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Original Article

Determination of Optimum Conditions for Membrane Synthesis using Crown Ethers

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Abstract - *Based on hydroxyl-substituted mono-crown ethers, new bis-crown ethers have been synthesized. A perfect membrane for ion-selective electrodes based on crown compounds has been synthesized.*

A mathematical model of membranes synthesis for ion-selective electrodes has been developed. Based on the obtained mathematical model, synthesizing membranes for ion-selective electrodes was optimized, and the optimal regime condition for the synthesized membrane was determined. To determine the optimal parameters of the synthesized membrane, the Minitab 17 software package was used.

Keywords *- Synthesis, Membrane, ion-selective electrode, Model, Optimization.*

1. Introduction

The use of modern scientific equipment and instruments, in terms of their technical character of analogs corresponding or being superior to foreign analogs, should contribute to the solution of priority tasks,s for the development of science, technology, and technology. In this regard, the task was to improve ion-selective electrodes (ISE) characteristics using synthesized membranes. The electrochemical properties are the membrane for ion-selective electrodes isaref great practical importance. These devices with ion-selective electrodes have many advantages. They are easy to handle. Hcompositionstive, analyze liquids of different compositions. AseawatAseawatersis: natural waters, rainfall, seawater, ice, at the analysis of soils.

At present can be used to conduct medical and biological research, as well as analyzes carried out to determine the ionic composition of various environmental media [1].

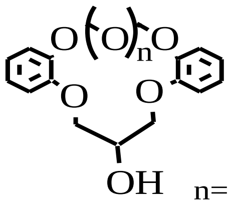
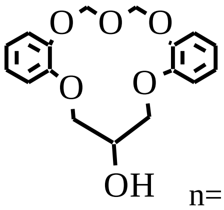
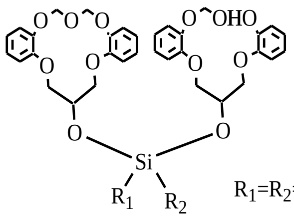
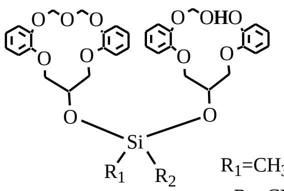
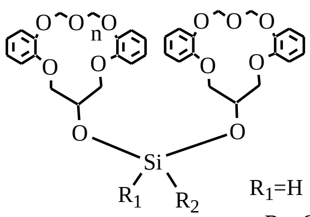
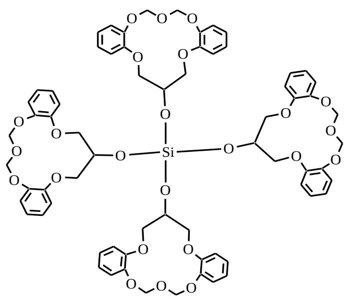
There are works [2-][3] where macrocyclic compounds were used as electrode-active elements. Ion-selective electrodes are the most promising among modern analyzes that allow you to quickly and with great accuracy determine small amounts of the concentration of metal ions, electrically neutral substances d ions [4][5]. Ion-selective electrodes that are selective for cations and anions are, first of all, integral electrochemical systems, where the potential depends on the processes of distribution of ions between the membrane and the solution, i.e., these are electrochemical electrodes that give a signal depending on the content of the measured ions in the solution [6][7]. The membrane-type does not affect the accuracy of the ISE indicators since the electrode works according to general patterns. However, the difference is revealed in the stages of the passage of the ion between the phase boundaries and within the membrane. Suppose the membrane is the boundary for separating two electrolyte solutions. In that case, the movement of specific ions occurs only in one direction - At preseIISEs can be used to conduct medical and biological research, as well as analyzes carried out to determine the ionic composition of various environmental media [1].

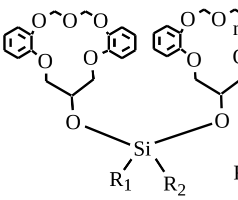
There are works [6][7] where macrocyclic compounds were used as electrode-active elements. Ion-selective electrodes are the most promising among modern analyzes that allow you to quickly and with great accuracy determine small amounts of the concentration of metal ions, electrically neutral substances, and anions [8][9]. Ion-selective electrodes that are selective for cations and anions are, first of all, integral electrochemical systems, where the potential depends on the processes of distribution of ions between the membrane and the solution, i.e., these are electrochemical electrodes that give a signal depending on the content of the measured ions in the solution [11] The membrane-type does not affect the accuracy of the ISE indicators since the electrode works according to general patterns. However, the difference is revealed in the stages of other passages of the ion between the phase boundaries and within the membrane. Suppose the membrane is the boundary for separating two electrolyte solutions. In that case, the movement of specific ions occurs only in one direction where the concentration of moving ions is the lowest. When dynamic equilibrium is reached at the phase boundary, a potential arises on the membrane surface with a value that helps prevent the subsequent movement of ions. A dynamic equilibrium is established on the membrane surface, at which the emerging potential corresponds to the value necessary to prevent further movement of ions [12][13].

2. Method and Discussion

Based on hydroxyl-substituted mono-crown ethers, new bis-crown ethers containing a silicon atom and an alkyl radical were synthesized [14]. Physico-chemical data of the obtained substances are shown in Table1.

Table 1. Physicochemical constants and elemental analysis data compounds (I-VII)

№	Crown ether structures	Exit %	T.mt ^{0}C	Found,% C	Found,% H	Found,% Si	Gross formula
I	 n=1	27	116	65.88	6.40	-	$C_{19}H_{22}O_6$
II	 n=2	25	135	64.60	6.71	-	$C_{21}H_{26}O_7$
III	 $R_1=R_2=CH_3$	98.15		64.15	6.46	3.75	$C_{40}H_{48}O_{12}Si$
IV	 $R_1=CH_3$ $R_2=CH_2=CH$	97.85	7-168	64.71	6.35	3.69	$C_{41}H_{48}O_{12}Si$
V	 $R_1=H$ $R_2=CH_3$	98.35	155-156	63.72	6.31	3.82	$C_{39}H_{46}O_{12}Si$
VI		98.6	280-284	64.76	6.00	1.99	$C_{76}H_{84}O_{24}Si$
VII		98.3	165-166	63.14	6.74	3.35	$C_{44}H_{56}O_{14}Si$

	 R$_1$=R$_2$=CH$_3$						

Potassium-selective polyvinyl chloride membrane electrodes based on silicon-containing bis(dibenzo-16-crown-6) ethers (III-VII) were prepared with the expectation of high electrochemical selectivity from these electrodes under operating conditions. The electrode properties of potassium selective electrodes based on crown ethers are given in Table 2.

Table 2. Electrode Properties of Potassium Selective Electrodes Based on Crown Ethers

crown ethers	plasticity-tori	Max slope mv/decade	Interval pK+	mula	K_{K^+/M^+}			
				Na^+, mcg/ml		NH_4^+, mcg/ml	Rb^+, mcg/ml	Cs^+, mcg/ml
bis-crown-ether (III)	o-nitrophenyl octyl ether	62	7-2	2.5×10^{-5}		2×10^{-2}	3.4×10^{-2}	3.6×10^{-2}
	dibutyl phthalate	58	3-1	1.2×10^{-3}		1.3×10^{-2}	1.1×10^{-1}	1.1×10^{-1}
bis-crown-ether (III (IV)	o-nitrophenyl octyl ether	56	6-2	8.2×10^{-4}		3.5×10^{-2}	4.1×10^{-2}	4.8×10^{-2}
	dibutyl phthalate	57	6-2	7.1×10^{-4}		3.8×10^{-2}	4.3×10^{-2}	4.4×10^{-2}
bis-crown-ether (III (V)	o-nitrophenyl octyl ether	51	5.5-1.5	6.5×10^{-4}		2.5×10^{-2}	8.7×10^{-2}	9.2×10^{-2}
	dibutyl phthalate	44	5.5-1,5	4.2×10^{-4}		2.1×10^{-2}	4.8×10^{-2}	6.4×10^{-2}
Mono-macro-cyclic crown ether (VI	o-nitrophenyl octyl ether	27	5-1.5	5.7×10^{-3}		7×10^{-5}	2.4×10^{-1}	2.7×10^{-1}
	dibutyl phthalate	18	5-1.5	4.2×10^{-3}		8.4×10^{-2}	2.5×10^{-1}	2.8×10^{-1}
valino mycin	o-nitrophenyl octyl ether	52	5.5-1,5	9.5×10^{-5}		2.2×10^{-2}	8.3×10^{-1}	8.8×10^{-1}
	dibutyl phthalate	50	5.5-1,5	$8.4\times10^{-}$		1.7×10^{-2}	6.8×10^{-1}	7.8×10^{-1}
Crown ether(VI)	o-nitrophenyl octyl ether	41	6-2	5×10^{-3}		1.5×10^{-2}	8×10^{-1}	8.4×10^{-1}
	dibutyl phthalate	39	6-2	6×10^{-3}		1.3×10^{-2}	7.5×10^{-1}	8.7×10^{-1}
Bis Crown Ether(VII)	dibutyl phthalate	50	6-2	8.4×10^{-4}		8.7×10^{-3}	7.7×10^{-2}	7.5×10^{-2}

One of the important characteristics of an ion-selective electrode is its response time (table 3).

Table 3. Response time of ion-selective electrodes based on crown compounds (III - VII)

crown ether	III	IV	V	VI	VII
Response time, sec	10	40	45	90	50

In this regard, it is important to study the improvement of the optimal parameters for the synthesis of the membrane for the electrode. At present, it is difficult to name a field of science the success of which would not be associated with the use of computer technology. At present, the use of computer technology in conducting various studies in the field of chemistry and chemical technology has become a prerequisite. It is mainly due to decreased transition time from laboratory research to industrial implementation. In this regard, the automation and planning of the experiment and the processing of the obtained data play a special role. To this end, we have carried out the following actions:

1. compiled a planning matrix for conducting experimental studies;
2. determined the coefficients of the regression equations;
3. checked the reliability of the obtained quantitative information;
4. checked the adequacy of the obtained regression model for the technological process

To fulfill these goals, it is necessary to determine the optimization criterion (U) [15][16][17][18]. Establishing the order of the measured process parameters and defining the regression model variables is also necessary. Next, find out the degree of influence of technological parameters. The goal of the multifactorial design of an experiment is the optimal design, which will allow one to study the quantitative applications of all technological parameters of synthesis that affect the synthesis of membranes for an ion-selective electrode. The result of planning an experiment is the possibility of establishing the degree of interaction between the parameters and reducing the total number of experiments to a sufficient extent.

3. Results

When researching and planning an experiment, the regression equation based on experimental data is described as follows (separation of the Taylor series).

$$y = b_0 + \sum_{j=1}^{N} b_j \cdot x_j + \sum_{\substack{U,j=1 \\ U\neq j}} b_{U,j} \cdot x_U \cdot x_j + \sum_{j=1}^{N} b_{jj} \cdot x_j^2 + \cdots \quad (1)$$

where b_0 - free term of the regression equation; bj - linear effect; B JJJ- square effect; $b_{U,j}$- - pair interaction effects.

The following indicators were chosen as the main factors affecting the deviation time (mg):

m(X1) amount of polyvinyl chloride (PVC); w(X2) is the number of crown ethers (C.E.); v(X3) is the amount of dibutyl phthalate plasticizer (PDBP).

The main levels for the factors are summarized in Table 4.

Table 4. Basic levels for factors

Designation	m	w	v
factors	X_1	X_2	X_3
Top-level+1 basic level 0 lower level -1	300 200 100	15 10 5	600 500 400

For example, according to the orthogonal central compositional plan of the 2nd order for a three-factor process, it is necessary to conduct experiments on the planning matrix presented in Table 4.

In the process we are studying, the number of factors is n=3.

After optimizing the composition of the ion-selective electrode membrane, the response time noticeably decreased. For example, the response time of ion-selective electrodes based on crown compounds (III) decreased from 10 to 6.3 seconds.

To determine the optimal parameters of the synthesized membrane for the electrode, the Minitab 17 software package for processing static data was used.

On fig. 1 shows the influence of various factors on the qualitative properties of the membrane.

Based on the Minitab 17 software package, it was found that factors such as the amount of polyvinyl chloride, crown ethe, s, and dibutyl phthalate plasticizer simultaneously affect the properties of the membrane.

Where: ПВХ-PVC, КЭ-CE, ПДБФ- dibutyl phthalate.Approximation confidence level,%

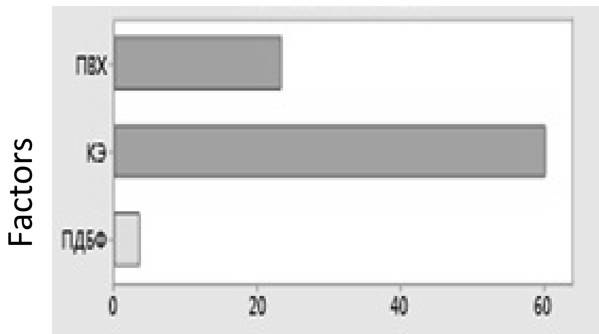


Fig. 1 Approximation confidence level

As can be seen from Fig. 1, the properties of the membrane are slightly affected by the plasticizer dibutyl phthalate, while crown ether significantly affects the properties of the electrode membrane.

R2the the corrected value of approximation reliability Fig. 2 shows the dependence of the influence of the amount of PVC and C.E. on the deflection that the

The 2 – the corrected value of approximation reliability

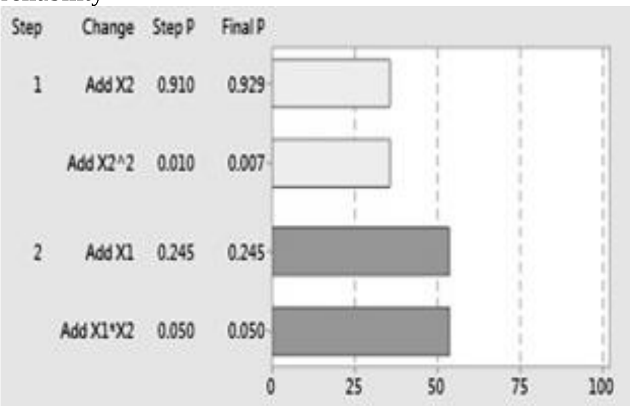


Fig. 2 Dependence of the influence of the amount of PVC and C.E. on the deflection time

The influence of the amount of PVC and C.E. on the deflection time was also studied (Fig. 3)

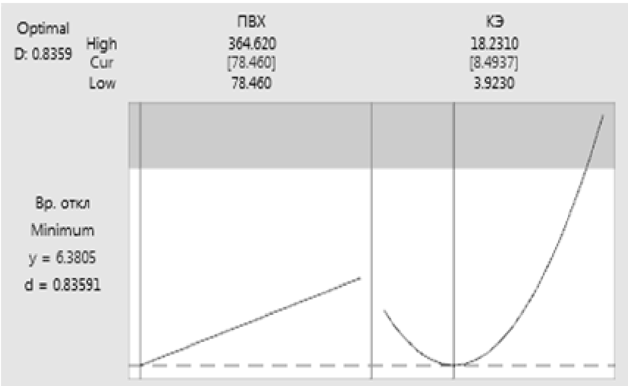


Fig. 3 The optimal value of the deviation time (s) depends on the amount of PVC and C.E., mg

The data obtained (Fig. 3) indicate the following direct relationship: the deflection time increases with an increase in the amount of PVC. At the same time, the number of crown ethers of the E.C. is dependent on the deflection time. When considering the obtained dependence, it can be seen (Fig. 2) that with an increase in the number of E.C. from 2 to 7 mg, the deviation time decreases, and after 7 mg, it increases. Thus, the optimal value of the deflection time was obtained under the following conditions for PVC and C.E. (Fig. 3).

Accordingly, the influence of PVC, C.E., and dibutyl phthalate on the deflection time was also studied (Fig. 4). The dependence of the quantity of C.E. codebases database based on regression analysis. As you can see, all points of this dependence are on a straight line.

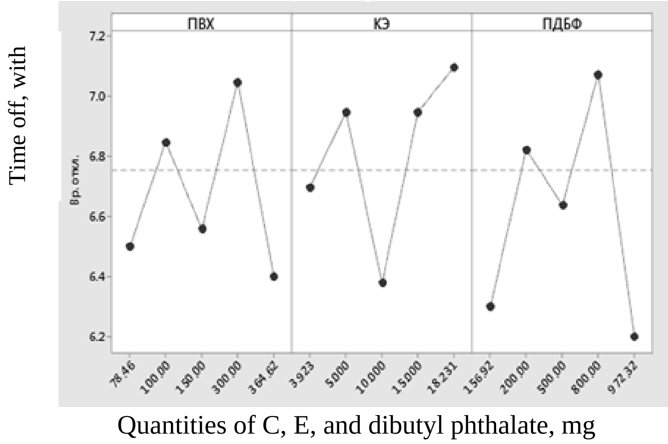


Fig. 4 Dependence of the deviation time (s) on the amount o,f,   C E, and dibutyl phthalate (mg).

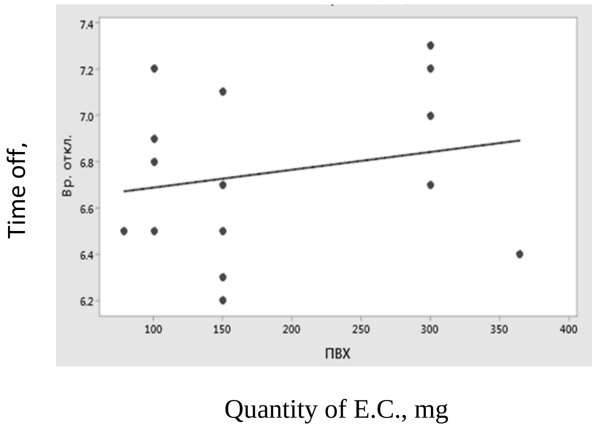


Fig. 5 Dependence of the value of the deviation time, cells of the amount of PVC and C.E., mg

As can be seen (Fig. 5), the optimal value of the deflection time (6.3 seconds) is obtained with the amounts of PVC - 150 mg and E.C. - 10 mg.

4. Conclusion

The development of new technologies and products of scientific instrumentation will entail the growth of science-intensive industries, providing our scientists with modern instrumentation and increasing the technical equipment of labor, accelerating the development of the scientific and innovative performance jobs, and increasing the investment attractiveness of our country, which has science-intensive technologies for the production of high-tech equipment.

Taking as a basis the developed model (2) of the process of synthesizing membranes for ion-selective electrodes using the "Minitab17" program, the optimal regime condition for the synthesized membrane for ion-selective electrodes was found.

The optimal output parameter (deviation time) was Y = 6.38 s. The values of the synthesis parameters that ensure the optimality of this condition are as follows

$$X_1(pvc)=78.46 \text{ mg}$$
$$X_2(ce) = 8.49 \text{ mg}$$

And the amount of X3 dibutyl phthalate does not significantly affect the deviation time.
The experiments carried out under the found optimal regime conditions fully confirmed the reliability of the results obtained.

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