



THE POTENTIOMETRIC SENSOR FOR EXPRESS DETERMINATION OF POLYHEXAMETHYLENE GUANIDINE SALTS

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ABSTRACT

A potentiometric sensor for the quantitative determination of polyhexamethylene guanidine salts was developed. The ionic associate of the degradation product of polyhexamethylene guanidine - hexamethylenediamine salts with heterogeneous acids with the Keggin structure was used as an electrode-active substance for the plasticized polyvinyl chloride membrane of the sensor. The anions of 12-molybdophosphate and 12-tungstenphosphate heteropolyacids were used as counterions for ionic associates. The influence of a qualitative and quantitative composition of the membrane, a type of degradation of polyhexamethylene guanidine salts, a nature of the membrane solvent-plasticizer, pH of the test solution, a presence of interfering ions in the solution on the electrode characteristics of the membrane of the developed sensor (tilt angle, minimum detectable concentration) were investigated. The optimum conditions for the quantitative determination of polyhexamethylene guanidine salts through the product of their degradation (hexamethylenediamine) by the potentiometric method with the developed sensor were established.

Keywords: polyhexamethylene guanidine phosphate, hexamethylene diamine, heteropolyanion, 12-molybdophosphate heteropoly acid, 12-tungsten phosphate heteropoly acid, potentiometric sensor.

1. INTRODUCTION

Alkylguanidine salts, like many other compounds containing a guanidine group, are used as physiologically active substances for various purposes because of its high efficacy and less toxicity than other biocides. Polyhexamethylene guanidine (PHMG) salts are diphilic and exhibit properties of surfactants due to the presence of polar guanidine and non-polar methylene groups in the molecule [1]. These compounds have high antimicrobial efficiency due to the structure of its molecules: hydrophobic polyethylene units promote adsorption of these substances on phospholipid cell membranes, and hydrophilic guanidine groups give these compounds biocidal properties. The various materials with prolonged antiseptic properties were also created based on polyhexamethylene guanidine (textiles, paper, film, plastics, rubber, paints, varnishes). Also PHMG salts are a part of cosmetics and medicines [2-8].

The salts of polyhexamethylene guanidine (PHMG) have the general formula with the ratio $m/n = 1 - 2$, $m = 10 - 100$ monomer units with M.m. = 142.

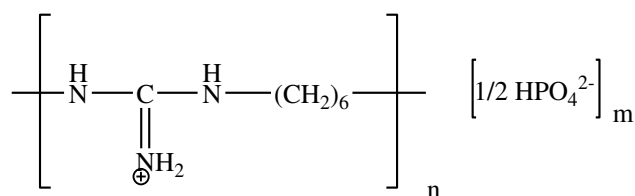


Figure-1. Polyhexamethylene guanidine phosphate structural formula.

Currently, spectrophotometric methods are used to determine the quantitative content of polyhexamethylene guanidine salts [9-14]. Titrimetric [15], electrochemical (amperometric titration [16] inversion voltammetry [17], capillary electrophoresis [18]) and fluorimetric methods for the quantitative determination of these compounds have been developed [19] as well as. The most existing methods are difficult to implement or the methods require expensive equipment. The common photometric methods cannot always be used to analyze complex objects involving many drugs and cosmetics. The direct potentiometric methods using sensors sensitive to cations of polyhexamethylene guanidine (PHMG) can be as an alternative solution.

The Keggin structures (HPA) of 12-molybdophosphate and 12-tungsten-phosphate heteropoly acids were used as counterions to obtain the ionic associates for plasticized membranes of potentiometric sensors. The degradation product of polyhexamethylene



guanidine - hexamethylenediamine (HMDA) salts were used as a substance for ionic associates because PHMG molecules, due to the large mass and length of the polymer

chain in solutions, can take a reduced conformation with the formation of macro coils [20].

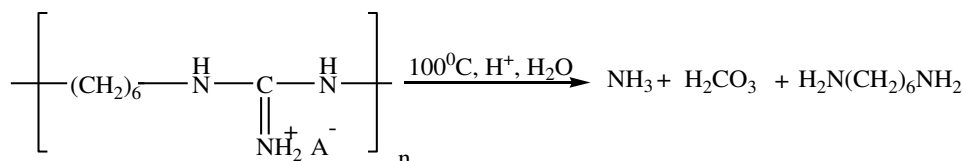


Figure-2. The reaction of destruction salts of polyhexamethylene guanidine.

The chemical degradation of polyhexamethylene guanidine salts with the formation of hexamethylenediamine occurs with boiling in alkaline or acidic solutions [1].

2. MATERIALS AND METHODS

2.1 Materials used in the work

The following reagents are used in the work:

- 12-molybdophosphate acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$ (analytical grade);
- 12- tungsten phosphate acid, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ (analytical grade);
- polyhexamethylene guanidine phosphate $\text{C}_{252}\text{N}_{108}\text{H}_{594}\text{O}_{72}$ (pure grade);
- sodium hydroxide (analytical grade);
- chloride acid (conc.) (analytical grade);
- polyvinyl chloride (PVC), brand C-70 (pure grade);
- cyclohexanone (CH), (analytical grade);
- dibutyl phthalate (DBP), (pure grade);
- dioctyl phthalate (DOP), (pure grade);
- tricresyl phosphate (TCP), (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 $\text{KCl}_{\text{sat.}}$) 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 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 0.01 g or 0.02 g of the ionic associate in 1.1 ml of a plasticizer solvent (dibutyl phthalate, dioctyl phthalate or tricresyl phosphate). The solutions were mixed and transferred to Petri dishes with a diameter of 50 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 2-3 days.

3. RESULTS AND DISCUSSIONS

The effect of the acidity of the solution on the electrode characteristics of the membranes of potentiometric sensors sensitive to the degradation product of polyhexamethylene guanidine - hexamethylenediamine was investigated using standard solutions of hexamethylenediamine with concentrations in the range of $1.0 \cdot 10^{-7}$ - $1.0 \cdot 10^{-2}$ mol/l (Figures 3 and 4).

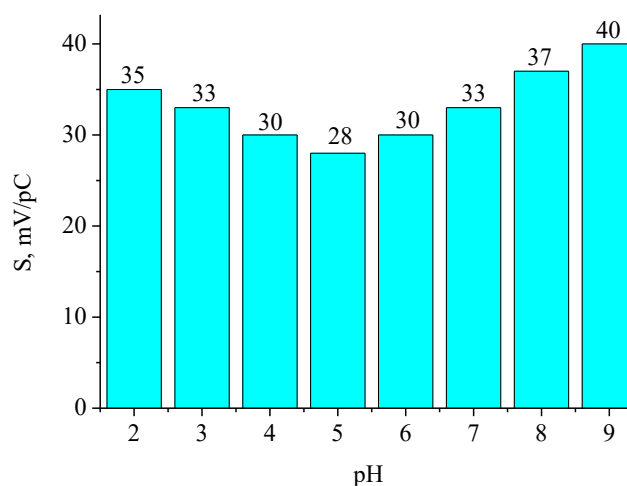


Figure-3. The influence of the pH on the slope of the electrode function of the sensor membrane.

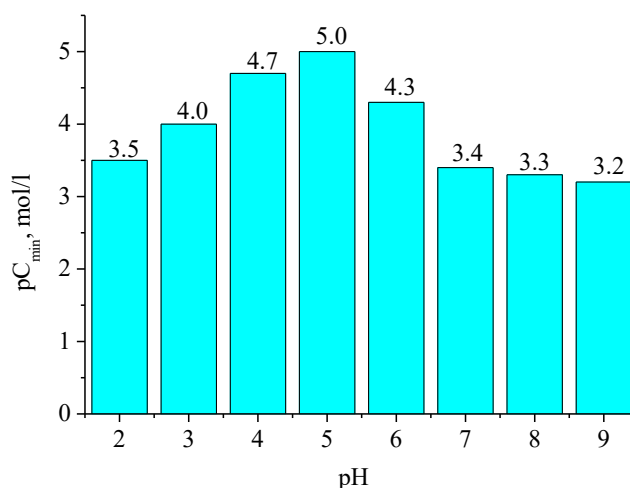


Figure-4. The influence of the pH on the value of the determined minimum for the membrane sensor.

The investigation of the dependence of the electrochemical properties of the developed potentiometric sensor's membrane on the pH of the solution shows that the slope of the calibration graphs in the pH range from 4.0 to 6.0 retains a constant value of $\sim 30 \text{ mV/pC}$ which is matched to the standard Nernst value for two charge ions. The optimum of pH for the hexamethylenediamine determination with the potentiometric method is 5.0 since the membrane of the potentiometric sensor is most sensitive to the content of hexamethylenediamine (minimum determined concentration is 10^{-5} mol/l) at this acidity of the solution.

The influence of various factors (the nature of the solvent of the plasticizer and the ionic associate, the pH of the pre-destruction of PHMG salts to HMDA, the quantitative content of the ionic associate in the membrane) on the electrode function of the membrane of the developed potentiometric sensor was investigated as well as (Figures 5-7).

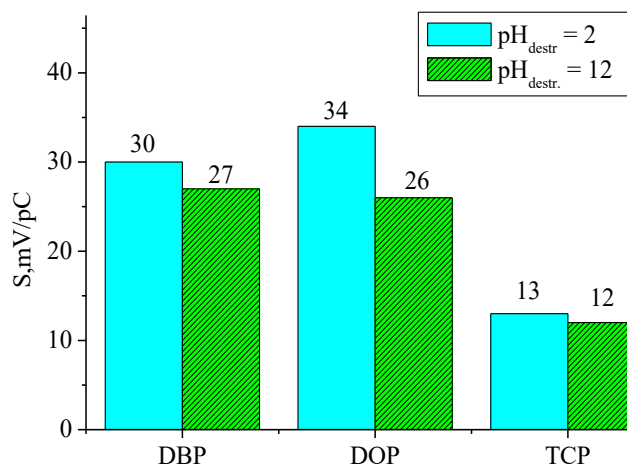


Figure-5. Dependence of the slope of the electrode function on the type of solvent (IA- $(\text{HMDA})_3(\text{PMo}_{12}\text{O}_{40})_2$; $\omega_{IA} = 0.17\%$ $\text{pH}=5$).

When using tricresyl phosphate as the solvent-plasticizer for the membrane, low values of the slope of the electrode function ($\sim 15 \text{ mV/pC}$) are observed in all cases. These values are very different from the theoretical Nernst's value for the two-charge cation as shown by the experimental data obtained (Figure-5). The steepness of the electrode function is close to the theoretical value ($\sim 30 \text{ mV/pC}$) using phthalic acid derivatives (dioctyl- and dibutyl phthalate). Therefore, further investigations were conducted using these solvents-plasticizer.

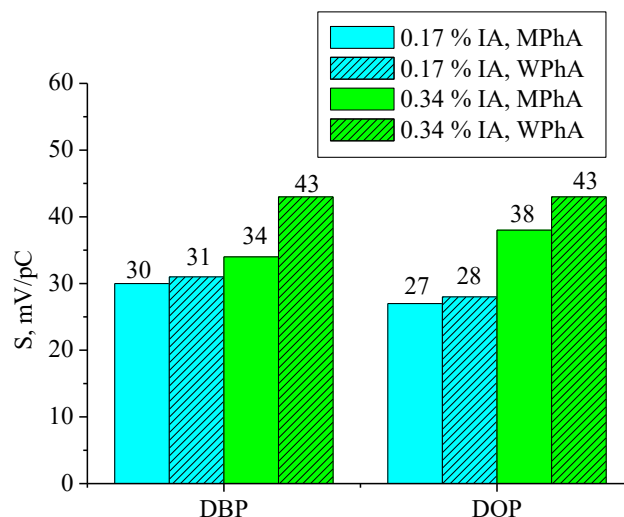


Figure-6. The dependence of the angle of inclination of the electrode function on the content of ionic associate in the membrane ($\text{pH}=5$; IA - $(\text{HMDA})_3(\text{PMo}_{12}\text{O}_{40})_2$).

The investigation of the influence of the quantitative content of the ionic associate in the membrane (Figure-6) showed that the optimal value of the angle inclination of the electrode function is close to the theoretical Nernst's value for two-charge cations ($\sim 30 \text{ mV/pC}$). This value is observed at the content of the ionic associate at the level of 0.17 % regardless of the type of plasticizer solution. As the content of ionic associate in the membrane increases, the angle of inclination and deviation of this parameter from the theoretical value are increased.

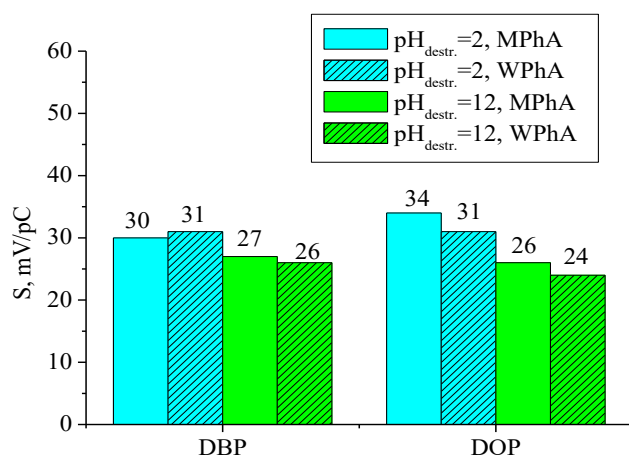


Figure-7. The dependence of the slope of the electrode function on the nature of the counterion ($\omega_{IA} = 0.17\%$).

The investigation of the influence of the type of pre-destruction and the nature of the counterion on the electrode characteristics of the membrane of the developed potentiometric sensor (Figure-7) showed that the experimentally determined value of the slope angle is close to theoretical at the carrying out the preliminary acid destruction of salts of polyhexamethylene guanidine regardless of the type of counter-ion.

According to the experimental data, the optimal value of the angle of inclination of the electrode function which is close to the theoretical Nernst value is observed for the acid type of degradation and at the content of ionic associate in the membrane at 0.17%. The nature of the electrode-active substance and the type of solvent-plasticizer don't affect significantly.

The results of the investigations of the dependence of the minimum detectable concentration of HMDA which can be determined with the developed potentiometric sensor on various factors are presented in Figure-8.

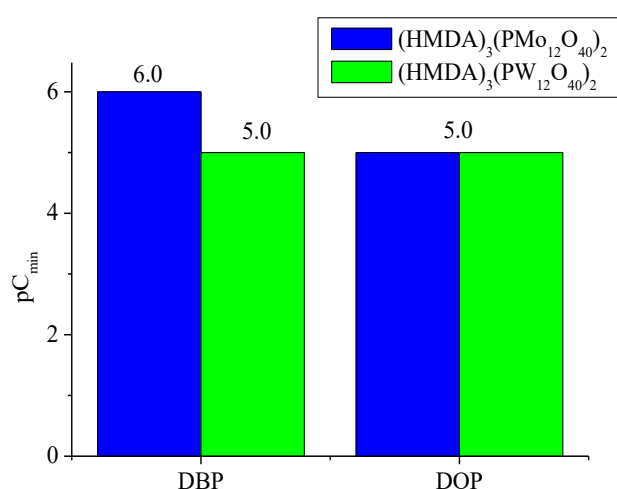


Figure-8. The dependence of the minimum determinable concentration on the type of solvent and counterion ($\text{pH}_{\text{destr.}} = 2$, $\omega_{IA} = 0.17\%$)

The lowest detectable concentration is observed at using a dibutyl phthalate and ionic associate composition (HMDA)₃(PMo₁₂O₄₀)₂ as a membrane solvent plasticizer according to the obtained experimental data (Figure-8)

The response time of plasticized sensor membranes is determined by the "immersion method" [21] when the concentration of the potentially detectable ion changes by an order of magnitude. It is 2 - 3 min at low concentrations and 40 - 50 sec at high concentrations ($1.0 \cdot 10^{-3}$ - $1.0 \cdot 10^{-2}$ mol/l).

The lifetime of the potentiometric sensor's membranes depends on its storage method: the membranes which are stored on the air have the longest one (50 - 60 days). These membranes must be immersed in a solution with a concentration corresponding to the middle range of the hexamethylenediamine content (10^{-4} mol/l) on 10 - 15 min before using.

A graphical dependence of the potential of the developed potentiometric sensor on the concentration of hexamethylenediamine in solution is shown in Figure-9.

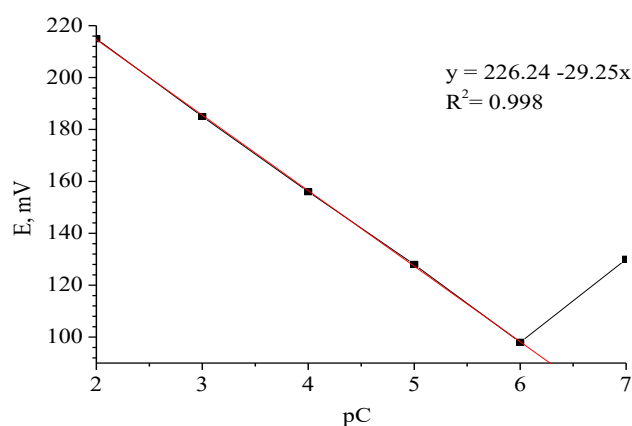


Figure-9. The dependence of the electrode potential of the developed sensor on the logarithm of concentration ($\text{pH} = 5.0$, $\text{pH}_{\text{destr.}} = 2$, $\omega_{IA} = 0.17\%$, solvent - DBP).



The selectivity coefficients of the membrane of the potentiometric sensor on HMDA are determined by the mixed solutions method. This method is based on the

measurement of potentials in mixed solutions with a stable content of interfering ion j and a variable concentration of the investigated ion i (Figure-10).

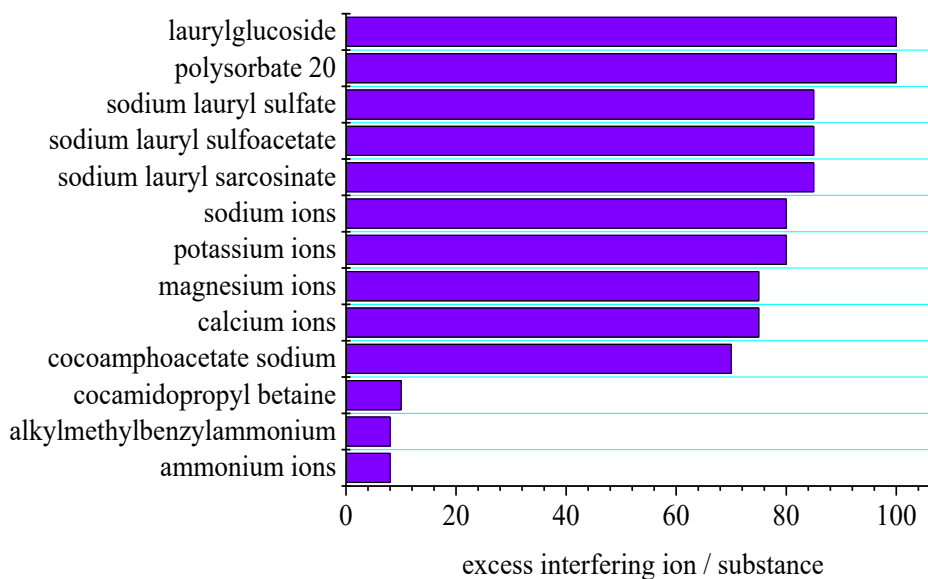


Figure-10. Obstructive excess of ions/substances in potentiometric determination of hexamethylenediamine.

According to the experimental data, nitrogen-containing substances and ions can influence the results of the potentiometric determination of the quantitative content of hexamethylenediamine using a developed sensor. Therefore, these substances or ions must be removed or masked while carrying out a sample preparation of a real sample. Other listed cations and substances don't have a significant interfering effect on the characteristics of the developed sensor.

4. CONCLUSIONS

- A potentiometric sensor for the determination of polyhexamethylene guanidine salts via the product of their destruction (hexamethylenediamine) has been developed.
- The influence of various factors (the nature of the solvent-plasticizer and ionic associate, pH of pre-destruction of PHMG salts to HMDA, the quantitative content of ionic associate in the membrane) on the electrode characteristics (the inclination angle of the electrode function, the minimum determined concentration) of the plasticized membrane of the developed sensor was investigated. The optimum conditions for carrying out the analysis were determined:
 - carrying out acid-type destruction of salts of polyhexamethylene guanidine to hexamethylenediamine;

- heteropolyanion of 12-molybdophosphoric acid is used as a counterion;
 - the content of anionic associate in the membrane of the sensor is 0.17%;
 - dibutyl phthalate is used as a membrane solvent-plasticizer;
 - pH of the researched solution is 5.0.
- The response time of the membrane and the lifetime of the sensor were experimentally determined.
 - The influence of different ions and substances in the researched solution on the results of the determination of hexamethylenediamine using the developed potentiometric sensor was investigated.

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