use of dibutyl phthalate solvent and the pH of the test solution is 8.0.

The influence of the pH of the solutions under study and the composition of the plasticized membrane on the minimum detectable concentration of benzalkonium chloride in the solution was also studied (Figures 4-5).

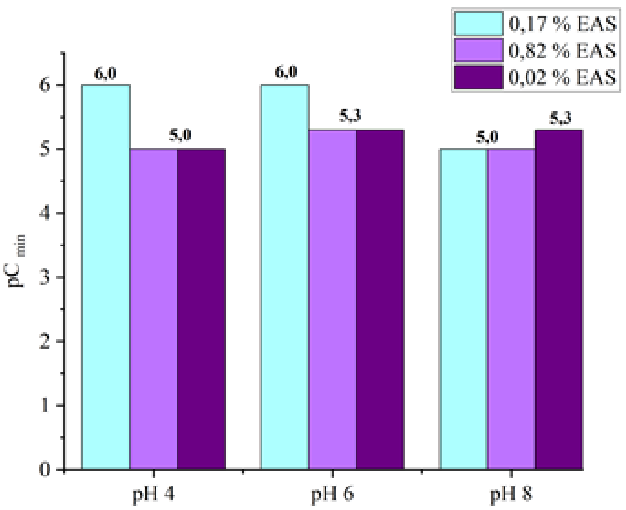

Figure-4. The influence of various factors on the minimum detectable concentration of BAC (plasticizer solvent - DOP).

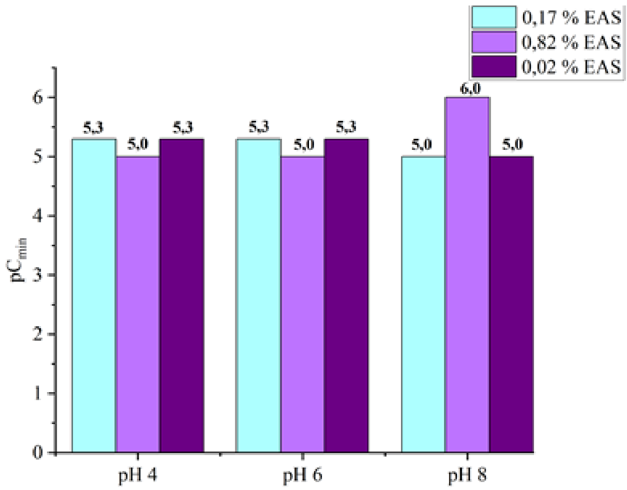

Figure-5. The influence of various factors on the minimum detectable concentration of BAC (solvent - DBP).

From the presented graphs it is clear that the minimum detectable concentration when using 0.17% of the electroactive substance (supramolecular complex of benzalkonium chloride with polyoxomolybdate) in the polymer membrane is observed at a level of $1.0 \cdot 10^{-6}$ mol/l, regardless of the pH of the test solution when using a solvent - plasticizer - dioctyl phthalate. Similar results are observed when using dibutyl phthalate solvent, the content of the supramolecular complex in the plasticized membrane is 0.82% and the pH of the test solution is 8.0. Other conditions make it possible to determine the concentration of catamine AB in the test solutions only at a level exceeding $7.5 \cdot 10^{-6}$ mol/l.

A study was also carried out on the numerical value of the slope of the electrode function of a polymer polyvinyl chloride membrane containing an electrode-active supramolecular substance based on benzalkonium chloride (Figures 6-7) from various factors.

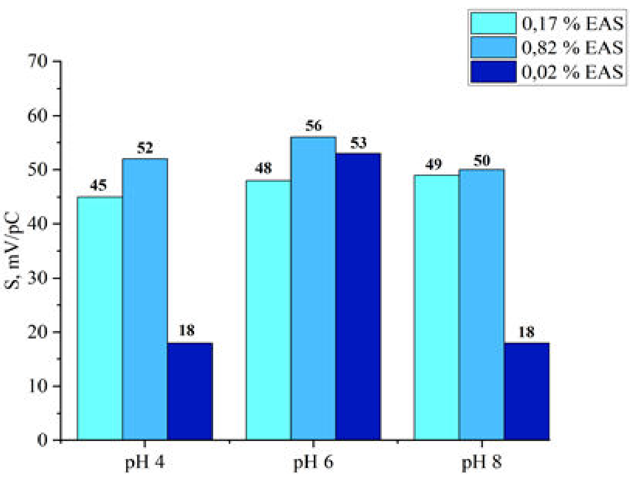

Figure-6. Dependence of the slope of the electrode function from various factors (plasticizer solvent - DOP).

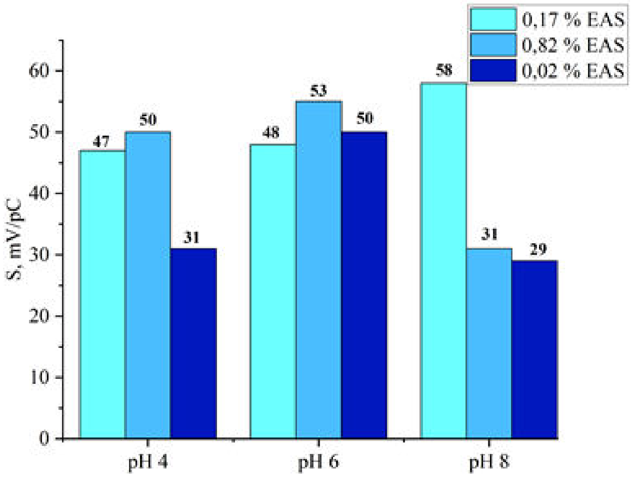

Figure-7. Dependence of the slope of the electrode function from various factors (plasticizer solvent - DBP).

When studying the slope of the electrode function of a plasticized polyvinyl chloride membrane based on the supramolecular complex of benzalkonium chloride and POM, it was found that the slope, depending on various conditions, ranges from 18 to 58 mV/pC. The theoretical value of the Nernst slope of the electrode function of the membrane of a singly charged cation should correspond to 59-60 mV/pC, and in real conditions, this value can be in the range of 40-60 mV/pC [27-29].

Based on the experimental data obtained, we can conclude that the slope of the electrode function, closest to the theoretical one, is observed at a percentage of the supramolecular complex in the membrane of 0.17 and 0.82%, regardless of the type of solvent-plasticizer. The slope of the electrode function when using membranes containing 0.02% electroactive species is closer to the Nernst slope for a doubly charged cation and is therefore not suitable for measuring catamine AB concentration using the electrode potential of a polyvinyl chloride membrane.

Having analyzed the entire complex of experimental data (linearity of the electrode function, the minimum detectable concentration of BAC, the slope of the electrode function), we can conclude that the rational conditions for obtaining a supramolecular complex of benzalkonium with 12-molybdophosphate heteropolyacid and a plasticized membrane for the determination of catamine AB in solutions based on them are as follows:

- EAB = 0.17%;
- solvent – dioctyl phthalate;
- pH=6,0.

Electrode characteristics of this membrane: linearity - $1.0\cdot 10^{-6}$ mol/l, minimum detectable concentration - $1.0\cdot 10^{-6}$ mol/l, slope of the electrode function - 48 mV/pC.

In Figure-8 shows the dependence of the electrode potential of the plasticized membrane of a potentiometric sensor for determining benzalkonium chloride based on the supramolecular compound BAC and POM on the concentration of the test solution.

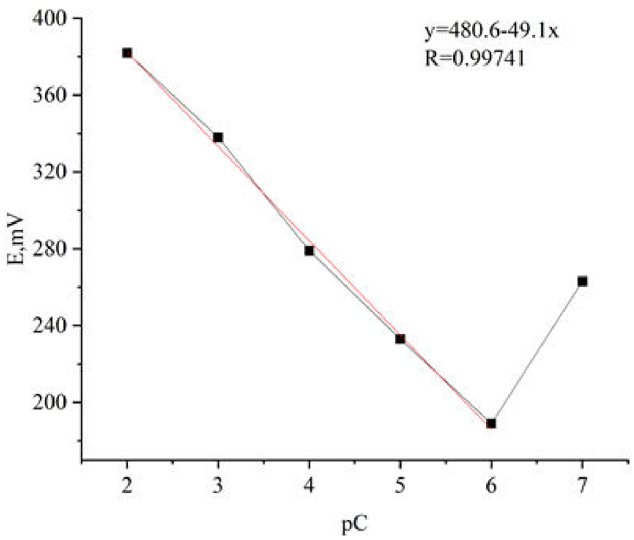

Figure-8. Dependence of the electrode potential of a polyvinyl chloride membrane on the logarithm of concentration (EAS = 0.17%, solvent – DOP, pH = 6.0).

4. CONCLUSIONS

An electroactive supramolecular substance based on benzalkonium chloride and molybdenum polyoxometalate has been synthesized. To select rational conditions for its use and study its electroactive properties, it was used as an electrode active substance for the construction of polyvinyl chloride plasticized membranes. For this purpose, the influence of various factors (the nature of the membrane solvent, the percentage of supramolecular substance in the membrane, and the pH of the solutions under study) on the electrode characteristics (minimum detectable concentration, linearity interval, and slope of the electrode function) of plasticized polyvinyl chloride membranes based on the supramolecular complex of benzalkonium chloride and polyoxomolybdate. Rational conditions for the production and use of a plasticized membrane based on a supramolecular complex were selected (percentage of electrode-active substance in the membrane, nature of the solvent-plasticizer, acidity of the test solution). The resulting platified membranes can be used for the further development of potentiometric sensors for determining the quantitative content of benzalkonium chloride in environmental objects.

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