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IONOMETRIC DETERMINATION OF COCAMIDOPROPYL BETAINE

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ABSTRACT

This article reports on the development of an ionometric sensor for the determination of the amphoteric surfactant cocamidopropyl betaine. It was found that low-soluble complex compounds with the composition $(CAPB)_3(PMo_{12}O_{40})_2$ and $(CAPB)_3(PW_{12}O_{40})_2$ are formed as a result of the interaction of the cation of the test substance with the anions of heteropoly acids. The obtained compounds were used as electrode active substances for polyvinyl chloride membranes of ionometric sensors. Phthalic acid derivatives (dibutyl and dioctyl phthalates) were used as solvents for plasticized membranes. The study of the dependence of the electrochemical properties of the obtained sensor membranes on various factors was carried out. This made it possible to choose the optimal conditions for the operation of the ionometric sensor. The detection limit of cocamidopropyl betaine using this sensor is $1.0 \cdot 10^{-6}$ mol/l and quantitative determination can be carried out in a fairly short time (5-10 minutes).

Keywords: cocamidopropyl betaine, heteropoly acid, ionometry, complex compound, 12-molybdophosphate acid, 12-tungstenphosphate acid, potentiometric sensor.

1. INTRODUCTION

The current trend in the development of the market for surfactants has mostly intensive character. It means that the new types of surfactants are implement in industrial producing along with an increasing in the release of "classical" surfactants, such as sodium lauryl sulfate or fatty acid salts. The new application areas of the long-known surfactants are discovering as well as [1].

The surface-active betaine derivatives, in particular cocamidopropyl betaine (lauramidopropyl betaine), are good example of the "new wave" of detergents. Cocamidopropyl betaine belongs to the class of ampholytic surfactants, because the molecule of this substance contains positively and negatively charged functional groups simultaneously, to wit, it is a dipole ion (a zwitterion) [2].

This compound is widely used as the main and auxiliary surfactant for the various types of cosmetic products, because it does not have a high level of irritating ability to the skin and mucous membranes of a person, unlike to other commonly used surfactants. This important factor usually significantly limits the possibilities of using other surfactants.

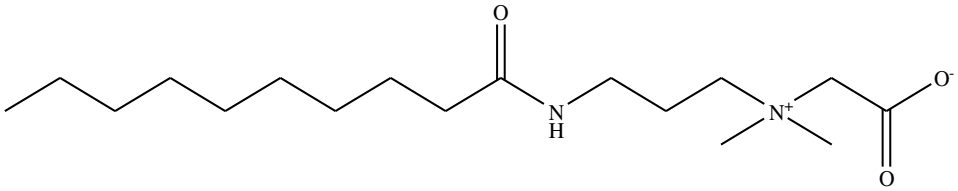

Figure-1. Cocamidopropyl betaine structural formula.

Lauramidopropyl betaine has a wide range of technological properties due to its structure and ampholytic nature: stabilizing of a foam, improving of the foaming capacity of anionic surfactants and reducing of its irritant ability; it has own high purifying properties and an antistatic and conditioning effect which inherent in cationic surfactants. In addition, this substance is well compatible with all types of surfactants and exhibits synergistic properties, which makes it possible to use it in combination with other surfactants, which leads to a significant improvement in the dermatological properties of the finish product [3].

However, cocamidopropyl betaine as a cosmetic component has two major disadvantages - a relatively high cost and the possibility of allergic reactions during using. As for the possibility of the allergic reactions to this substance, a lot of studies have been carried out to confirm the safety of cocamidopropyl betaine which is used in cosmetics in many countries according to the technologically justified concentrations (from 0.1-1 % to 3%) [4-7]. Therefore, the using of this surfactant is allow even in cosmetic products intended for children (toothpastes, shampoos, foams, etc.). The high cost of this compound is connect, first, with the complexity of the synthesis process of this detergent and the high cost of raw materials - dimethylaminopropylamine. It should be note that this surfactant is not produce in Ukraine that is why the using of this surfactant is considerably limited in our country by the necessity to import it from China, Great Britain, Germany and USA.

The amount of counterfeits is increasing along with an increasing in the level of industrial using of this detergent. That is why there is an important problem in the rapid and simple express method in determination of cocamidopropyl betaine.

Three main groups of methods for the quantifying determining of lauramidopropyl betaine currently exist: chromatographic, potentiometric and titrimetric. The determination of this substance by liquid chromatography [8] based on the using of a mixture of 70 % acetonitrile and 30 % 0.05 M solution of lithium hydroxide as a mobile phase. The disadvantages of the method are the complexity and duration of the sample preparation stages and the availability of expensive equipment for analysis. The method of acid-base titration of cocamidopropyl betaine [2] based on the adding of an excess of hydrochloric acid to the sample and a subsequent titration of potassium hydroxide. The disadvantage of this method is the lack of selectivity, i.e., the determination of the content of cocamidopropyl betaine is not possible at the presence of other bases. The basis of the potentiometric titration method of lauramidopropyl betaine [9] is a titration of a sample by 0.1 N solution of perchloric acid in dioxane with the glass electrode as an indicator. The disadvantages of the method include the necessity and complexity of the sample preparation, which increases the time of the analysis, as well as the using of auxiliary toxic reagents. Methods for determining the cocamidopropyl betaine by mass spectrometry [10] and spectrophotometry with using of the eryochormal black [11] are also know, but these methods require the expensive equipment and the complexity of the research like previous methods.

The development of ionometric sensors for various bioactive compounds and surfactants used in cosmetic and food technology is a promising direction in methods for the quantitative determination of these substances. This allows determining various components of food and cosmetic products quickly and quantitatively with high sensitivity and selectivity, and without additional costs [12-20].

The purpose of this work is to develop an express method for the determination of cocamidopropyl betaine. For the quantitative determination of this compound, it is suggest using the direct potentiometric method with using the potentiometric sensors, which are sensitive to the substance being determined.

2. MATERIALS AND METHODS

2.1 Materials Used in the Work

The following reagents used in this work:

- cocamidopropyl betaine, $C_{19}H_{38}N_2O_3$ (analytically pure);
- 12-molybdophosphate acid, $H_3PMo_{12}O_{40}x26H_2O$ (analytically pure);
- 12-tungstenphosphate acid, $H_3PW_{12}O_{40}x29H_2O$ (analytically pure);
- polyvinyl chloride (PVC), brand C-70 (chemically pure);
- cyclohexanone (CH), (analytically pure);
- dibutyl phthalate (DBP) (chemically pure);
- dioctyl phthalate (DOP) (chemically pure);
- sodium hydroxide (analytically pure);
- hydrochloric acid (conc.) (analytically pure).

2.2 Devices Used in the Work

An electrochemical cell 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 carried out with the ionomer I-130. To determine the pH the electrode with brand ESK-10601/4 used.

2.3 Method for the Synthesis of Membranes of Sensor

Plasticized polyvinyl chloride membranes were synthesize according to the following procedure: 0.45 g of polyvinyl chloride 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 of the complex compounds in 1.1 ml of a plasticizer solvent (dibutyl phthalate or dioctyl phthalate). The solutions 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 obtained from the mixture after complete evaporation of cyclohexanone in 2-3 days.

3. RESULTS AND DISCUSSIONS

The nature influence of the complex compound counterion on the membrane sensitivity of the developed ionometric sensor was studied using a series of cocamidopropyl betaine standard solutions in the pH= 1 – 9 and the concentration range $1.0 \cdot 10^{-6}$ – $1.0 \cdot 10^{-2}$ mol/l. Solutions with pH> 9 were not studied because of capability of heteropoly acids to decomposing in strongly alkaline media at pH more than 10 with the precipitation of oxides of the corresponding metals [22-23]. Dibutyl phthalate was used as a solvent for the membrane (Figures 2 and 3).

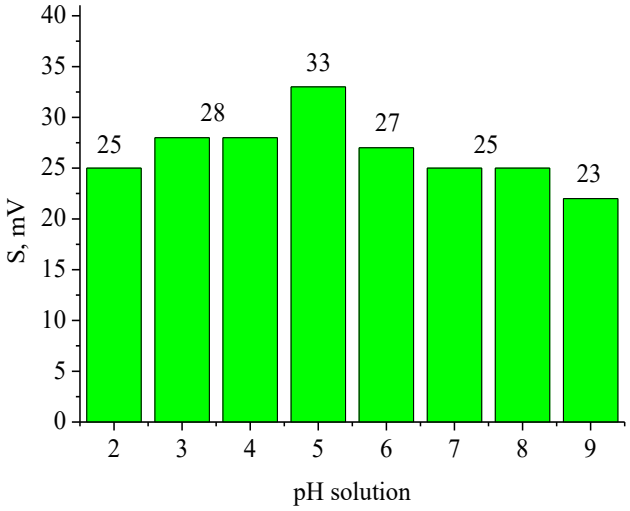

Figure-2. The influence of the pH on the slope of the electrode function of the sensor membrane (counterion $PMo_{12}O_{40}^{3-}$, solvent dibutyl phtalate).

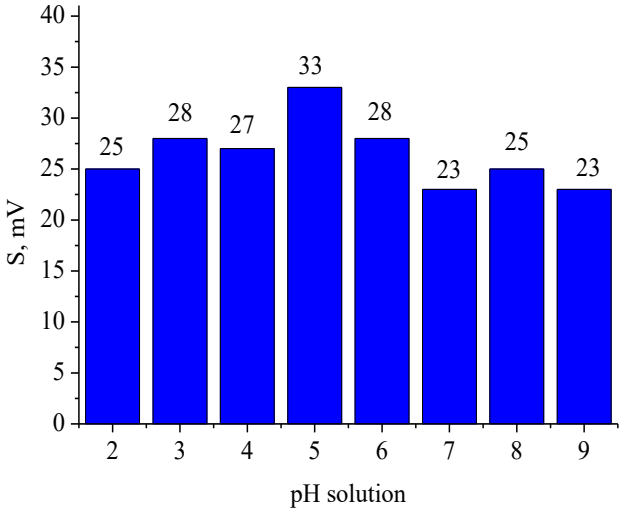

Figure-3. The influence of the pH on the slope of the electrode function of the sensor membrane (counterion $PW_{12}O_{40}^{3-}$, solvent dibutyl phtalate).

From the obtained experimental data, it can be seen that using as a counterion complex compound of 12-tungstophosphate heteropoly acid anion decrease the slope of the electrode function of the membrane sensor is observed. Such an effect indicates a decrease in the membrane sensitivity to cocamidopropyl betaine ions. The use of the anion of 12-molybdophosphate heteropoly acid as a counterion complex compound, on the contrary, makes it possible to determine the studied substance with greater accuracy. In addition, the slope of the electrode function is closer to the theoretical value in the Nernst equation for a doubly charged cation (~ 30 mV/pC).

In parallel, the nature effect of the complex compound counterion on the determining minimum of cocamidopropyl betaine was research depending on pH of the test solution (Figures 4 and 5).

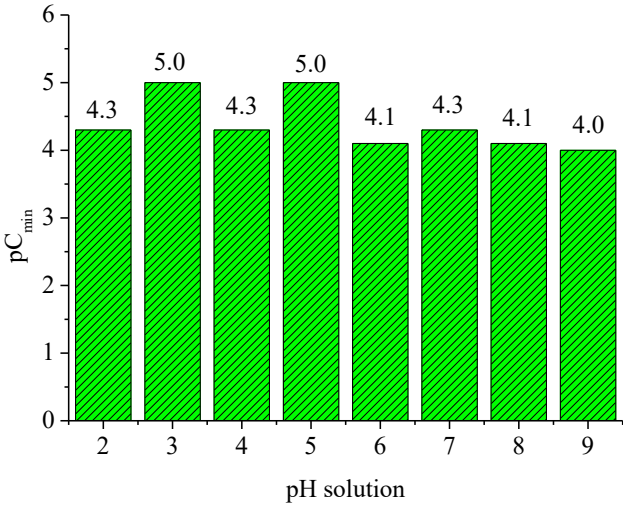

Figure-4. The influence of the pH on the value of the determined minimum for the membrane sensor (counterion $PMo_{12}O_{40}^{3-}$, solvent dibutyl phtalate).

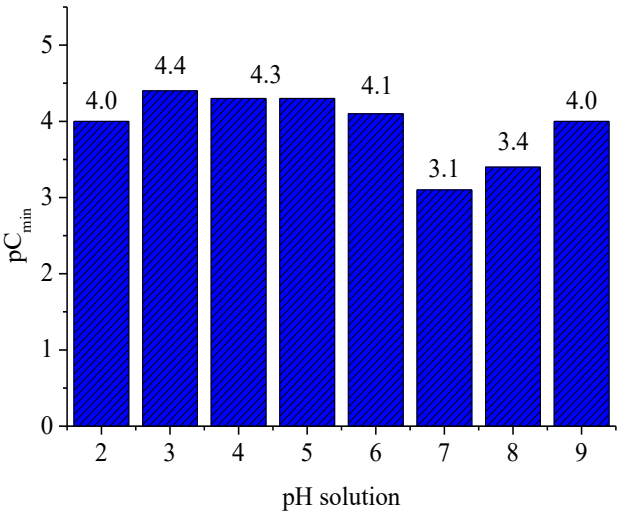

Figure-5. The influence of the pH on the value of the determined minimum for the membrane sensor (counterion $PW_{12}O_{40}^{3-}$, solvent dibutyl phtalate).

As can be seen from the obtained experimental data, when working within the pH range of 4-7, the cocamidopropyl betaine determined minimum does not depend on the nature of complex compound counterion and it is equal to 10^{-5} mol/l. When using a solution with pH = 3.0 and anion of 12-molybdophosphate heteropoly acid, the determined minimum is 10^{-5} mol/l, which correlates with the data of spectrophotometric studies of the interaction reactions of cocamidopropyl betaine with heteropoly acids [24].

It was also studied the nature effect of the solvent-plasticizer on the electrode characteristics of the membrane, depending on the acidity of the test solution (Figures 6 and 7).

From the obtained experimental data, it can be seen that using dioctyl phthalate as a solvent-plasticizer leads to a decrease in the inclination angle of the electrode

function and, accordingly, the sensitivity of the plasticized sensor membrane decreases. The determining minimum is also reduced compared to membranes based on dibutyl phthalate.

The response time of the membrane of the potentiometric sensor depends on the concentration and it is equal to 40-50 s for low concentrations ($1.0 \cdot 10^{-6}$ - $1.0 \cdot 10^{-5}$ mol/l) and it is equal to 10-20 s for high concentrations ($1.0 \cdot 10^{-2}$ - $1.0 \cdot 10^{-3}$ mol/l).

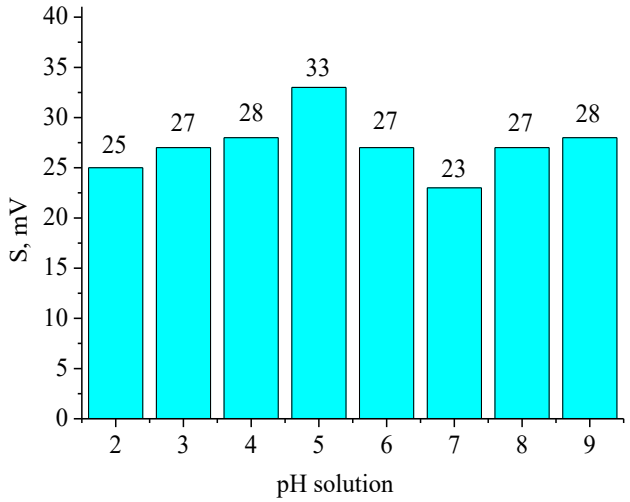

Figure-6. The influence of the pH on the slope of the electrode function of the sensor membrane (counterion $PMo_{12}O_{40}^{3-}$, solvent dioctyl phthalate).

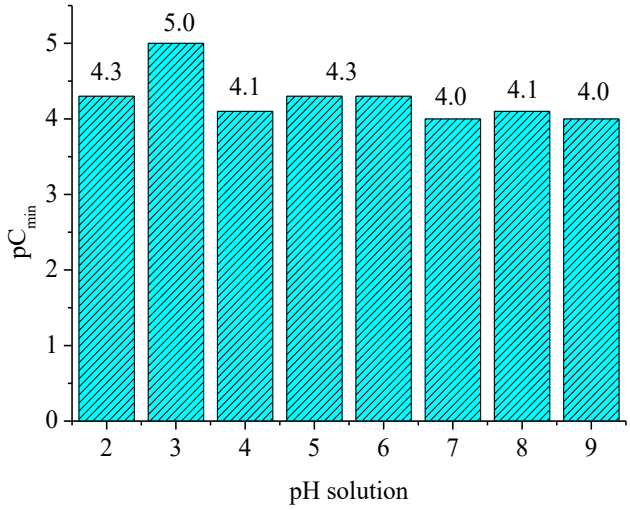

Figure-7. The influence of the pH on the value of the determined minimum for the membrane sensor (counterion $PW_{12}O_{40}^{3-}$, solvent dioctyl phtalate).

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 days). These membranes must be immersed in a solution with a concentration corresponding to the middle range of the cocamidopropyl betaine content ($1.0\ 10^{-4}$ mol/l) on ~ 15 min before using.

A graphical dependence of the potential of the developed ionometric sensor on the concentration of the cocamidopropyl betaine is show in Figure-8.

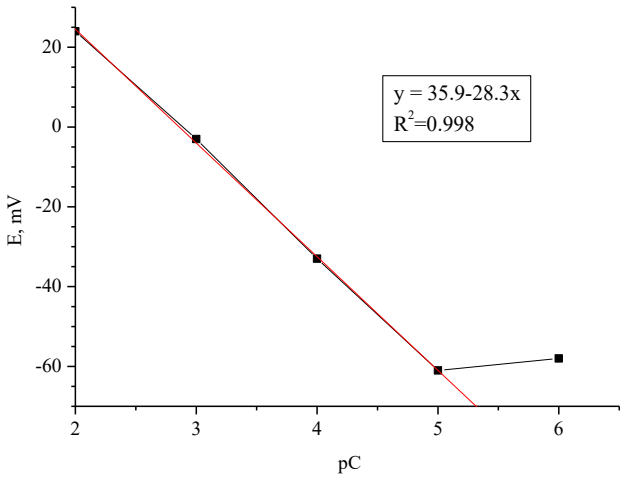

Figure-8. The dependence of the electrode potential of the developed sensor on the logarithm of concentration (pH=3.0, counterion $PMo_{12}O_{40}^{3-}$, solvent dibutyl phthalate).

4. CONCLUSIONS

a) A potentiometric sensor sensitive to an ampholytic surfactant cocamidopropyl betaine has been developed.

b) The influence of test solution pH, the nature of the complex compound counterion, the nature of the solvent-plasticizer for the membrane on the main electrode characteristics of the PVC membrane of the sensor was studied (the slope of the electrode function and the minimum determination limit of cocamidopropyl betaine). From the obtained experimental data, the optimal operating conditions for a potentiometric sensor based on cocamidopropyl betaine were determined:

- the anion of 12-molybdophosphate heteropoly acid should be used as a complex compound counterion;
- dibutyl phthalate should be used as a membrane solvent;
- pH of studied solution is 3.0.

c) The lifetime of the membrane of the potentiometric sensor was experimentally determined.

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