Original Research Article: full paper

(2019), «EUREKA: Physics and Engineering»
Number 4

DEVELOPMENT OF A POTENTIOMETRIC SENSOR SENSITIVE TO POLYSORBATE 20

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Abstract

Polyoxyethylated sorbitans (polysorbates) are widely used in the chemical, pharmaceutical, and cosmetic industries, but only quantitative determination is used mainly for chromatographic methods. In this paper, the results of the development and testing of a potentiometric sensor sensitive to nonionic surfactant polyoxyethylene sorbitan monolaurate (polysorbate-20) are presented. An anion of the heterogeneous acid of the Keggin structure (12-molybdophosphate heteropolyacid) was used as a counterion to obtain the electrode-active substance for the potentiometric sensor membrane. Polysorbate-20 does not form cations when dissociating in water and cannot directly interact with heteropolyanion; therefore, a cationic complex of polysorbate-20 with barium ions was previously prepared (similar to the interaction of metals with crown ethers). The resulting ion associate meets the basic requirement for the electrode-active substance of plasticized film polyvinyl chloride membranes of potentiometric sensors (poor water solubility and good solubility in organic solvents). Phthalic acid derivatives (dibutyl phthalate and dioctyl phthalate) were used as solvent-plasticizers for a polyvinyl chloride membrane. To determine the optimum conditions for the functioning of a potentiometric sensor sensitive to polysorbate-20, the influence of various factors on the electrode characteristics was studied. Quantitative content of the ionic associate in the polyvinyl chloride membrane, the nature of the membrane solvent-plasticizer, pH of a series of standard polysorbate-20 solutions) on the electrode characteristics

of the plasticized membrane of the potentiometric sensor (sensitivity or slope of the electrode function, lower limit of linearity and minimum detectable concentration of polysorbate-20, which can be determined with the help of the developed potentiometric sensor) was studied. The optimal conditions for using the developed potentiometric sensor were found. The developed sensor allows for a short period of time (5–10 min) determining the quantitative content of polysorbate-20 in industrial products at the level 10–5–10 6 mol/l. The potentiometric sensor sensitive to polysorbate-20 can be used for the development of a potentiometric method for determining the clinical reception of polysorbate-20 in various types of industrial products.

Keywords: 12-molybdophosphate heteropolyacid, polyoxyethylene sorbitans, polysorbate, potentiometric sensor, direct potentiometry, tween.

DOI: 10.21303/2461-4262.2019.00942

1. Introduction

Polysorbates (trade name "tween") are ethoxylated sorbitans exhibiting the properties of non-ionic surfactants. These compounds are widely used in industry as fiber softeners, defoamers, antistatic agents, emulsifiers and solubilizes [1].

Polyoxyethylene sorbitan monolaurate (Polysorbate-20) is a non-ionic surfactant with a degree of ethoxylation at 20 (**Fig. 1)**. It was chosen as the object of a study.

Polysorbate-20 is used in the cosmetic industry [1–4]: to improve the dissolution of essential oils; in foam-washing compositions, which are moisturizing well, don't irritate and don't overdry the skin; in decorative cosmetics.

Currently, IR spectroscopy is used to identify ethoxylated sorbitans [5], and high-performance liquid chromatography [6–10] is used to quantify the content. According to previous studies [11–20], direct potentiometry using sensors which are sensitive to organic cations and substances is a simple, rapid and sensitive method of determination. The purpose of this study was to develop a potentiometric sensor which would allow to quickly and efficiently determine polysorbate-20 in various environmental objects and industrial products.

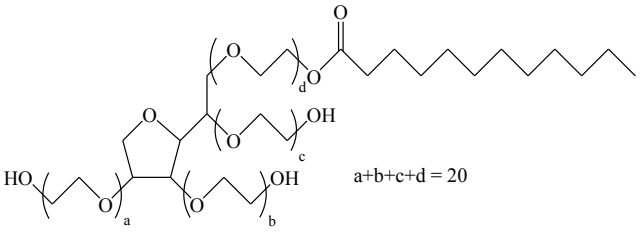

Fig. 1. Polysorbate 20 structural formula

Inasmuch as the ethoxylated sorbitans are non-ionic surfactants and don't form ions upon dissolution, a cationic complex of polysorbate-20 with barium ions was obtained in advance to obtain an associate with a 12-molybdophosphate heteropolyacid.

2. Methods, materials, and devices, used for making and testing of the potentiometric sensor for polysorbate 20 detection

2. 1. Materials used for developing and testing of the potentiometric sensor for polysorbate 20 detection

The following reagents are used in the work:

– 12-molybdophosphate acid, $H_3PMo_{12}O_{40}\times 26H_2O$ (analytically pure);

– Polysorbate-20, C58H114O26 (pure grade);

– Sodium hydroxide (analytically pure);

– Chloride acid (conc.) (analytically pure);

– Barium nitrate (analytically pure).

The following reagents were used to manufacture membranes potentiometric sensors:

– PVC (polyvinyl chloride), brand C-70 (pure grade) is a membrane matrix;

– CH (cyclohexanone), (analytically pure) is a matrix solvent.

The phthalic acid esters are used as membrane solvent-plasticizers:
– dibutyl phthalate (DBF), pure grade;
– dioctyl phthalate (DOF), pure grade.

Ionic associate of the cationic complex of polysorbate with barium ions and 12-molybdophosphate acid was used as an electrode active substance.

2. 2. Devices used for making and testing of the potentiometric sensor for polysorbate 20 detection

An electrochemical cell (**Fig. 2**) was used for direct potentiometric studies:

Ag	AgCl, KClsat.	Investigated solution	Membrane	$5.0 \cdot 10^{-5}$ solution PS-Ba^{2+}	AgCl, KClsat.	Ag

Fig. 2. The electrochemical circle of special cell for direct potentiometry

The galvanic cell consisted of a film potentiometric sensor (with an internal solution $5.0 \cdot 10^{-5}$ 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. Measurement of EMF is carried out with the ionomer I-130. To determine the pH has used the electrode with brand ESK-10601/4.

2. 3. Method for the synthesis of a plasticized membrane potentiometric sensor sensitive to polysorbate-20

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 0.10 g of the ionic associate in 1.1 ml of a plasticizer solvent. The phthalic acid esters were chosen as a plasticizer solvent via dibutyl phthalate (DBF) or dioctyl phthalate (DOF). 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.

2. 4. Determination of optimal conditions for the functioning of the membrane of a potentiometric sensor sensitive to polysorbate-20

The membranes were soaked in a solution of polyoxyethylene sorbitan monolaurate with a concentration of $5.0 \cdot 10^{-5}$ mol/l before starting measurements for the correct operation of a potentiometric sensor. The electrode function of a potentiometric sensor depends on the properties of the ionic associate and on the nature of the plasticizer solvent for the membrane. The characteristics of potentiometric sensors sensitive to the cationic polysorbate - Ba^{2+} particle were studied on various model solutions. A series of standard solutions PS-20 with concentrations from $1.0 \cdot 10^{-6}$ to $5.0 \cdot 10^{-3}$ mol/l was used to build the calibration graphs inasmuch the critical concentration of micelle-forming of polysorbate-20 is ~$1.5 \cdot 10^{-3}$ mol/l. This fact means that micelles and molecules appear in the solution which can influence on the determination results. Barium nitrate with volume 1.0 ml and concentration at 0.1 mol/l was added to 25.0 ml of each solution in the series to obtain a cationic complex.

The electrode characteristics of the developed sensors (minimum detectable concentration, linearity interval, and sensitivity S) were investigated depending on the various factors to determine the optimal conditions.

3. The results of the development of a potentiometric sensor sensitive to polysorbate20: determination of optimal conditions for the functioning of the membrane

3. 1. Study of the influence of various factors on the slope of the electrode membrane function of a potentiometric sensor sensitive to polysorbate 20

Fig. 3, 4 shows the study results of the effect of pH of the test solution, the nature of the membrane solvent and the quantitative content of the ionic associate in the membrane on the

amount of slope (steepness) of the electrode function of the potentiometric sensor sensitive to polysorbate-20.

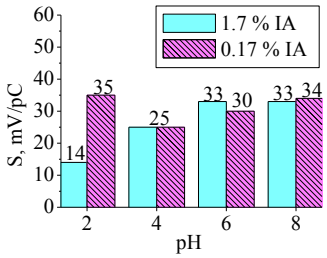

Fig. 3. Dependence of the slope of the electrode function from various factors (plasticizer solvent – dioctyl phthalate)

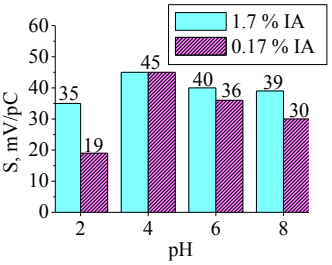

Fig. 4. Dependence of the slope of the electrode function from various factors (plasticizer solvent – dibutyl phthalate)

In the study of the influence of pH of solutions of the standard polysorbate-20 series, it can be seen that the numerical values of the inclination of the electrode function close to the theoretical one are observed at pH=6–8. The nature of the plasticizer solvent and the quantitative content of the ionic associate in the membrane do not have a significant effect on the inclination value of the electrode function of the developed potentiometric sensor sensitive to polysorbate-20

3. 2. The study of the dependence of the minimum determined concentration of polysorbate 20 on various factors

Fig. 5, 6 show the results of a study of the effect of the nature of the solvent, the content of the ionic associate in the membrane and the pH of the test solution on the minimum detectable concentration for the developed potentiometric sensors for polyoxyethylene sorbitan monolaurate.

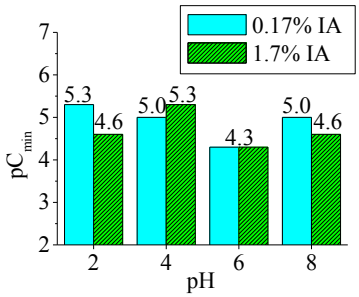

Fig. 5. The influence of various factors on the minimum detectable concentration of PS-20 (plasticizer solvent – dioctyl phthalate)

When investigating the effect of the nature of the solvent-plasticizer on the value of the minimum determined concentration, it was found that the lowest concentrations (the highest values of pC) were detected using dibutyl phthalate as a solvent. The acidity of the investigated solution and the quantitative content of the ionic associate in the membrane do not significantly affect this parameter.

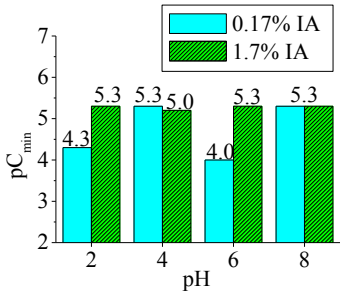

Fig. 6. The influence of various factors on the minimum detectable concentration of PS-20 (solvent – dibutyl phthalate)

3. 3. Investigation of the influence of various factors on the lower limit of the determination of potentiometric sensors sensitive to polysorbate-20

Fig. 7, 8 show the results of a study of the effect of the pH of the test solution, the nature of the solvent and the content of the ionic associate in the membrane on the lower limit of linearity for the developed potentiometric sensors for polyoxyethylene sorbitan monolaurate.

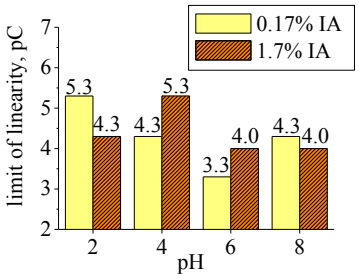

Fig. 7. The influence of various factors on the lower limit of the linearity of the E – pC dependence (solvent – dioctyl phthalate)

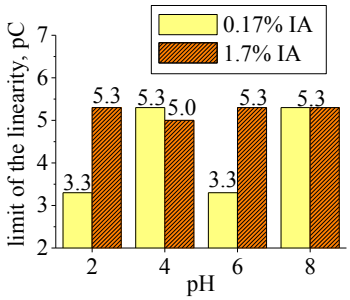

Fig. 8. The influence of various factors on the lower limit of the linearity of the E – pC dependence (solvent – dibutyl phthalate)

The study of the influence of various factors on the lower limit of the linearity of the electrode function showed that the maximum values of pC are observed with the use of a diluent-plasticizer of dibutyl phthalate, the quantitative content of the ionic associate in the membrane and the pH of the solution investigated do not significantly affect this parameter.

4. Discussion of development results and testing of a potentiometric sensor sensitive to polysorbate-20

It was found during the study of the influence of various factors on the steepness of the electrode function of the membrane of the obtained sensor that the slope value is 27–33 mV/pC for

both solvents at a pH of 6 (for DOF) and 8 which corresponds to the theoretical Nernst's value for a double charged cation.

It can be seen from the obtained experimental data, that the best parameters (maximum range of operating concentrations of potentiometric sensors, the lowest detectable concentration (~5×10^{-6} mol/l) and the linearity of the calibration graph up to the concentration of 5.0×10^{-6} M) are observed for membranes with an inclination of the electrode function characteristic of a doubly charged cation under pH=6 and 8 and using of dibutyl phthalate as a membrane solvent and the content of the ionic associate is 0.17 % (0.01 g).

Accordingly, the optimal operating conditions of the potentiometric sensor for polysorbate-20 (linearity interval of the dependence $E=f(PC)$ from $5.0\cdot10^{-6}$ to $5.0\cdot10^{-3}$ mol/l with the slope of the electrode function $S\approx30$ mV/pC equal to the Nernst's value for doubly charged cations) are:

– m_{IA}=0.01 g (0.17 %);

– a solvent is dibutyl phthalate;

– pH=8.

In **Fig. 9** shows the dependence of the electrode potential of the developed potentiometric sensor for polysorbate-20 on the concentration of the test solution.

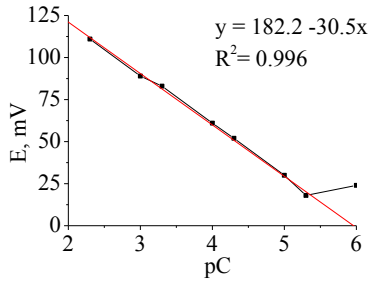

Fig. 9. The dependence of the electrode potential of the developed sensor on the logarithm of concentration (m_{1A}=0.01 g, solvent – DBF, pH=8)

It was experimentally established that the response time of the sensor is 30–50 s depending on the concentration of the test solution, the sensor's lifetime is ~50 days at stored dry and soaked for 10–15 minutes in a PS-Ba^{2+} solution with concentration $5.0\cdot10^{-5}$ mol/l.

5. Conclusions

The ion associate of the composition $(PS–Ba)_3(PMo_{12}O_{40})_2$ with Keggin structure has been synthesized. It was used as electrode active substances for the construction of polyvinyl chloride membranes of potentiometric sensors sensitive to polysorbate-20. The influence of various factors (the nature of the membrane solvent, the amount of associate in the membrane and the pH of a series of standard solutions) on the electrode characteristics (minimum detectable concentration, linearity interval, and sensitivity S**)** of the developed sensors was investigated. The optimum composition of the membrane of a potentiometric sensor and the conditions of its operation were selected (the content of the ion associate in the membrane is 0.17 %, a solvent is dibutyl phthalate and pH=8). The developed sensor can be used to determine the quantitative content of polysorbate 20 in various types of industrial products.

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Received date 24.06.2019
Accepted date 12.07.2019
Published date 31.07.2019