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### **Application of composite materials based on polyvinyl alcohol in phytoremediation soil**

Oil production, transportation, transshipment and storage lead to accidental soil pollution with oil products. To solve this problem, the researchers proposed the possibility of using polymer films for the rehabilitation of oil-contaminated soils. In the present work, in order to clean the soil from oil products, films based on polyvinyl alcohol and chitosan were obtained, their main physical and mechanical properties were investigated. The results of IR spectrometric analysis showed good compatibility of the starting components. It was found that the films obtained possess rather high indices of mechanical strength. Moreover, films containing 80 % synthetic polymer — PVA showed the highest mechanical properties. The latter is apparently associated with the formation of a network of intermolecular hydrogen bonds between chitosan and PVA, which favorably affects their operational characteristics. Pollution modeling was carried out by applying oil to the soil of the Karazhanbass field. The resulting films based on polyvinyl alcohol and chitosan were used as recultivates, which were applied in concentrations of 0.2 g/kg of soil. The effectiveness of remediation of oil-contaminated soils was evaluated by measuring the content of oil products and conducting phytotests of the studied soil samples. The results of the assessment of the degradation of oil products in the process of reclamation and the phytotesting indicators obtained in the dynamics of the experiment allow us to conclude the effectiveness and feasibility of using polymer films based on polyvinyl alcohol and chitosan to clean oil-contaminated soils.

*Keywords:* polyvinyl alcohol, chitosan, glycerol, polymer films, oil-contaminated soils, oil products, phytoremediation, remediation.

#### *Introduction*

Soil belongs to the most important natural resources, the state of which mostly provides the ecological equilibrium of the planet. The main characteristic of the soil is fertility, which is formed by the microorganisms' activity. Economic activity contaminates oil, that leads to a decreasing in economic and potential fertility [1]. Soil pollution by oil and oil products is currently an actual problem. Oil production from the bowels, processing and transportation are not only technically difficult, but also dangerous processes, since it is impossible to preserve the natural environmental conditions during field development. Inevitably, each stage of oil production is accompanied by an oil leak, which can cause irreparable phenomena. Chronic oil spills pose a serious threat to the environment and human health [2].

Restoration of the environment with the help of plants is of wide interest due to the opportunities that this technology opens up in the cleaning of contaminated areas. Over the past decade, phytoremediation has become very popular, as this technology is much cheaper than methods based on the application of technology, and is also used directly in the area of pollution [3].

The purpose of this work is to study the possibility of using composite materials based on polyvinyl alcohol and chitosan for purification of oil-contaminated soil in the process of phytoremediation.



### Experimental

In our work we used polyvinyl alcohol (PVA) with molecular weights 72,000 and 145,000 kDa, chitosan (CT) produced by «Fluka Chemie GmbH» (Switzerland), acetic acid and glycerin from «SCAT» (Kazakhstan) without additional purification. The synthesis of polyvinyl alcohol and chitosan copolymers is described in work [4]. In this article, initial polymer solutions are prepared in advance to obtain films based on a mixture of polyvinyl alcohol and chitosan. To do this, in distilled water, the PVA suspension is dissolved at a temperature of 70–75 °C, the chitosan suspension is dissolved in acetic acid at room temperature. After complete dissolution of chitosan, a cooled PVA solution was introduced into the solution with constant stirring to homogenize the solution. After a certain time, continuing mixing, glycerin was added as a plasticizer. Before molding, the resulting solution was kept at room temperature for 10 to 12 hours for de-airing and stabilization. The films were formed in Petri dishes by evaporation of the solvent at room temperature for 1–2 days under the drying cabinet. The mass of the films was 7–8 g. The films were obtained at different ratios of polyvinyl alcohol/chitosan — 20:80; 50:50 and 20:80 wt.%.

Organic solvents (acetone, ethyl alcohol, benzene, a mixture of alcohol: benzene in a 1:1 ratio) and distilled water were used to study the solubility of films.

The IR spectra of the obtained films were recorded on an IR spectrometer with a Fourier Converter («LOMO», Russia).

The mechanical properties of the films (tensile strength) were studied on a discontinuous machine «TEXTURE ANALYSER» (UK) with a break rate of 10 mm/min, with a force of 20,000 kg.

To study the phytoremediation process, the experiment was carried out under laboratory conditions in 500 ml polyethylene cups filled with oil-contaminated soil (the oil content was 15g/500g, 30g/500g, 45g/500g % of the total mass). In the experiment we used the oil from the Karazhanbas field.

To determine the oil content in the soil, we used the extraction method on the Soxhlet apparatus. Extraction of petroleum hydrocarbons from contaminated soil samples were performed after 60 days of their interaction with each other. Benzene was used as a solvent. The flask with the solvent is heated to the boiling point of the solvent, the vapors of which enter continuously into the cooler, into the ground mixture, dissolve the hydrocarbon part and secrete from the mixture. After filling the extraction flask with a siphon tube, the solvent flows in enters the flask. Before the solvent color is lost, the organic part is extracted. The sample from the extractor is dried in a drying cabinet to a constant mass at a temperature of 60–70 °C. The mixture of the organic part of the solvent and the oil residue is separated by simple distillation here.

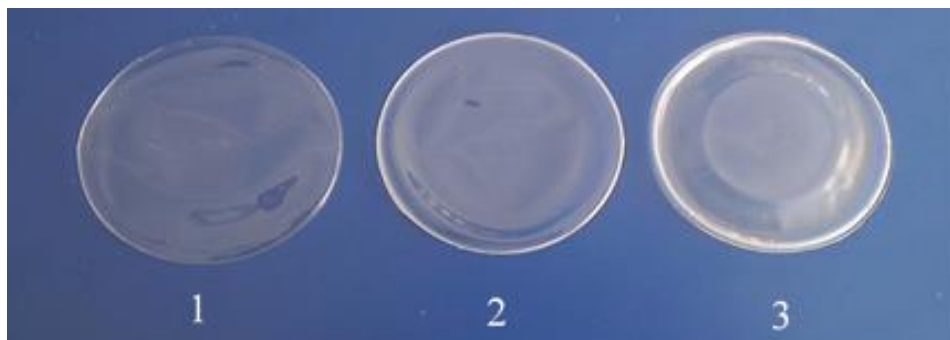
### Results and Discussion

Hydrophilic polymers, which include polyvinyl alcohol (PVA), are widely used in medicine, biochemistry, biotechnology. The possibility of their modification, including by mixing with other polymers, contributes to the expansion of areas and efficiency of application of hydrophilic polymers. The most promising are mixtures of PVA with the natural polysaccharide chitosan, which can be obtained in the form of films from a common solvent. It is established that this leads to an increase in the stability of the films, improves their physical and mechanical parameters, etc.

In the proposed work, films based on polyvinyl alcohol and chitosan are obtained by mechanical mixing of specified ratios of components, glycerin is used as a plasticizer. The ratio of the initial polymers was varied in the preparation of films. Thus, films with the content of PVA/CT = 20:80, 50:50 and 20:80 wt.% were obtained, the uniformity and transparency of which indicates the compatibility of the original components. Moreover, an increase in the chitosan content in the initial polymer mixture affects the transparency: less transparent films are formed. Pictures of the films are shown in Figure 1.

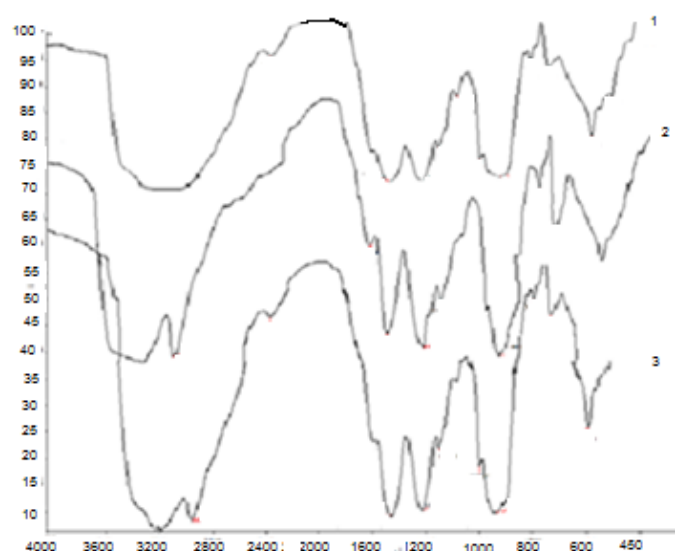
The compatibility of the initial components is indicated by the IR spectra of films based on PVA/CT, presented in Figure 2 and in which you can see the presence of the composition of the two components of the film. It is known that absorption bands of NH<sub>2</sub>-groups are present on the IR spectra of chitosan, as well as absorption bands characteristic of the polysaccharide structure at 1,050 cm<sup>-1</sup> and 851 cm<sup>-1</sup> [5]. Intense fluctuations at 1,645 cm<sup>-1</sup> and at 1,565 cm<sup>-1</sup>, characteristic of the amide groups, indicates that the initial chitosan has a high degree of deacetylation. In the spectra of PVA/CT mixtures, there are changes in the position and intensity of the absorption bands: the presence of a weak absorption band of the carbonyl C=O group at 1,735 cm<sup>-1</sup> in the PVA spectrum indicates that part of the OH groups of the polymer is acetylated during dissolution in acetic acid solution. Judging by the low intensity of this band and the high intensity of the OH-group band (947 cm<sup>-1</sup>), the degree of acetylation is very insignificant. An increase in the chitosan content in the mixture

causes a gradual shift of the absorption band C=O of the PVA groups at  $1,735\text{ cm}^{-1}$  (this band is absent in the chitosan film) to the lower frequencies. This may suggest a possible interaction between the C=O groups of partially acetylated PVA and the active groups of chitosan. From the analysis of IR spectra, it follows that the interaction of polyvinyl alcohol and chitosan leads to molecular interaction between the hydroxyl groups of alcohol macromolecules and the amide groups of chitosan, and hydrogen bonds are formed according to the scheme below.



1 — 80:20; 2 — 50:50; 3 — 20:80 wt.%

Figure 1. Films based on PVA/CT at different ratios of the initial components



PVA/CT: 1 — 20:80; 2 — 50:50; 3 — 80:20 wt.%;  $M_w[\text{PVA}] = 145,000$

Figure 2. IR spectra of films based on PVA/CT

The solubility of these films in distilled water and in organic solvents was studied. The dissolution process was carried out at room temperature for 24 hours. This study showed that films based on PVA/CT in organic solvents such as acetone, ethyl alcohol, benzene, alcohol-benzene mixture, do not dissolve in distilled water organic solvents. This is probably due to the impossibility of breaking the bonds between the polymers in the macromolecule. Since organic solvents are unable to break the bonds of polymer macromolecules in the model. While these polymers are dissolved in distilled water during the day due to the processes of solvation and hydration. The effect of the molar mass of PVA on the solubility of films based on PVA/CT was established. Thus, films with a molecular weight  $MW(\text{PVA}) = 72,000$  are dissolved within 18 hours, and the solubility of films based on PVA with a molecular weight of 145,000 is 24 hours (Table 1).

**Results of mechanical stretching of the films of PVA/CT**

Parameter	Film ratio = PVA/CT, wt.%					
	20:80		50:50		80:20	
$M_w$ (PVA)	72,000	145,000	72,000	145,000	72,000	145,000
Pressure, MPa	37.44	61.78	22.21	33.76	57.60	29.47
Stretching, %	4.63	18.95	47.32	40.37	116.75	198.12
Young's modulus, kPa	1.9±5	1.4±5	2.3±5	2.0±5	2.9±5	2.9±5

The mechanical properties of the obtained films were investigated. All obtained films have good mechanical strength. An increase in chitosan content leads to a decrease in elongation and an increase in the modulus of elastic, and as a result, to an increase in brittleness. The highest rates of mechanical parameters were shown by films containing 80 % synthetic polymer — PVA. The latter is apparently due to the formation of a grid of intermolecular hydrogen bonds between chitosan and PVA.

The issues of remediation of oil-contaminated soils are relevant in connection with the rapid development of oil and gas industry and infrastructure [6]. Increasing oil production continues to increase the risk of soil contamination with oil. Every year, oil-contaminated areas expand, and land used for agriculture and forestry remains unusable. Due to the high adsorption, oil can be observed in the soil for a long time, shifting the soil balance from the equilibrium level. Plants are the key contributor to the high fertility of the soil. However, unfavorable growing conditions on oil-contaminated soils of any plants, excludes the possibility of cleaning such soils by phytoremediation. Natural polymers are not xenobiotics and their use is the most environmentally and economically rational for exosystems. Their low cost and simple preparation technology together with high performance properties make it possible to effectively clean the soil from oil products.

Chitosan is a natural biopolymer, an aminopolysaccharide, which has no pronounced substrate specificity, which means approximately the same ability to bind both hydrophilic and hydrophobic compounds. Chitosan has ion-exchange, chelation-forming and complex-forming properties [7]. Chitosan is similar in composition to nonspecific organic compounds of soils, this eliminates the possibility of a negative impact on the processes of decomposition, synthesis of organic compounds, humus formation.

We studied for the first time the possibility of using synthetic films based on PVA/CT for soil detoxification with simultaneous planting of technical crops.

Modeling of biodegradation of oil products was carried out at temperatures of about 25–30 °C, simulating the temperature regimes of the summer months in Atyrau, Mangistau and West Kazakhstan regions. The soil selected within Almaty was subjected to researches. Soil sampling was carried out in accordance with State Standard 7.4.3.01–831. The soil was freed from stones and roots of plants, dried in the absence of sunlight to an air-dry state, sifted and placed in open containers. Pollution modeling was carried out by means of introduction of oil of the Karazhanbas field into the soil and according to gradation of soils on degree of pollution with oil products (OP) developed by V.S. Khomich [8], introducing oil before achievement of mass concentration of oil products in the soil of 15g/500g, 30g/500g, 45g/500g that corresponded to the category «very strongly polluted soils». The effectiveness of remediation of soils contaminated with oil products was estimated by measuring the content of oil products and phytotesting of studied soil samples.

Phytotesting is based on the sensitivity of plants to exogenous chemical effects, which affects the growth and morphological functions of test cultures. Dry seeds of the selected test cultures were placed at intervals of 1 cm in polyethylene cups (with mixed and moistened soil samples). As a control, samples of the studied soil without the introduction of oil products were used. As indicators of the phytotest, test functions of the height of seedlings were adopted.

The dynamics of changes in the concentration of oil products was evaluated by the method of their extraction from contaminated soils. The analysis of quantitative composition of hydrocarbons of the Karazhanbas oil was carried out on the soxlet apparatus. Analysis of changes in oil content in the studied soil samples showed that during the first two weeks, the level of oil dropped significantly compared to the original values as in the control sample (to 25.6 %) and in samples containing OP, which is obviously related to the first phase of degradation of oil products evaporation of light fractions and photooxidation. At the same time, in soil samples containing films based on PVA/CT, the loss of oil products on day 14 was 36.0 %.

After 14 days of the experiment, the achieved concentration of petroleum products in the control soil sample (which does not contain petroleum products) remained almost unchanged until the end of the

experiments. In soil samples with films, there is a decrease in the concentration of petroleum products. This, apparently, indicates the end of the process of degradation of petroleum products in these conditions.

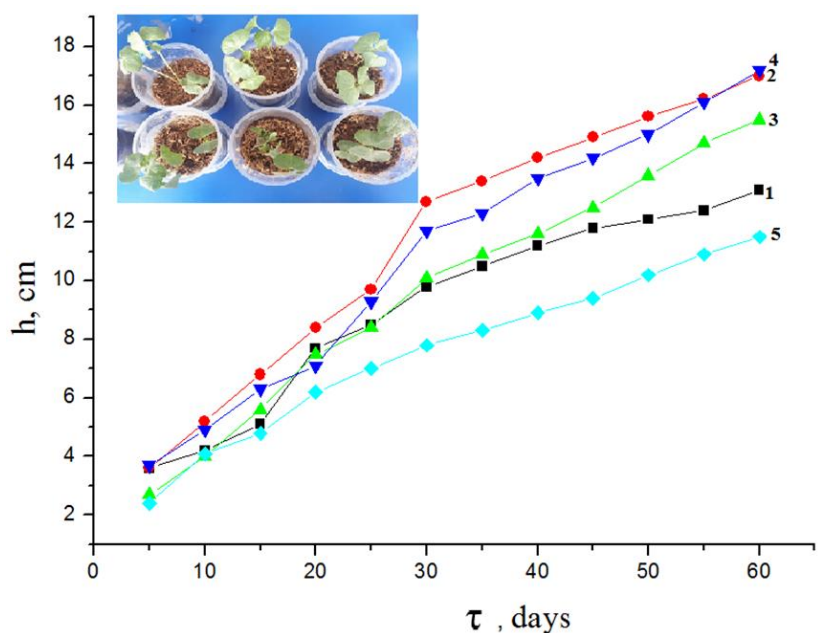
In soil samples with the addition of films based on PVA/CT, the dynamics of reducing the concentration of oil products up to 21 days was approximately 40 %. It can be noted that the degradation of oil hydrocarbons was accelerated by films based on PVA/CT, increasing the efficiency of soil purification from oil products in comparison with the self-cleaning ability of the soil, the level of which was 25.6 %. In addition, the work assessed the degree of soil purification from oil products. The data are presented in Table 2.

Table 2

**The purification degree of soils contaminated with oil**

Concentration of oil products in soil samples, g/500g	Polymer concentration, g	Purification degree, %
15	0.1	86.9
30	0.1	82.3
45	0.1	78.7

In the process of transformation of oil products, intermediates are formed, which no longer fall under the definition of «oil products» and are not taken into account in the gross definition of OP. At the same time, these compounds can have a significantly greater toxic potential and have a positive ecotoxic effect. Carrying out ecotoxicological phytotesting in addition to the instrumental method of assessing the content of OP in the process of remediation allows to quickly and fully assess the environmental quality of the soil environment [9]. Assessment of soil samples by indicators of test functions of test crops Figure 3 established the effectiveness of using films based on PVA/CT as recultivants to reduce the level of oil pollution in the studied soil samples.



1 — soil; 2 — soil with films; 3 — 15g/500g; 4 — 30g/500g; 5 — 45g/500g

Figure 3. Length of test plant seedlings in soil samples

According to the results of the study, the indicator «seedling length» for control soil samples without films after 60 days was 10 cm in the case of reclamation of soil samples using films without refining waste, the length of the seedling on day 60 of the study reached 17 cm after 60 days, the least phytotoxic effect (along the length of the seedling) was observed for soil samples using films based on PVA/CT with a maximum content of OP.

The maximum length of the seedling is typical for soil samples uncontaminated by oil waste containing films based on PVA/CT. Slightly different indicators for soil samples contaminated with oil products.

Probably, due to the presence of free amino groups in the macromolecule of the polymer, chitosan effectively clears the soil, which is explained by the process of complexation of oil products by amino groups, with the formation of polynuclear compounds. Also because of the abundance of hydrogen bonds between chitosan molecules — not soluble in water, but swells in organic acids, in the swollen state is able to firmly hold various intoxicants (pollutants).

The studies suggest that films based on polyvinyl alcohol/chitosan will be widely used in solving the problems of cleaning soils contaminated with oil products. When PVA/CT films are introduced into the soil as a remediant, they do not need to be collected and disposed of, as they are capable of undergoing enzymatic degradation, increasing the level of natural soil carbon.

### Conclusions

We obtained films based on polyvinyl alcohol and chitosan. By IR spectroscopy it is shown that polyvinyl alcohol and chitosan form a mixture stabilized by a hydrogen bond. It is established that with increasing content of polysaccharide in the composition of the film, their strength properties decrease. The results of the assessment of degradation of oil products in the process of reclamation and phytotesting indicators obtained in the dynamics of the experiment allow us to conclude about the effectiveness and feasibility of using polymer films based on polyvinyl alcohol and chitosan as recultivants of oil-contaminated soils.

### Acknowledgment

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## Поливинил спирті негізіндегі композициялық материалдарды топырақ фиторемедиациясында қолдану

Мұнайды өндіру, тасымалдау, ауыстырып тиеу және сақтау топырақтың мұнай өнімдерімен авариялық ластануына әкеп соғады. Осы мәселені шешу барысында зерттеушілер мұнаймен ластанған топырақты қалпына келтіру үшін полимерлі үлдірлерді қолдану мүмкіндігін ұсынған. Мақалада топырақты мұнай

өнімдерінен тазартуда қолдану мақсатында поливинил спирті мен хитозан негізінде үлдірлер алынған, олардың негізгі физика-механикалық қасиеттері зерттелген. Зерттеуде ИК-спектрометриялық талдау нәтижелері бастапқы компоненттердің жақсы үйлесімділігін көрсетті. Алынған үлдірлер жоғары механикалық беріктік көрсеткіштерге ие екені анықталған. Сонымен қатар, механикалық параметрлердің барынша жоғары көрсеткіштерінің құрамында 80 % синтетикалық полимер-ПВС бар екенін үлдірлер көрсетті. Бұл жағдай хитозан мен ПВС арасындағы молекулааралық сутегі байланыстары торының түзілуімен байланысты болуы мүмкін, бұл олардың қолданылу сипаттамаларына жағымды әсер етеді. Ластануды модельдеу Қаражанбас кен орнының мұнайын топыраққа енгізу арқылы жүргізілді. Поливинил спирті мен хитозан негізіндегі алынған үлдірлер 0,2 г/кг топырақ концентрациясына енгізілген рекультивант ретінде қолданылды. Мұнаймен ластанған топырақты ремедиациялау тиімділігі мұнай өнімдерінің құрамын өлшеу және зерттелетін топырақ үлгілерін фитотестілеуді жүргізу барысында бағаланды. Қайта құнарландыру процесінде мұнай өнімдерінің ыдырауын бағалау нәтижелері және эксперимент динамикасында алынған фитотестілеу көрсеткіштері поливинил спирті мен хитозан негізіндегі полимерлі пленкаларды мұнаймен ластанған топырақты тазалау үшін пайдаланудың тиімділігі мен орындылығы туралы қорытынды жасауға мүмкіндік береді.

*Кілт сөздер:* поливинил спирті, хитозан, глицерин, полимерлі үлдірлер, мұнаймен ластанған топырақ, мұнай өнімдері, фиторемедиация, ремедиация.

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### Применение композиционных материалов на основе поливинилового спирта в фиторемедиации почв

Добыча, транспортировка, перевалка и хранение нефти приводят к аварийным загрязнениям почв нефтепродуктами. При решении данной проблемы исследователями рассматривалась возможность применения полимерных пленок для рекультивации нефтезагрязненных почв. В настоящей работе с целью очистки почвы от нефтепродуктов получены пленки на основе поливинилового спирта и хитозана, исследованы их основные физико-механические свойства. Результаты ИК-спектрометрического анализа показали хорошую совместимость исходных компонентов. Обнаружено, что полученные пленки обладают достаточно высокими показателями механической прочности. Причем максимально высокие показатели механических параметров показали пленки, содержащие 80 % синтетического полимера — ПВС. Последнее, видимо, связано с образованием сетки межмолекулярных водородных связей между хитозаном и ПВС, что благоприятно влияет на их эксплуатационные характеристики. Моделирование загрязнения проводилось посредством внесения в почву нефти Каражанбасского месторождения. Полученные пленки на основе поливинилового спирта и хитозана использовали в качестве рекультивантов, которые вносились в концентрации 0,2 г/кг почвы. Эффективность ремедиации загрязненных нефтью почв оценивалась в ходе измерения содержания нефтепродуктов и проведения фитотестирования исследуемых образцов почв. Результаты оценки деградации нефтепродуктов в процессе рекультивации и показатели фитотестирования, полученные в динамике эксперимента, позволяют сделать вывод об эффективности и целесообразности использования полимерных пленок на основе поливинилового спирта и хитозана для очистки нефтезагрязненных почв.

*Ключевые слова:* поливиниловый спирт, хитозан, глицерин, полимерные пленки, нефтезагрязненные почвы, нефтепродукты, фиторемедиация, ремедиация.

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## N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine synthesis and structure

New stilbene fulleropyrrolidine has been synthesized by C<sub>60</sub> fullerene triple-component condensation with sarcosine and trans-4-stilbene carboxaldehyde in Prato reaction conditions. It was demonstrated that primary factor having influence on this reaction *final* product yield is the homogeneity of the reaction medium. The highest yield of N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine is observed when reaction performed in xylene and reactive medium is heated. Synthesized compound structure has been studied by IR-, UV-, NMR <sup>1</sup>H and <sup>13</sup>C spectroscopy as well as by two-dimensional COSY (<sup>1</sup>H-<sup>1</sup>H) and HMQC (<sup>1</sup>H-<sup>13</sup>C) spectra data. The purity and individuality of obtained fulleropyrrolidine have been evaluated using HPLC analysis. N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine synthesis proceeds by the 1,3-dipolar addition to fullerene C<sub>60</sub> mechanism through formation of active azomethinilides. N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine and poly-N-vinylpyrrolidone water-soluble complex has been obtained in dichloromethane. It was shown that complex formation is outcome of fulleropyrrolidine solubilization by PVP chains and lactamic group physical interaction with the fullerene sphere.

**Keywords:** fullerene C<sub>60</sub>, trans-4-stilbencarboxaldehyde, sarcosine, fulleropyrrolidine, Prato reaction, NMR specters, poly-N-vinylpyrrolidone, three-component condensation.

### Introduction

Nowadays biological properties of fullerenes and their functional derivatives are massively researched for the purpose of creating new pharmaceuticals and biomaterials based on them. Compounds found among fullerene derivatives possess various types of pharmacological activity. The development of C<sub>60</sub> fullerene functionally substituted derivatives synthesis methods is essential for creating new materials and obtaining biologically active substances. Fulleropyrrolidine derivatives obtained through Prato reaction are some of the most promising for this purpose within the wide range of derivatives known today. This way, natural fullerene-containing aminoacid derivatives, such as fulleropyrrolidineglutamine acid and fulleroproline, have been synthesized. Some biologically active peptides and other derivatives advantageous for use in medicine and engineering have been obtained based on them [1–3].

A highly promising fulleropyrrolidine research area is the study of pyrrolidine scaffold containing new «pharmacophoric» groups [4]. One of such «pharmacophoric» groups is stilbene fragment, as stilbene (1,2-diphenylethylene) functional derivatives are widespread in plant life and have been used in traditional medicine for a long time [5–8]. These compounds' (as well as other arylpolyenes) electronic structure peculiarities provide strong physiological activity and valuable physical-chemical properties for their molecules. Synthetic stilbenoids with various functions and stilbenoid-containing polymers are used for the production of laser dyes, sensors, light-sensitive markers and composite materials [9]. Stilbenoids show antioxidant, anticarcinogenic, antibacterial and other therapeutic activities. Due to high derivative pharmacological activity stilbene fragment is considered as one of privileged structure blocks while creating pharmacologically important substances [10, 11]. However, compounds containing both stilbene fragment and fullerene sphere are not sufficiently researched.

### Experimental

NMR <sup>1</sup>H and <sup>13</sup>C (DMSO-d<sub>6</sub>) spectra were registered at JNM-ECA Jeol400 spectrometer (399.78 and 100.53 MHz respectively) regarding deuterated solvent carbon residual protons or atoms signals. IR spectra (KBr) were registered at Nicolet 5700 spectrometer. The reaction progress and the identity of the synthesized



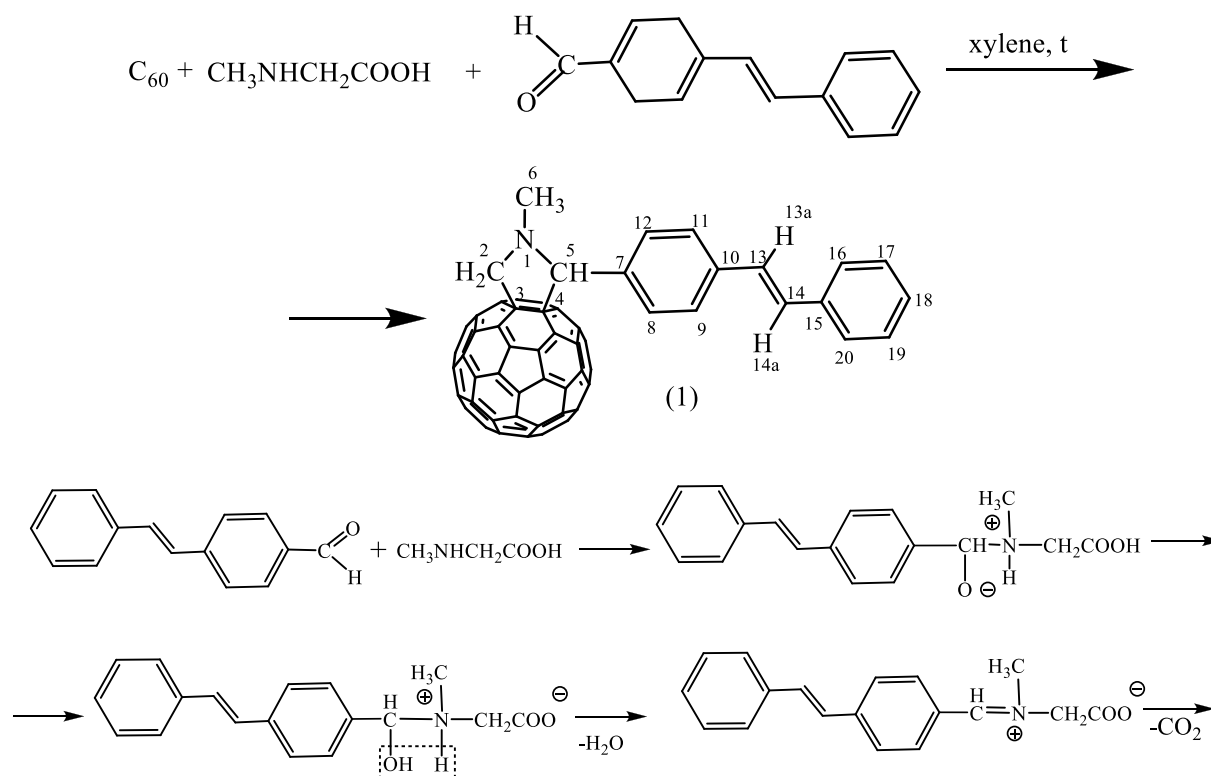
compounds were monitored by TLC on Sorbfil plates (Russia). Plates development was done in isopropyl alcohol — ammonia (25 % in water) — water (7:2:1), treatment by iodine vapor.

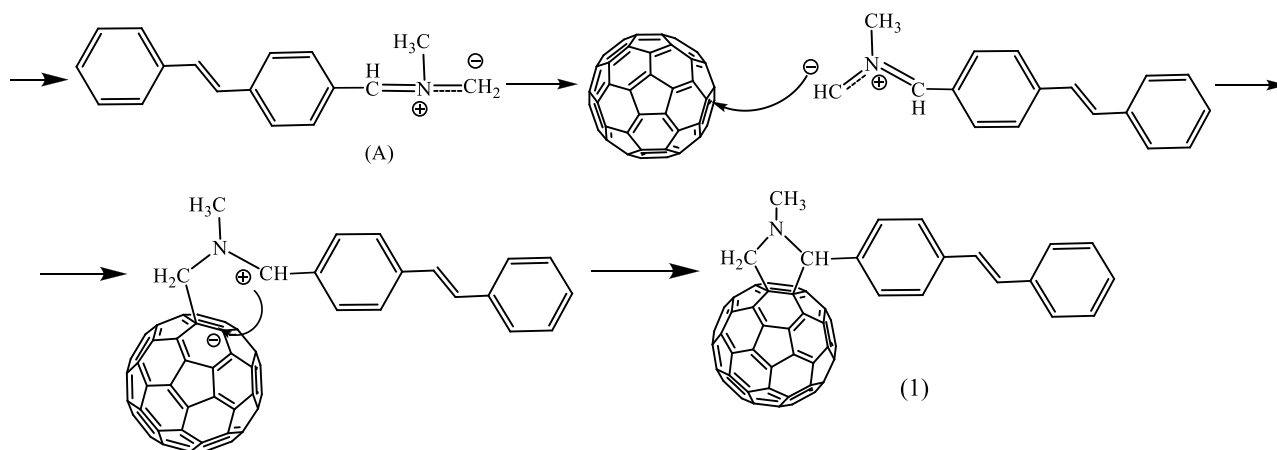
N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine (1). 100 mg  $C_{60}$  solution (0.1388 mmol) in 20 ml xylene was added to 57.81 mg (0.2776 mmol) trans-4-stilbenecarboxaldehyde and 123.6 mg (1.388 mmol) sarcosine (reacting agents' molecular ratio was 1:2:5 respectively). Reaction mixture was boiled for three hours at 110–120°C. After solvent removal residue was chromatographed on silicagel column eluting unreacted  $C_{60}$  and the product with toluene. Product yield was 14.7 mg (10.8 %). NMR spectra  $^1H$ ,  $\delta$ , ppm (J, Hz): 2.87 s (3H, H-6,6), 4.31 d (1H, H-2ax,  $^2J$  9.2), 4.98 s (1H, H-5), 5.02 d (1H, H-2eq,  $^2J$  9.2), 7.0 d (1H, H-14,  $^3J$  3.6), 7.25 t (1H, H-18,  $^3J$  7.2), 7.27 d (2H, H-17,19,  $^3J$  8.4), 7.34 t (2H, H-16,20,  $^3J$  7.6), 7.47 d (2H, H-9,11,  $^3J$  7.6), 7.57 d (2H, H-8,12,  $^3J$  8.0), 7.81 w. s (1H, H-13). NMR spectra  $^{13}C$ ,  $\delta_c$ , ppm: 40.12 (C-6), 70.12 (C-2), 83.47 (C-5), 126.70 (C-9,11), 126.99 (C-8,12), 127.85 (C-18), 128.36 (C-14), 128.79 (C-16,20), 129.36 (C-13), 137.73 (C-15), 139.69 (C-10), 156.22 (C-7).

Complex obtaining technique (1a). 2 mg fulleropyrrolidine 1 solution in 2 ml xylene were added to 200 mg PVP in 3 mg xylene. Reaction mixture was stirred for 30 minutes at room temperature. After solvent removal the residue was dried in vacuum.

### Results and Discussion

Considering stilbenoids and fullerenes derivatives' scientific and applied prospects, we have performed synthesis and NMR spectroscopic research of new fulleropyrrolidine structural peculiarities.  $C_{60}$  fullerene, sarcosine and trans-4-stilbenecarboxaldehyde triple-component condensation took place in Prato reaction conditions. One of major factors having influence on this reaction final product yield is the homogeneity of the reaction medium. So stilbenefulleropyrrolidine 1 synthesis was done in medium of various solvents such as benzene, toluene, chlorobenzene and xylene and while reactive medium was heated for 4–5 hours. It is possible that present in reaction medium amino acid (which is a zwitterionic compound) has negative impact on the reaction rate (heterogeneity factor). The highest yield of target fulleropyrrolidine 1 was obtained in xylene medium. Obtained fulleropyrrolidine 1 purity and individuality were analyzed using HPLC analysis.





New obtained fulleropyrrolidine 1 structure was found using IR, NMR <sup>1</sup>H and <sup>13</sup>C spectroscopy as well as two-dimensional COSY (<sup>1</sup>H-<sup>1</sup>H) and HMQC (<sup>1</sup>H-<sup>13</sup>C) spectra data.

There are pyridine ring C-N bond lines and fullerene scaffold, C-H and N-H vibrational frequencies in compound 1 IR spectra. Compound 1 UV spectra has 254, 319 and 431 nm peaks. Low intensity peak at 431 nm is typical for all C<sub>60</sub> fullerene [6, 8] closed adducts (Fig. 1).

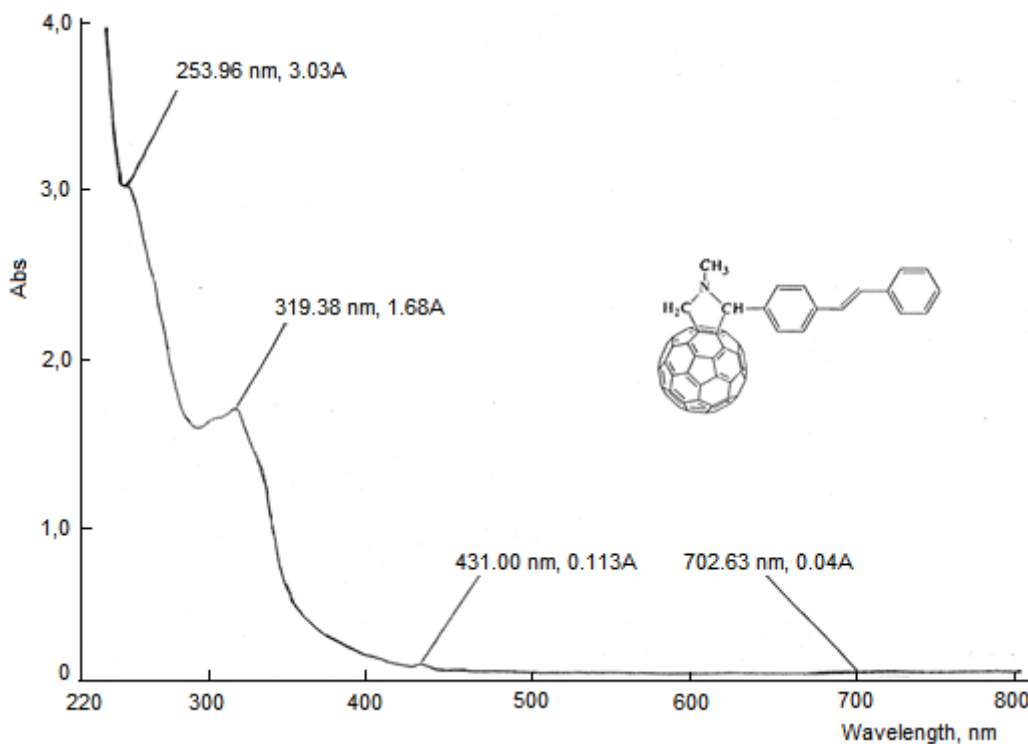


Figure 1. Compound 1 UV spectra

Compound 1 NMR <sup>1</sup>H spectra is characterized by three-proton singlet signal presence at 2.87 ppm of H-6,6,6 N-methyl fragment protons in pyrrolidine ring. One-proton singlet signal at 4.92 ppm indicates presence of H-5 methyne proton in pyrrolidine cycle. Two one-proton duplicate signals appearance at 4.31 and 5.02 ppm with the same spin-spin interaction constant <sup>2</sup>J 9.2 Hz proves presence of two pyrrolidine ring H-2ax and H-2eq protons (axial and equatorial) connected to fullerene nucleus. H-14 and H-13 protons of ethane chain appear as one-proton duplicate at 7.09 ppm and <sup>3</sup>J 3.6 Hz extended one-proton singlet at 7.81 ppm respectively. Aromatic protons H-18 and H-9,11 appear as one- and two-proton triples at 7.25 ppm and <sup>3</sup>J 7.2 Hz and 7.34 ppm and <sup>3</sup>J 7.6 Hz respectively. H-17 and H-19 protons appear as two-proton duplicates at 7.27 ppm and <sup>3</sup>J 8.4 Hz, H-9 and H-11 protons appear as two-proton duplicates at 7.47 ppm and <sup>3</sup>J 7.6 Hz, H-8 and H-12 protons appear as two-proton duplicates at 7.57 ppm and <sup>3</sup>J 8.0 Hz respectively.

Pyrrolidine ring signals with N-methyl substituent can be seen at 40.12 (C-6), 70.12 (C-2) and 83.47 (C-5) ppm in compound 1 NMR  $^{13}\text{C}$  spectra. Aromatic and unsaturated fragments carbon atoms resonated at 126.70 (C-9,11), 126.99 (C-8,12), 127.85 (C-18), 128.36 (C-14), 128.79 (C-16,20), 129.36 (C-13), 137.73 (C-15), 139.69 (C-10) and 156.22 (C-7) ppm. Multiple signals in 136–148 ppm area belong to fullerene nucleus  $\text{sp}^2$ -hybridized carbon atoms.

Compound 1 structure was also confirmed by two-dimensional NMR COSY ( $^1\text{H}$ - $^1\text{H}$ ) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) spectroscopy data, which allowed finding spin-spin interactions of homo- and heteronuclear nature. Correlations observed in molecule are shown in Figure 2. In compound 1  $^1\text{H}$ - $^1\text{H}$  COSY pectras there are spin-spin correlations through two bonds of methylene protons  $\text{H}^{2\text{ax}}$ - $\text{H}^{2\text{eq}}$  (4.31, 5.02 and 5.02, 4.31) ppm and through three bonds of protons in adjacent methyne groups  $\text{H}^{16,20}$ - $\text{H}^{18}$  (7.34, 7.26 and 7.26, 7.34),  $\text{H}^{16,20}$ - $\text{H}^{9,11}$  (7.34, 7.48 and 7.48, 7.34), and  $\text{H}^{8,12}$ - $\text{H}^{13}$  (7.56, 7.81 and 7.81, 7.56) ppm aromatic rings. Protons and carbon atoms heteronuclear interactions through one bond were found using  $^1\text{H}$ - $^{13}\text{C}$  HSQC for the following couples present in the compound:  $\text{H}^6$ - $\text{C}^6$  (2.87, 40.12),  $\text{H}^{2\text{ax}}$ - $\text{C}^2$  (4.31, 70.16),  $\text{H}^{2\text{eq}}$ - $\text{C}^2$  (5.02, 70.16),  $\text{H}^5$ - $\text{C}^5$  (4.98, 83.47),  $\text{H}^{14}$ - $\text{C}^{14}$  (7.10, 128.36),  $\text{H}^{18}$ - $\text{C}^{18}$  (7.24, 127.84),  $\text{H}^{16,20}$ - $\text{C}^{16,20}$  (7.34, 129.11),  $\text{H}^{9,11}$ - $\text{C}^{9,11}$  (7.48, 126.70),  $\text{H}^{8,12}$ - $\text{C}^{8,12}$  (7.57, 126.99),  $\text{H}^{13}$ - $\text{C}^{13}$  (7.80, 129.36).

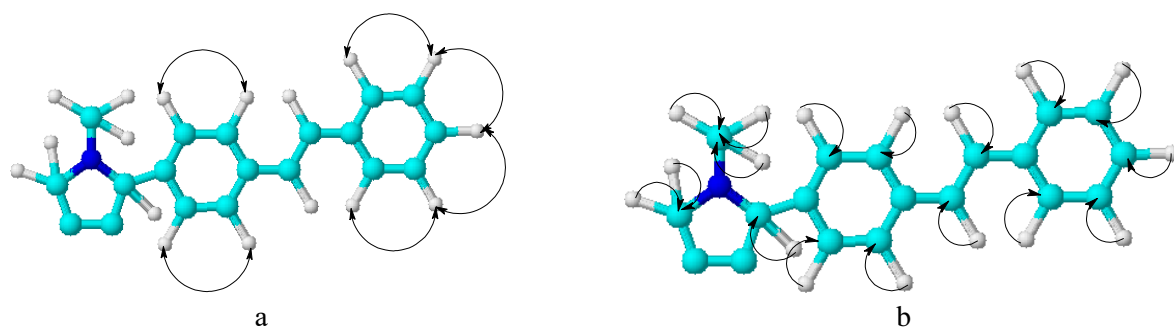
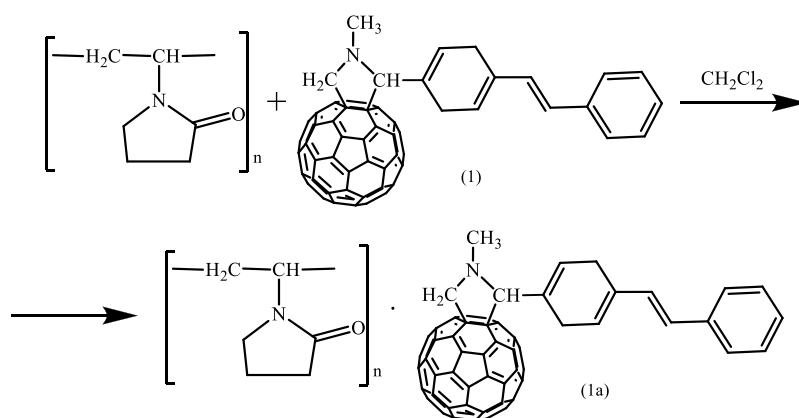


Figure 2. Compound 1 correlations in COSY ( $^1\text{H}$ - $^1\text{H}$ ) (a) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) (b) spectra

The insolubility of fullerenes in water is the main problem that impedes the biological studies of fullerene derivatives and the creation of therapeutic agents based on them. One of the possible ways to overcome this problem is to obtain water-soluble polymers approved for use in medicine, for example, with poly-N-vinylpyrrolidone.

In this regard, a complex of compound 1 with poly-N-vinylpyrrolidone in dichloromethane medium was obtained:



1a complex formation proceeds as a result of fullerene-pyrrolidine 1 solubilization by PVP chains and lactamic group physical interaction with fullerene sphere. Obtained complex 1a dissolves well in water.

### Conclusion

New stilbenefulleropyrrolidine has been synthesized by  $\text{C}_{60}$  fullerene triple-component condensation with sarcosine and trans-4-stilbenecarboxaldehyde in Prato reaction conditions. It was demonstrated that the

homogeneity of the reaction medium is the primary factor having influence on this reaction final product yield. The highest yield of N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine was observed when reaction performed in xylene and reactive medium heated. N-methyl-2-(4-styrylphenyl)-3,4-fulleropyrrolidine compound water-soluble complex with poly-N-vinylpyrrolidone in dichloromethane has been obtained. Synthesized compound structure has been studied by IR-, UV-, NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectroscopy as well as two-dimensional COSY ( $^1\text{H}$ - $^1\text{H}$ ) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) spectra data.

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### **N-Метил-2-(4-стирилфенил)-3,4-фуллеропирролидиннің синтезі және құрылымы**

Стильбенқұрамды фуллеропирролидинге әкелетін *транс*-4-стильбенкарбоксальдегидтің C<sub>60</sub>-фуллеренге Прато реакциясы бойынша циклоқосылу реакциясы зерттелген. Бұл реакцияда соңғы өнімнің шығуына әсер ететін негізгі фактор реакциялық ортаның гомогенділігі болып табылады. N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидиннің ең жоғары шығымы ксилол ортасында реакция жүргізу және реакциялық ортаны қыздыру кезінде байқалады. Синтезделген қосылыстың құрылымы ИҚ-, УК-, ЯМР <sup>1</sup>H және <sup>13</sup>C спектроскопия әдістерімен, сондай-ақ COSY (<sup>1</sup>H-<sup>1</sup>H) және HMQC (<sup>1</sup>H-<sup>13</sup>C) екі өлшемді спектрлерінің деректерімен зерттелген. Алынған фуллеропирролидиннің даралығы мен тазалығы ЖТСХ талдауды қолдана отырып, анықталған. N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидиннің түзілуі белсенді азотинилидтердің аралық түзілуі арқылы C<sub>60</sub> фуллереніне диполярлы қосылыс механизмі бойынша жүреді. Дихлорметан ортасында N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидинді поли-N-винилпирролидонмен қосудың суда еритін комплексы алынған. Комплексінің фуллеренопирролидинді ПВП тізбектерімен солубилизациялау және лактам тобының фуллерендік сферамен физикалық өзара әрекеттесуі нәтижесінде пайда болатыны көрсетілген.

*Кілт сөздер:* фуллерен C<sub>60</sub>, *транс*-4-стильбенкарбоксальдегид, саркозин, фуллеропирролидин, Прато реакциясы, ЯМР-спектрлер, поли-N-винилпирролидон, үшкомпонентті конденсация.

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### **Синтез и строение N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидина**

Изучена реакция [2+3] циклоприсоединения *транс*-4-стильбенкарбоксальдегида к C<sub>60</sub>-фуллерену по реакции Прато, приводящая к стильбенсодержащему фуллеропирролидину. Показано, что основным фактором, влияющим на выход конечного продукта в этой реакции, является гомогенность реакционной среды. Наиболее высокий выход N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидина наблюдается при проведении реакции в среде ксилола и нагревании реакционной среды. Строение синтезированного соединения исследовано методами ИК-, УФ-, ЯМР <sup>1</sup>H и <sup>13</sup>C спектроскопии, а также данными двумерных спектров COSY (<sup>1</sup>H-<sup>1</sup>H) и HMQC (<sup>1</sup>H-<sup>13</sup>C). Чистота и индивидуальность полученного фуллеропирролидина проанализированы с применением ВЭЖХ анализа. Образование N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидина протекает по механизму 1,3-диполярного присоединения к фуллерену C<sub>60</sub> через промежуточное образование активных азотинилидов. Получен водорастворимый комплекс соединения N-метил-2-(4-стирилфенил)-3,4-фуллеропирролидина с поли-N-винилпирролидоном в среде дихлорметана. Показано, что образование комплекса происходит в результате солубилизации фуллеропирролидина цепями ПВП и физического взаимодействия лактамной группы с фуллереновой сферой.

*Ключевые слова:* фуллерен C<sub>60</sub>, *транс*-4-стильбенкарбоксальдегид, саркозин, фуллеропирролидин, реакция Прато, ЯМР-спектр, поли-N-винилпирролидон, трехкомпонентная конденсация.

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## Supramolecular inclusion complexes of functionally substituted N-benzylidene- and allylidene- isonicotinohydrazides with oligosaccharides and their properties

This paper presents the results of a study of the synthesis and structural features of supramolecular inclusion complexes of N-benzylidene- and allylidene- isonicotinohydrazides with cyclic oligosaccharides (with  $\beta$ - and 2-hydroxypropyl- $\beta$ -cyclodextrins). The results of studying the synthesis and structural features of supramolecular inclusion complexes of N-benzylidene and allylideneisonicotinohydrazides with cyclic oligosaccharides ( $\beta$ - and 2-hydroxypropyl- $\beta$ -cyclodextrins) are presented. The structure of the obtained supramolecular inclusion complexes was studied using one-dimensional <sup>1</sup>H, <sup>13</sup>C and DEPT NMR and two-dimensional spectroscopy of COSY (<sup>1</sup>H-<sup>1</sup>H), HMQC (<sup>1</sup>H-<sup>13</sup>C) and TOCSY (<sup>1</sup>H-<sup>1</sup>H). The formation of supramolecular inclusion complexes was established on the basis of changes in the chemical shifts of the NMR of the substrate and receptor atoms. Based on the analysis of spectral data, the proposed schemes of the obtained supramolecular inclusion complexes are presented. It was found that the interaction of the studied hydrazone substrates with cyclodextrins forms inclusion complexes 1:1 and 1:2 with the entry of the substrate molecule into the internal cavity of the receptor. The resulting products are able to dissolve in water or form stable aqueous dispersions. The antiradical effect of the synthesized supramolecular inclusion complexes with respect to the 2,2-diphenyl-1-picrylhydrazide radical was evaluated. Under the conditions of this test system, antiradical activity was detected in the supramolecular complex of N-(diethylamino)benzylidene-isonicotinohydrazide. The concentration of the complex was determined, capable of reducing the optical density of 100  $\mu$ M of the test system solution by 50 %.

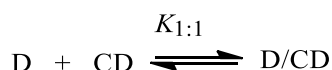
*Keywords:* oligosaccharides, hydrazones, cyclodextrin, inclusion complexes, NMR spectroscopy, substrate.

### Introduction

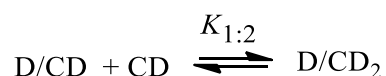
A well-known drawback of many modern drugs is the rapid decrease in their plasma levels after reaching peak metabolic destruction in the stomach of the body. This fact necessitates an increase in dose loads and, accordingly, increases the likelihood of side effects. In this regard, one of the most important attributes of drug delivery systems is the controlled release profile of the latter in the patient's body. Every year, many researchers find that biologically active substances cannot be obtained from clinical trials [1–3]. Therefore, one of the urgent tasks of modern pharmacological science is the targeted delivery of drug systems. Currently, biodegradable oligosaccharides (cyclodextrins) have been used to transport drugs [4–6]. Cyclodextrins (CDs) are complex natural cyclic oligosaccharides consisting of D-glucopyranose residues connected by an  $\alpha$ -1,4-glycosidic bond. On the basis of wide distribution and commercial use,  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins were obtained, the macro rings of which consist of 6, 7 and 8 residues of D-glucose, respectively. They are unique natural nanostructures equipped with a hydrophobic internal cavity and a hydrophilic external surface. They are able to form various forms: micelles, vesicles and more complex forms. The formation of all these complex forms is governed by a hydrophobic effect.

These are «molecular containers» that are capable of holding non-polar, non-ionized molecules of the «guest» substance in the internal cavity. This leads to the formation of complexes, which include a hydrophobic molecule of the «guest» substance, a unique property to dissolve in the aqueous phase due to the hydrophilic outer surface of the molecular container [7–12]. Molecules of cyclodextrins contain both polar and non-polar parts. They form very complex structures: micelles, vesicles, layers and more complex forms. The formation of all these complex forms is governed by the hydrophobic effect [8–11].

The most common type of complex includes cyclodextrin and the drug/cyclodextrin (D/CD) complex in a 1:2–1 ratio, which contains one drug (D), which forms a complex with one cyclodextrin (CD) molecule [13–15]:



Cyclodextrins can form higher-order drug / cyclodextrin complexes, depending on the nature and structure of the ligand-substrate, in a 1:2 ratio:



Currently, CDs are widely used in the food, cosmetic, pharmaceutical industries, in analytical chemistry, and in protecting the environment from ecotoxicants and others [9–12]. Further prospects for the use of diabetes in pharmacology and medicine are associated with the development of so-called targeted drugs for antitumor and gene therapy [16–19]. If the receptor acts as a target, then the bioactive drug will be a ligand with respect to it, i.e. a compound specifically interacting with the active center of the receptor. The formation of such a supramolecular complex causes high selectivity and lower toxicity of the drugs. In this regard, in recent years, CDs and their derivatives have been actively used for targeted drug delivery in the form of a molecular container. Such encapsulation protects the «guest» molecule from damage by various reactive molecules and thereby reduces the rate of oxidation, steric rearrangements, hydrolysis, racemization and enzymatic degradation, as well as enhances its water solubility and, as a result, a more effective pharmacological effect.

For analysis of supramolecular inclusion complexes, the methods of proton magnetic resonance spectroscopy on  $^1\text{H}$  nuclei and nuclear magnetic resonance spectroscopy on  $^{13}\text{C}$  nuclei are mainly used. The most informative method for confirming the formation of inclusion complexes is  $^1\text{H}$  NMR spectroscopy [13–15, 20–24]. This analysis method allows one to fix a pronounced chemical shift in the vibrational spectra of H3, H5  $\beta$ -CD protons oriented inside the torus cavity, which is due to the placement of the «guest» substance molecule in the hydrophobic cyclodextrin cavity. In this case, insignificant chemical shifts are observed in the vibrational spectra of the H1, H2, and H4 atoms localized on the outer surface of the molecule.

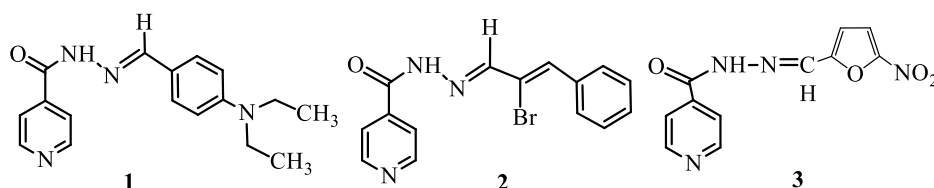
The  $^{13}\text{C}$ -NMR spectroscopy method allows one to detect chemical shifts in the electronic environment of carbon atoms of the cavity of a cyclodextrin molecule resulting from the van der Waals and electrostatic interaction of the molecules of the «guest» substance with the molecules of the host substance [13–15]. With an increase in the concentration of the «guest» substance in the system, a proportional increase in the chemical shift in the vibrational spectra is observed, due to a shift in the equilibrium state towards the formation of inclusion complexes [19–28].

### Experimental

$\alpha$ -,  $\beta$ -,  $\gamma$ - and 2-Hydroxypropyl- $\beta$ -cyclodextrins were used by Fluka, 99 % pure. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the compounds were recorded on a Jeol JNM-ECA 400 spectrometer (399.78 and 100.53 MHz on  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively) in a DMSO- $d_6$  solution at room temperature. Chemical shifts are measured relative to the residual signals of protons or carbon atoms of DMSO- $d_6$ .

In this work, we selected spectroscopic methods to study supramolecular complexes for the inclusion of functionally substituted isonicotinic acid hydrazone with cyclodextrins ( $\beta$ -CD, 2-hydroxypropyl- $\beta$ -CD). Hydrazones — N-(diethylamino)benzylidene isonicotinohydrazide (1), N-(2-bromo-3-phenyl)allylidenisonicotinohydrazide (2) and N'-((5-nitrofuran-2-yl) methylene) was chosen as hydrazone substrates isonicotinohydrazide (3). The procedures for the preparation of inclusion complexes of functionally substituted N-benzylidene- and allylidene- isonicotinohydrazide (1–3) with  $\beta$ - and hydroxypropyl- $\beta$ -cyclodextrins were described by us in [29–31].

Preliminary bioprognosis (1–3) using the PASS program showed high rates of their manifestation of antituberculosis, antimycobacterial, antioxidant activity and inhibitors of glutaminophenylpurivate transaminase and threonine aldolase. The above compounds (1–3) are characterized by their poor solubility in water. The inclusion of substrates (1–3) in the cavity of the host molecule will increase the solubility of the substance, improve bioavailability and contribute to obtaining more in-depth data on their biological properties.





### Results and Discussion

The NMR spectroscopic study of supramolecular inclusion complexes (4–6), obtained on the basis of functionally substituted hydrazone (1–3) of isonicotinic acid and cyclodextrins, is based on determining the difference in the values of chemical shifts  $^1\text{H}$  and  $^{13}\text{C}$  of substrates and receptor ( $\alpha$ -,  $\beta$ -,  $\gamma$ -CD) in the free state and in the composition of complexes as a result of intermolecular interaction.

The NMR spectrum of an individual  $\beta$ -CD (Fig. 1) is characterized by the manifestation of six groups of signals in the region 3.23–3.32; 3.45–3.60; 4.47–4.49; 4.77–4.78; 5.66; 5.71–5.73 ppm.

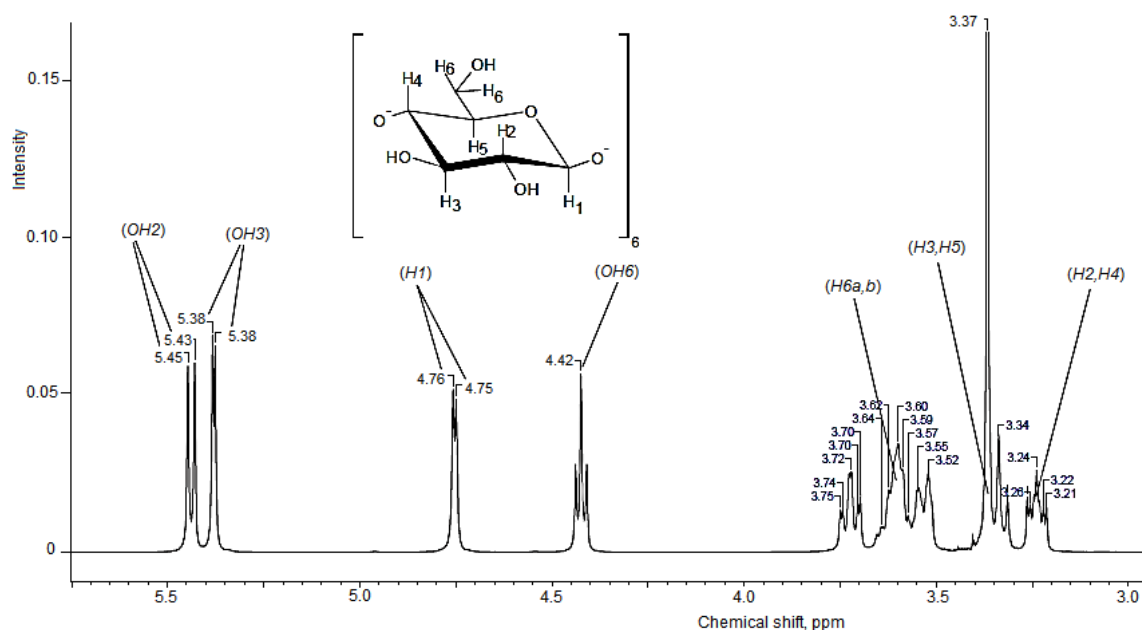


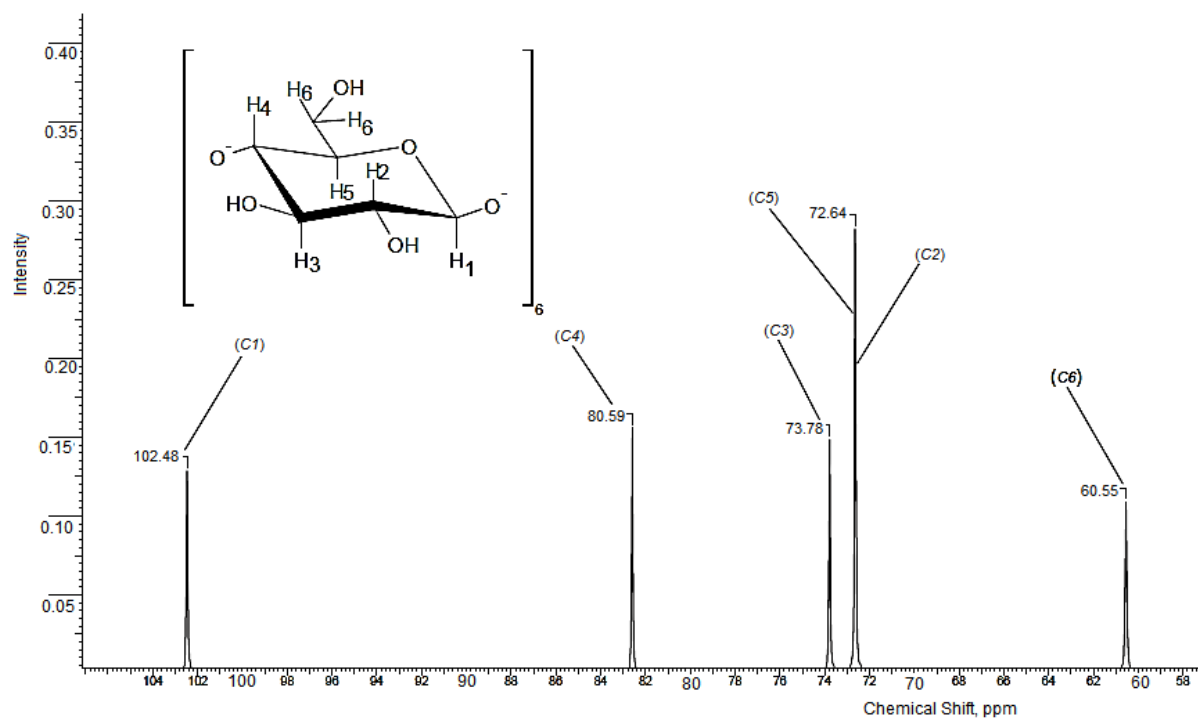
Figure 1.  $^1\text{H}$  NMR spectrum of  $\beta$ -CD

Doublet signal in the range 5.71–5.73 ppm with a splitting of 4 Hz, it belongs to the proton of the hydroxyl group at the C-2 atom. The proton of the OH group of a neighboring atom (OH-3) located in the internal cavity of the  $\beta$ -CD molecule ( $\delta=5.66$  ppm, doublet) also resonates in the low-field region. Doublet signal in the region of 4.77–4.78 ppm corresponds to the proton H-1  $\beta$ -CD. The location of this proton in a weaker field compared to the protons of other CH groups is due to the influence of the oxygen atom. The hydroxyl group OH-6 resonates, splitting into a triplet with a center at 4.48 ppm. In the region of a strong field at 3.49–3.60 ppm signals of protons H-6a, b of the methylene group are observed. High-intensity signal at 3.45 ppm corresponds to the protons H-3 and H-5 of the glucopyranose link. In the range from 3.23 to 3.32 ppm. methine protons H-2 and H-4 are manifested [8, 11, 23, 29, 30].

The carbon NMR spectrum of  $\beta$ -CD (Fig. 2) represents six signals of  $^{13}\text{C}$  nuclei of the elementary unit. In the strong-field part, the signal of the C-6 carbon atom appears at 60.41 ppm. Signals at 72.49, 72.85 and 73.51 ppm are caused by C-5, C-2 and C-3 atoms, respectively. In the region of a weaker field at 82.02 and 102.41 ppm signals of carbon atoms C-4 and C-1 are observed, respectively, directly connected to the adjacent glucopyranose link through the oxygen bridge.

Studying the one-dimensional spectra of  $\beta$ -CD in the free and bound state) reveals the pattern of displacement of all  $^1\text{H}$  and  $^{13}\text{C}$  signals of the host molecule to the weak field region, which confirms the non-valent binding with the guest.

For proton spectra, the largest difference in the values of the chemical shift ( $\Delta\delta = +0.10$  ppm) is characteristic of the intraspheric protons N-3 and N-5, on the basis of which it can be concluded that an internal (inclusion) complex with a substrate is formed. In the case of the carbon spectrum, the difference is more significant and ranges from 0.05–0.25 ppm. Thus, the formation of supramolecular inclusion complexes is established on the basis of changes in the NMR chemical shifts of the substrate and receptor atoms [28–33].

Figure 2.  $^{13}\text{C}$  NMR spectrum of  $\beta$ -CD

The study by NMR spectroscopy of supramolecular complexes is based on determining the difference in the chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  of substrates (12–14) and receptors ( $\beta$ -CD, 2-hydroxypropyl  $\beta$ -CD) in the free state and in the composition of the complexes as a result of intermolecular interaction. By the magnitude of the chemical shifts of the internal or external protons of the receptor, it is possible to reveal the formation of internal (inclusion) or external (without inclusion) complexes, respectively. A change in the chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  in the spectra of the substrates allows us to determine the direction of their entry into the cavity of CD.

The structure of substrates for supramolecular self-assembly (1) and (2) was established based on the results of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy obtained in  $\text{DMSO-d}_6$  (Table 1, 2 (1) and 1, 3, 4 (2)). One-dimensional  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (1) and (2) was confirmed by two-dimensional correlation data of  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectra (Table 1).

Table 1

 **$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectroscopy data,  $^1\text{H}$ - $^{13}\text{C}$  HMQC substrates (1) and (2)**

Substrate	$\delta$ , ppm, J, Hz			
	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$ - $^1\text{H}$ COSY	$^1\text{H}$ - $^{13}\text{C}$ HMQC
1	2	3	4	5
1	1.06 t (6H, H-20,22, $^3\text{J}$ 6.9), 3.31–3.35 m (4H, H-19,21), 6.66 d (2H, H-14,16, $^3\text{J}$ 8.7), 7.48 d (2H, H-13,17, $^3\text{J}$ 8.7), 7.77 d (2H, H-3,5, $^3\text{J}$ 4.6), 8.25 s (1H, H-23), 8.72 d (2H, H-2,6, $^3\text{J}$ 4.6), 11.72 s (1H, H-9)	12.96 (C-20,23), 44.26 (C-19,21), 111.56 (C-14,16), 120.76 (C-12), 122.00 (C-3,5), 129.56 (C-13,17), 141.37 (C-4,11), 149.57 (C-2,6), 150.41 (C-15), 161.48 (C-7)	$\text{H}^{19,21}$ - $\text{H}^{20,22}$ (1.03, 3.33; 3.32, 1.05); $\text{H}^{13,17}$ - $\text{H}^{14,16}$ (6.65, 7.48; 7.48, 6.66); $\text{H}^{3,5}$ - $\text{H}^{2,6}$ (7.76, 8.72; 8.71, 7.77)	$\text{H}^{20,22}$ - $\text{C}^{20,22}$ (1.03, 12.93); $\text{H}^{14,16}$ - $\text{C}^{14,16}$ (6.63, 111.53); $\text{H}^{13,17}$ - $\text{C}^{13,17}$ (7.45, 129.54); $\text{H}^{3,5}$ - $\text{C}^{3,5}$ (7.76, 121.92); $\text{H}^{2,6}$ - $\text{C}^{2,6}$ (8.70, 150.73)
2	7.38–7.43 m (3H, H-15,19,17), 7.67 s (1H, H-13), 7.77 d (2H, H- 3,5, $^3\text{J}$ 1.8), 7.84 d (2H, H-16,18, $^3\text{J}$ 6.4), 8.34 s (1H, H-11), 8.75 d (2H, H-2,6), 12.19 s (1H, H-9)	119.50 (C-12), 122.07 (C-3,5), 128.99 (C-15,19), 130.01 (C-17), 130.34 (C-16,18), 135.04 (C-14), 139.37 (C-13), 140.85 (C-4), 149.53 (C-11), 150.90 (C- 2,6), 162.27 (C-7)	$\text{H}^{16,18}$ - $\text{H}^{15,17,19}$ (7.40, 7.84; 7.83, 7.43); $\text{H}^{2,6}$ - $\text{H}^{3,5}$ (7.76, 8.75; 8.74, 7.77)	$\text{H}^{15,19}$ - $\text{C}^{15,19}$ (7.40, 129.31); $\text{H}^{13}$ - $\text{C}^{13}$ (7.67, 139.39); $\text{H}^{3,5}$ - $\text{C}^{3,5}$ (7.76, 122.07); $\text{H}^{16,18}$ - $\text{C}^{16,18}$ (7.85, 130.14); $\text{H}^{11}$ - $\text{C}^{11}$ (8.32, 119.49); $\text{H}^{2,6}$ - $\text{C}^{2,6}$ (8.74, 150.97)

The ratio of the integral intensities of protons in the compounds under consideration corresponded to the presented structures (1) and (2).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\beta$ - and 2-hydroxypropyl- $\beta$ -CD in the free state and supramolecular complexes (4–6) based on them with substrates (1) and (2) are presented in Tables 2–4.

Table 2

**Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei of the substrate (1) and 2-hydroxypropyl- $\beta$ -cyclodextrin in the free state ( $\delta_0$ ) and in the complex (4) ( $\delta$ )**

Atom number	Group	$\delta_0$ , ppm		$\delta$ , ppm		$\Delta\delta=\delta-\delta_0$	
		$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$
Substrate (1)							
2	CH	8.72	149.57	8.71	150.75	-0.01	1.18
3	CH	7.77	122.00	7.76	121.99	-0.01	-0.01
4	C		141.37		141.69		0.32
5	CH	7.77	122.00	7.76	121.99	-0.01	-0.01
6	CH	8.72	149.57	8.71	150.75	-0.01	1.18
7	C		161.48		163.82		2.34
9	NH	11.72		11.63		-0.11	
11	CH		141.37		141.69		0.32
12	C		120.76		120.94		0.18
13	CH	7.48	129.56	7.48	129.55	0	-0.01
14	CH	6.66	111.56	6.68	111.60	0.02	0.04
15	C		150.41		151.53		1.12
16	CH	6.66	111.56	6.68	111.60	0.02	0.04
17	CH	7.48	129.56	7.48	129.55	0	-0.01
19	CH <sub>2</sub>	3.35	44.26	3.36	44.27	0.01	0.01
20	CH <sub>3</sub>	1.06	12.96	1.00	12.84	-0.06	-0.12
21	CH <sub>2</sub>	3.35	44.26	3.36	44.27	0.01	0.01
22	CH <sub>3</sub>	1.06	12.96	1.00	12.84	-0.06	-0.12
23	CH	8.25		8.26		0.01	
2-HP- $\beta$ -CD							
1	CH	4.79	102.33	4.80	102.29	0.01	-0.04
2	CH	3.26	72.56	3.28	72.94	0.02	0.38
3	CH	3.70	73.56	3.73	73.55	0.03	-0.01
4	CH	3.18	82.11	3.21	82.20	0.03	0.09
5	CH	3.56	72.56	3.60	72.30	0.04	-0.26
6	CH <sub>2</sub>	3.56	60.40	3.60	60.43	0.04	0.03

Table 3

**Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei of the substrate (2) and  $\beta$ -cyclodextrin in the free state ( $\delta_0$ ) and in the complex (5) ( $\delta$ )**

Atom number	Group	$\delta_0$ , ppm		$\delta$ , ppm		$\Delta\delta=\delta-\delta_0$	
		$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$
1	2	3	4	5	6	7	8
Substrate (2)							
2	CH	8.75	150.90	8.38	150.98	-0.37	0.08
3	CH	7.77	122.07	7.95	124.49	0.18	2.42
4	C		140.85				
5	CH	7.77	122.07	7.95	124.49	0.18	2.42
6	CH	8.75	150.98	8.38	150.98	-0.37	0.08
7	C		162.27				
9	NH	12.19		12.19		0	
11	CH <sub>a</sub>	8.34	149.53	8.38		0.04	
12	C		119.50				
13	CH <sub>a</sub>	7.67	139.37	7.95		0.28	

Continuation of Table 3

1	2	3	4	5	6	7	8
14	C		135.04		133.50		-1.54
15	CH	7.43	128.99	7.53	129.42	0.10	0.43
16	CH	7.84	130.34	7.95	131.17	0.11	0.83
17	CH	7.43	130.01	7.53	132.11	0.10	2.10
18	CH	7.84	130.34	7.95	131.17	0.11	0.83
19	CH	7.43	128.99	7.53	129.42	0.10	0.43
β-CD							
1	CH	4.77	102.40	4.79	102.46	0.02	0.06
2	CH	3.26	72.83	3.27	72.93	0.01	0.10
3	CH	3.58	73.54	3.60	73.57	0.02	0.03
4	CH	3.28	81.98	3.31	82.07	0.03	0.09
5	CH	3.50	72.50	3.51	72.56	0.01	0.06
6	CH <sub>2</sub>	3.58	60.42	3.60	60.45	0.02	0.03

Table 4

**Chemical shifts of <sup>1</sup>H and <sup>13</sup>C nuclei of the substrate (2)  
and 2-hydroxypropyl-β-cyclodextrin in the free state (δ<sub>0</sub>) and in the complex (δ)**

Atom number	Group	δ <sub>0</sub> , ppm		δ, ppm		Δδ=δ-δ <sub>0</sub>	
		<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C
Substrate (2)							
2	CH	8.75	150.90	8.78	149.72	0.03	-1.82
3	CH	7.77	122.07	7.87	124.04	0.10	1.97
4	C		140.85		140.25		-0.60
5	CH	7.77	122.07	7.87	124.04	0.10	1.97
6	CH	8.75	150.98	8.78	149.72	0.03	-1.82
7	C		162.27		163.61		1.34
9	NH	12.19		12.19		0	
11	CH <sub>a</sub>	8.34	149.53	8.38	149.72	0.04	0.19
12	C		119.50				
13	CH <sub>a</sub>	7.67	139.37	7.87	139.64	0.20	0.27
14	C		135.04		131.18		-3.86
15	CH	7.43	128.99	7.52	129.00	0.09	0.01
16	CH	7.84	130.34	7.87	129.42	0.03	-0.62
17	CH	7.43	130.01	7.52	129.42	0.09	-0.59
18	CH	7.84	130.34	7.87	129.42	0.03	-0.62
19	CH	7.43	128.99	7.52	129.00	0.09	0.01
2-HP-β-CD							
1	CH	4.79	102.33	4.80	102.36	0.01	0.03
2	CH	3.26	72.56	3.28	72.91	0.02	0.35
3	CH	3.70	73.56	3.73	73.53	0.03	-0.03
4	CH	3.18	82.11	3.21	82.01	0.03	-0.10
5	CH	3.56	72.56	3.60	72.91	0.04	0.35
6	CH <sub>2</sub>	3.56	60.40	3.60	60.66	0.04	0.20

Comparison of the integral intensities of <sup>1</sup>H NMR signals of substrate molecules (1 and 2) and receptors (β- and 2-hydroxypropyl-β-CD) in supramolecular complexes (4–6) showed that in all cases «guest-host» complexes are formed. During the formation of the supramolecular complex (4), changes in proton chemical shifts in the cyclodextrin molecule Δδ occurred to a greater extent in the internal hydrophobic protons H-3, H-5, H-6. The protons H-1, H-2 and H-4 located in the outer hydrophilic surface have insignificant changes.

In molecule (1), the largest changes in the proton spectra are observed for the diethylamine protons H-20, H-22, H-19, H-21, and also for the phenylidene protons H-14 and H-16. Screening during complexation requires protons and aromatic pyridine hydrophobic protons H-2.6 and H-3.5. It can be assumed that the higher

supramolecular interaction of guest and host molecules is carried out using the above-mentioned protons in the process of complex formation (4) (1: 2) (Figure 3).

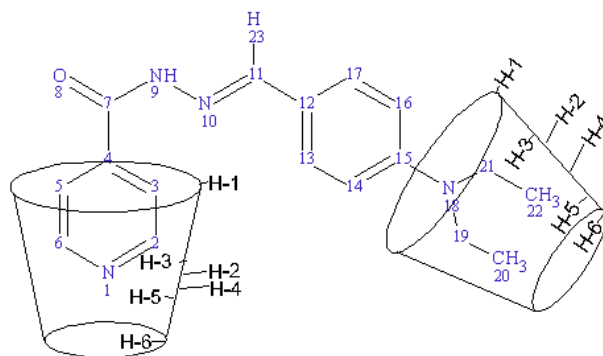


Figure 3. Estimated supramolecular inclusion complexes (4)

The screening of external cyclodextrin protons is probably due to the intermolecular interaction of hydrophilic protons with the external hydroxyl groups of 2-hydroxypropyl- $\beta$ -CD, as well as the possible slight formation of external complexes [19–24]. A significant change in the chemical shifts of the imine proton H-9 is probably due to hydrophilic interaction with its hydroxy groups of the receptor.

The supramolecular self-assembly of the substrate (2) with  $\beta$ - and 2-hydroxypropyl- $\beta$ -CDs with the formation of supracomplexes (5) and (6) was also accompanied by a change in the internal hydrophobic protons of the CDs and a slight screening of the external protons of the receptor. In molecule (1), the largest changes in proton chemical shifts occurred in the phenyl and pyridine fragments. When using  $\beta$ -CD-receptor as the receptor, the greatest changes in proton chemical shifts were observed in the protons of the pyridine fragment of the complex (5), while the use of 2-hydroxypropyl- $\beta$ -CD in supramolecular self-assembly with substrate 2 leads to the greatest change in the chemical shifts of protons phenyl radical in the supracomplex (6). The proposed models of supramolecular complexes (5) and (6) are similar in structure and are presented in Figure 4.

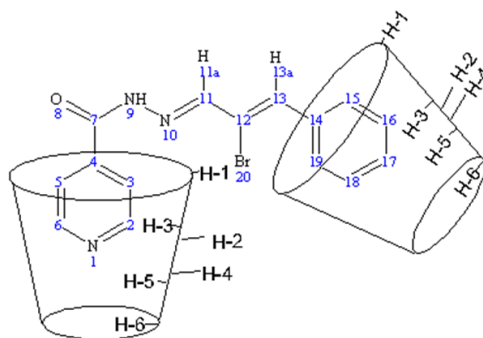


Figure 4. Estimated supramolecular inclusion complexes (5) and (6)

In the  $^1\text{H}$  NMR spectrum of compound (3), the proton H4 of the furan fragment appeared as a single-proton doublet at 7.29 ppm. with  $3J$  4.4 Hz. The remaining furan proton H3 resonated together with the pyridine protons H15.19 with a three-proton multiplet at 7.76–7.79 ppm. The pyridine protons N-16.18 manifested themselves as a two-proton doublet at 8.77 ppm. with  $3J$  5.6 Hz. The proton H8 at the unsaturated carbon atom and the amide proton H10 appeared as single-proton singlets at 8.36 and 12.41 ppm. respectively.

In the  $^{13}\text{C}$  NMR spectrum of compound (3), the signals of the carbon atoms of the furan fragment appeared at 115.08 (C3), 11.61 (C4), 151.83 (C5) and 152.59 (C2) ppm. The signals of the carbon nuclei of the pyridine ring are observed at 122.07 (C15.19), 140.35 (C14) and 150.99 (C16.18) ppm. The unsaturated carbon atom C8 resonated at 137.20 ppm. Chemical shift signal at 162.53 ppm corresponds to the carbon atom C11 of the urea group [28–30].

The structure of compound (3) was also confirmed by the methods of two-dimensional NMR spectroscopy COSY ( $^1\text{H}$ - $^1\text{H}$ ) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature. The observed correlations in the molecule are shown in Figure 5. In the  $^1\text{H}$ - $^1\text{H}$  COSY

spectrum of compound (3), spin-spin correlations are observed through three bonds of the neighboring methine-methine protons of the H4-H3 furan ring (cross-peak coordinates, ppm: 7, 28, 7.76 and 7.76, 7.28) and aromatic protons H15.19-H16.18 (coordinates of cross peaks, ppm: 7.78, 8.76 and 8.7, 7.77) pyridine ring. Heteronuclear interactions of protons with carbon atoms through one bond were established using  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectroscopy (Figure 5) for all pairs present in the compound: H4-C4 (7.27, 116.62), H3-C3 (7.75, 115, 04), H15.19-C15.19 (7.76, 122.10), H8-C8 (8.35, 137.21), H16.18-C16.1 (8.77, 150.96).

As a result of the studies, the supramolecular complexes (7) and (8) were first obtained on the basis of functionally substituted N' - ((5-nitro-furan-2-yl) methylene) isonicotinohydrazide with cyclodextrins ( $\beta$ -CD and 2-hydroxypropyl- $\beta$ -CD).

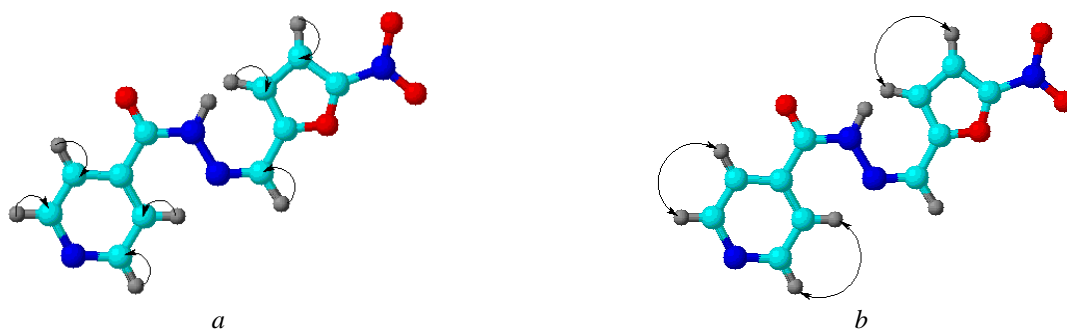
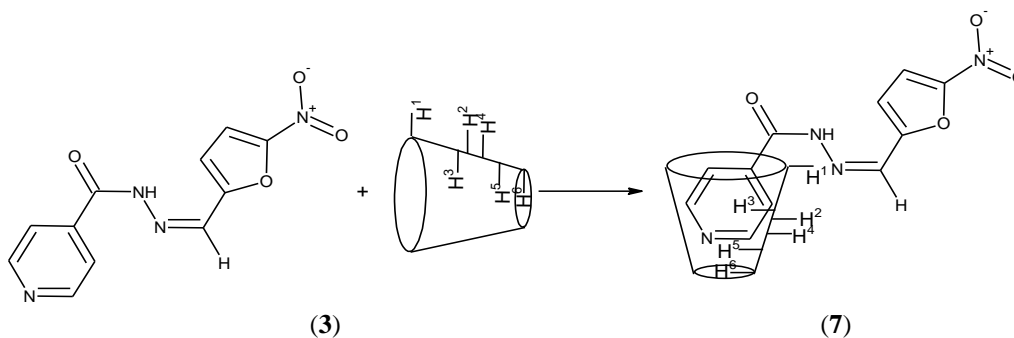
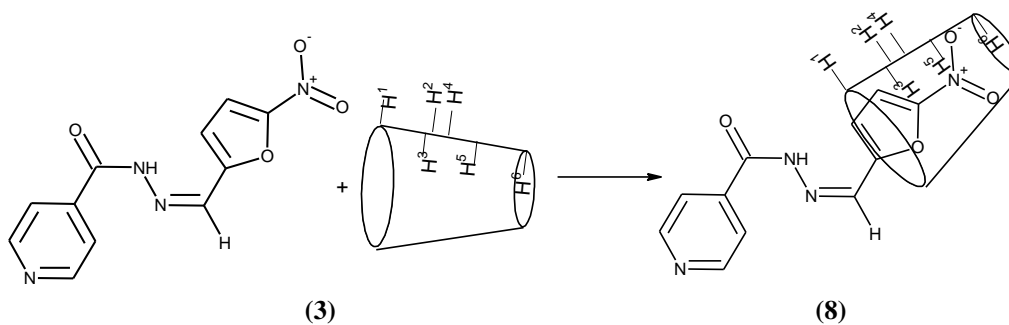


Figure 5. Correlation scheme in the spectra of HMQC (a) and COZY (b) compounds (3)

The study of supracomplexes with  $\beta$ -CD (7) and 2-hydroxypropyl- $\beta$ -CD (8) showed that in both cases substrate inclusion complexes (3) with a cyclodextrin receptor cavity are formed. The greatest change in the chemical shifts of protons in the process of formation of supra-molecular complexes occurs with the internal protons H-3 and H-5 of the cyclodextrin cavity. In the formation of a substrate inclusion complex (3) with  $\beta$ -CD, the greatest change in chemical shifts occurs with protons of the pyridine fragment. In the case of using 2-HP- $\beta$ -CD, a proton of the furan cycle undergoes a greater change in chemical shifts. This indicates the entry of the substrate molecule into the cyclodextrin cavity by the pyridine fragment in the case of using  $\beta$ -CD-Na (Scheme 1) and the furanose cycle in the case of 2-HP- $\beta$ -CD (Scheme 2).



Scheme 1. The formation of supramolecular complex (7)



Scheme 2. Formation of a supramolecular complex (8)

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound (3) in the free state and in the composition of supramolecular complexes (7) and (8) obtained in  $\text{DMSO-d}_6$  are presented in Tables 5 and 6.

Table 5

**Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei of the substrate (3) in the free state ( $\delta_0$ ) and in the complexes (7) ( $\delta_1$ ), (8) ( $\delta_2$ )**

Atom number	Group	$^{13}\text{C}$	$^1\text{H}$				
		$\delta_0$	$\delta_0$	$\delta_1$	$\Delta\delta_1 = \delta_1 - \delta_0$	$\delta_2$	$\Delta\delta_2 = \delta_2 - \delta_0$
2	>C<	152.59					
3	CH	115.08	7.78	7.77	-0.01	7.90	0.12
4	CH	140.35	7.29	7.28	-0.01	7.26	-0.03
5	>C<	151.83					
8	=CH	137.20	8.36	8.35	-0.01	8.38	0.02
10	NH		12.41	12.41	0		
11	>CO	162.53					
14	>C<	140.35					
15	CH	122.07	7.78	7.75	-0.03	7.78	0
16	CH	150.99	8.77	8.75	-0.02	8.75	-0.02
18	CH	150.99	8.77	8.75	-0.02	8.75	-0.02
19	CH	122.07	7.78	7.75	-0.03	7.78	0

A comparison of the integral intensities of  $^1\text{H}$  NMR signals of molecule (3) with  $\beta$ - and 2-hydroxypropyl- $\beta$ -CD in supracomplexes showed that in both cases complexes of the composition of one substrate molecule per one receptor molecule are formed. The resulting products form a mixture capable of dissolving in water or forming stable aqueous dispersions.

To obtain inclusion complexes of functionally substituted N'-((5-nitrofuranyl)methylene) isonicotinohydrazide (3) with  $\beta$ -cyclodextrins, we chose the coprecipitation method, since this method is simple and easy to implement.

Table 6

**Chemical shifts of  $^1\text{H}$  nuclei of  $\beta$ - and 2-hydroxypropyl- $\beta$ -CD in the free state ( $\delta_0$ ) and as part of complexes (7) ( $\delta_1$ ) and (8) ( $\delta_2$ ), ppm**

Atom number	$\beta$ -CD			2-HP- $\beta$ -CD		
	$\delta_0$	$\delta_1$	$\Delta\delta_1 = \delta_1 - \delta_0$	$\delta_0$	$\delta_2$	$\Delta\delta_2 = \delta_2 - \delta_0$
1	4.77	4.77	0	4.79	4.79	0
2	3.26	3.25	-0.01	3.26	3.27	0.01
3	3.58	3.52	-0.06	3.70	3.73	0.03
4	3.28	3.28	0	3.26	3.27	0.01
5	3.50	3.58	0.08	3.54	3.50	-0.04
6	3.58	3.55	-0.03	3.56	3.58	0.02
7				3.26	3.26	0
8				3.70	3.70	0
9				0.98	0.96	-0.02

In order to study the biological activity of the obtained supramolecular inclusion complexes (4–6), we evaluated their antiradical effect against 2,2-diphenyl-1-picrylhydrazide (DPPH). The antiradical effect of the presented samples was investigated in relation to the radical 2,2-diphenyl-1-picrylhydrazide (DPPH•).

For the initial assessment of the antiradical activity of the studied samples in the test with the DPPH radical, a methanol solution of DPPH (100  $\mu\text{M}$ ) was used. To select substances with a pronounced anti-radical activity, 2 ml of 100  $\mu\text{M}$  DPPH methanol solution was mixed with 20  $\mu\text{l}$  of the test object dissolved in DMSO at a concentration of 5 mM. Thus, the final concentration of the test substance in the reaction mixture was 50  $\mu\text{M}$ . 10 minutes after adding the solution of the test compound to the solution of the DPPH radical, we measure the decrease in optical density at 515 nm. For substances capable of reducing the optical density by more than 30 %, a test was carried out for interaction with the DPPH radical in the final concentrations of the investigated substances 100, 75, 50, 25, 20, 10, and 5  $\mu\text{M}$ . After that, the concentration of the test substance was determined,

capable of 50 % reduction in optical density —  $IC_{50}$  (DPPH) (Table 7). In a control in a 100  $\mu\text{M}$  DPPH solution, 20  $\mu\text{l}$  of a DMSO solvent was added.

Table 7

**The optical density of a solution of 100  $\mu\text{M}$  DPPH radical after 10-minute incubation with the test substance in a final concentration of 50  $\mu\text{M}$**

№	Connection cipher	Optical density	The magnitude of the decrease in optical density of the initial solution of the DPPH radical, in % of control
1	(4)	0.535	52.3
2	(5)	1.094	2.5
3	(6)	1.058	5.7
4	Control (DPPH solution without test sample)	1.122	-

From Table 7 we see that compound (4) in a final concentration of 50  $\mu\text{M}$  reduces the optical density of the initial solution of the DPPH radical by 52.3 %, and therefore, is promising for further studies. The remaining compounds did not show pronounced antiradical activity under the conditions of this test system.

In the second series of experiments, we studied the ability of compound (4) and of ascorbic acid at various concentrations (from 5.0 to 100  $\mu\text{M}$ ) to interact with the DPPH radical (Tables 8, 9). Using the calibration curves, we determined the concentrations of compound (4) and of ascorbic acid, capable of 50 % reduction in the optical density of a 100  $\mu\text{M}$  solution of the DPPH radical. For compound (4), the  $IC_{50}$ (DPPH) was found to be 46.4  $\mu\text{M}$ . For ascorbic acid, the  $IC_{50}$  (DPPH) was found to be 21.14  $\mu\text{M}$ .

Table 8

**The optical density of a solution of 100  $\mu\text{M}$  DPPH radical after a 10-minute incubation with compound (4) in final concentrations in the reaction mixture of 100, 75, 50, 25, 20, 10 and 5  $\mu\text{M}$**

№	The final concentration of compound (4) in the reaction mixture, $\mu\text{M}$	Optical density
1	100	0.079
2	75	0.275
3	50	0.491
4	25	0.723
5	20	0.798
6	10	0.907
7	5	0.963
	Control (DPPH solution without test sample)	1.042

Table 9

**The optical density of a solution of 100  $\mu\text{M}$  DPPH radical after a 10-minute incubation with ascorbic acid in final concentrations in the reaction mixture of 25, 20, 10 and 5  $\mu\text{M}$**

№	The final concentration of ascorbic acid in the reaction mixture, $\mu\text{M}$	Optical density
1	25	0.429
2	20	0.545
3	10	0.792
4	5	0.914
	Control (DPPH solution without test sample)	1.042

### Conclusions

Thus, supramolecular complexes based on functionally substituted N-benzylidene and allylideneisonicotinohydrazide with cyclodextrins ( $\beta$ -CD, 2-hydroxypropyl- $\beta$ -CD) were obtained and their structures were studied by NMR spectroscopy. It was shown that the products obtained form a mixture capable of dissolving in



water or forming stable aqueous dispersions. The antiradical effect of the synthesized supramolecular inclusion complexes with respect to the DPPH radical was evaluated. The antiradical activity in the conditions of this test system was shown by the sample (4). The concentration was determined, capable of 50 % reduction in the optical density of 100  $\mu\text{M}$  solution of the DPPH radical. For compound (4), the  $\text{IC}_{50}$  (DPPH) was 46.4  $\mu\text{M}$ .

According to our data,  $\text{IC}_{50}$  (DPPH) ( $\mu\text{M}$ ) for the reference sample, in this case, for ascorbic acid was 21.1  $\mu\text{M}$ . The activity of the sample of compound (4), for which the  $\text{IC}_{50}$  (DPPH) was equal to 46.4  $\mu\text{M}$  and is inferior to the reference sample of ascorbic acid.

According to the literature [18–26], the  $\text{IC}_{50}$  (DPPH) ( $\mu\text{M}$ ) for ascorbic acid is 27, for glutathione is 49, for hydroquinone is 27, for trolled is 28, for  $\alpha$ -tocopherol is 28. Thus, the activity of the compound (4) is comparable to the activity of the glutathione known antioxidant.

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### Функционалды ауысқан N-бензилиден- және аллилиденизоникотингидразидтердің олигосахаридтермен супрамолекулярлы қосылу кешендері және олардың қасиеттері

N-бензилиден- және аллилиденизоникотингидразидтердің циклдік олигосахаридтермен ( $\beta$ - және 2-гидроксипропил- $\beta$ -циклодекстриндермен) қосылудың супрамолекулярлық кешендерінің синтезі мен құрылымдық ерекшеліктерін зерттеу нәтижелері ұсынылған. Алынған супрамолекулярлы қосу кешендерінің құрылымы ЯМР бір өлшемді  $^1\text{H}$ ,  $^{13}\text{C}$  және қос өлшемді COSY ( $^1\text{H}$ - $^1\text{H}$ ), HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) және TOCSY ( $^1\text{H}$ - $^1\text{H}$ ) спектроскопия әдістерін қолдана отырып зерттелген. Супрамолекулярлы қосу кешендерінің түзілуі субстрат атомдары мен рецепторлардың ЯМР химиялық ығысуының өзгеру негізінде белгіленген. Спектрлік деректерді талдау негізінде алынған супрамолекулярлық қосылым кешендерінің болжамды схемалары берілген. Зерттелетін гидразинді субстраттардың циклодекстриндермен өзара әрекеттесуі кезінде субстрат молекуласының рецептордың ішкі қуысына енуімен 1:1 және 1:2 кешендері түзілетіні анықталған. Алынған өнімдер суда еруге немесе тұрақты су дисперсияларын құруға қабілетті. 2,2-дифенил-1-пикрил-гидразид-радикалға қатысты синтезделген супрамолекулярлы қосу кешендерінің антирадикалды әсері бағаланды. Осы тест-жүйе жағдайында антирадикалды белсенділікті тек N-(диэтиламино)бензилиденизоникотингидразид супрамолекулярлық кешені ғана көрсетті.

*Кілт сөздер:* олигосахаридтер, гидразондар, циклодекстрин, қосылу кешендері, ЯМР спектроскопиясы, субстрат.

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### Супрамолекулярные комплексы включения функционально-замещенных N-бензилиден- и аллилиденизоникотингидразидов с олигосахаридами и их свойства

Рассмотрены результаты изучения синтеза и структурных особенностей супрамолекулярных комплексов включения N-бензилиден- и аллилиденизоникотингидразидов с циклическими олигосахаридами (с  $\beta$ - и 2-гидроксипропил- $\beta$ -циклодекстринами). Строение полученных супрамолекулярных комплексов включения изучено с применением методов ЯМР одномерной  $^1\text{H}$ ,  $^{13}\text{C}$  и ДЕРТ и двумерной спектроскопии COSY ( $^1\text{H}$ - $^1\text{H}$ ), HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) и TOCSY ( $^1\text{H}$ - $^1\text{H}$ ). Образование супрамолекулярных комплексов включения выявлено на основе изменений химических сдвигов ЯМР атомов субстрата и рецептора. На основании анализа спектральных данных представлены предполагаемые схемы полученных супрамолекулярных комплексов включения. Установлено, что при взаимодействии изучаемых гидразоновых

субстратов с циклодекстринами образуются комплексы включения 1:1 и 1:2 с вхождением молекулы субстрата во внутреннюю полость рецептора. Полученные продукты способны растворяться в воде или образовывать устойчивые водные дисперсии. Оценено антирадикальное действие синтезированных супрамолекулярных комплексов включения в отношении 2,2-дифенил-1-пикрил-гидразид-радикала. Антирадикальную активность в условиях данной тест-системы проявил только супрамолекулярный комплекс N-(диэтиламино)бензилиденизоникотиногидразида.

*Ключевые слова:* олигосахариды, гидразоны, циклодекстрин, комплексы включения, спектроскопия ЯМР, субстрат.

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### **Investigation of intermolecular proton exchange of 3,6-di-tert-butyl-2-oxyphenoxyl with N-phenylanthranilic acid by ESR spectroscopy method**

In this work we studied the intermolecular proton exchange (IPE) reaction between the spin probe of 3,6-di-tert-butyl-2-hydroxyphenoxyl (I) and the aromatic amino acid N-phenylanthranilic acid (N-PhAA). The experimental spectra of the 3,6-di-tert-butyl-2-hydroxyphenoxyl-N-phenylanthranilic acid system were recorded using dynamic EPR spectroscopy. The studies were carried out in a non-aqueous indifferent solvent toluene in a wide temperature range. The theoretical EPR spectra of the radical I — N-PhAA system corresponding to various process rates were successfully simulated using the ESR-EXCHANGE program. This program is written in the modern version of the algorithmic language Fortran 90. The general line-form equation for the four-jump model have been derived from the modified Bloch equations. The second-order rate constants for the intermolecular proton exchange process between radical I and N-PhAA were determined by comparison of the experimental and simulated EPR spectra. The iterative least squares procedure was used for computer analysis of the kinetic data of intermolecular proton exchange and for obtaining activation parameters of the reaction. From kinetic data it follows that N-phenylanthranilic acid has the lowest value of protolytic ability in comparison with aminobenzoic acids.

*Keywords:* ESR-spectroscopy, spin probe, semiquinone radical, anthranilic acid, N-phenylanthranilic acid, 3,6-di-tert.butyl-2-hydroxyphenoxyl, OH-acids, proton exchange reactions, Bloch equation.

#### *Introduction*

It is well known that amino acids play an important role in chemical and biological processes [1]. Anthranilic acid (AA) is an indispensable participant in various biosynthesis processes. Currently, anthranilic acid and its derivatives including N-phenylanthranilic acid are actively studied by both experimental and quantum-chemical methods. Such interest is caused by the widespread use of these aromatic amino acids in both pharmaceutical and organic chemistry and serves as the starting material for the synthesis of various substances [2–4].

The stable semiquinone radical 3,6-di-tert.butyl-2-oxyphenoxyl (I) was used as acid spin probe for investigations of protolytic ability of different acids and bases such as carbonic acids, alcohols, tertiary amines, alkaloids, nitrogen heterocycles in organic solutions [5–8].

Thus the aim of this paper was to investigate the protolytic properties of N-phenylanthranilic acid with 3,6-di-tert.butyl-2-oxyphenoxyl spin probe by ESR spectroscopy method.

#### *Experimental*

N-phenylanthranilic acid ( $C_{13}H_{11}NO_2$ ,  $T_m = 182\text{--}183\text{ }^\circ\text{C}$ ) was purified by recrystallization of the acid from ethanol [9].

3,6-di-tert-butyl-o-benzoquinone ( $C_{14}H_{20}O_2$ ) and 3,6-di-tert-butylpyrocatechol ( $C_{14}H_{22}O_2$ ) were purified by recrystallization from tetrahydrofuran.

3,6-di-tert-butyl-2-hydroxyphenoxy radicals was obtained by dissolving the mixture of 3,6-di-tert-butyl-o-benzoquinone and 3,6-di-tert-butylpyrocatechol in toluene in vacuum. Toluene was dried by standard procedures before use [9].

ESR spectra were recorded on a RE-1306 spectrometer (X-band) using a temperature block in the range of 200–400 K. The theoretical EPR spectra were calculated using the modified version ESR-EXCHANGE program [10]. The program was written in Fortran language using the Visual Studio 2019 software package.

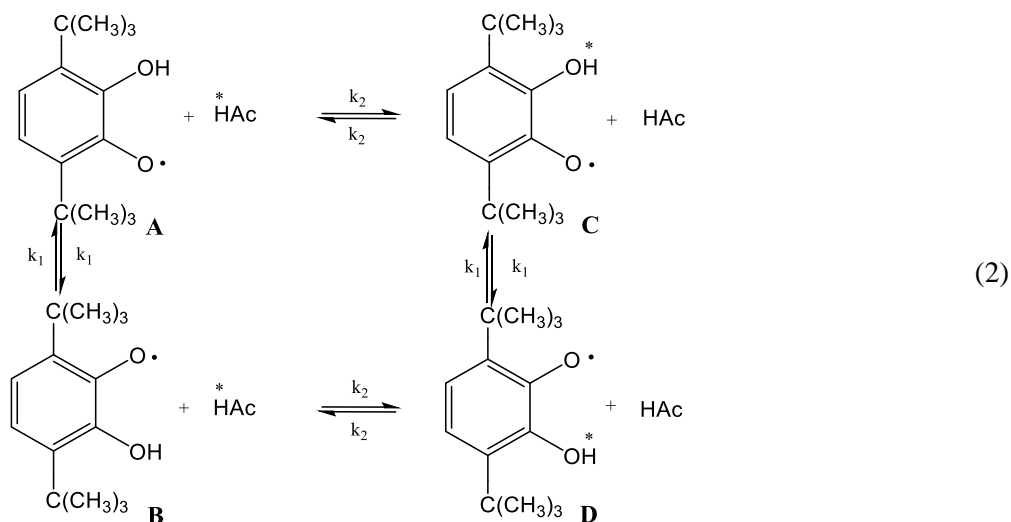
Intermolecular proton exchange can be represented for semiquinone radicals, taking into account the intramolecular processes by the following schemes:



Four-jump model and the modified Bloch equation is the basis of the developed program for the simulation of the ESR spectra of the radical and comparison with experimental data. ESR spectra are calculated from the coupling constants, the populations, the rate constants and the line widths of the all chemical configurations of radicals. The obtained kinetic data are subjected to statistical processing by the least squares method [10].

### Results and Discussion

Intermolecular proton exchange for 3,6-di-tert-butyl-2-oxyphenoxy with N-phenylanthranilic acid taking into account tautomeric transformations can be represented by the following scheme:



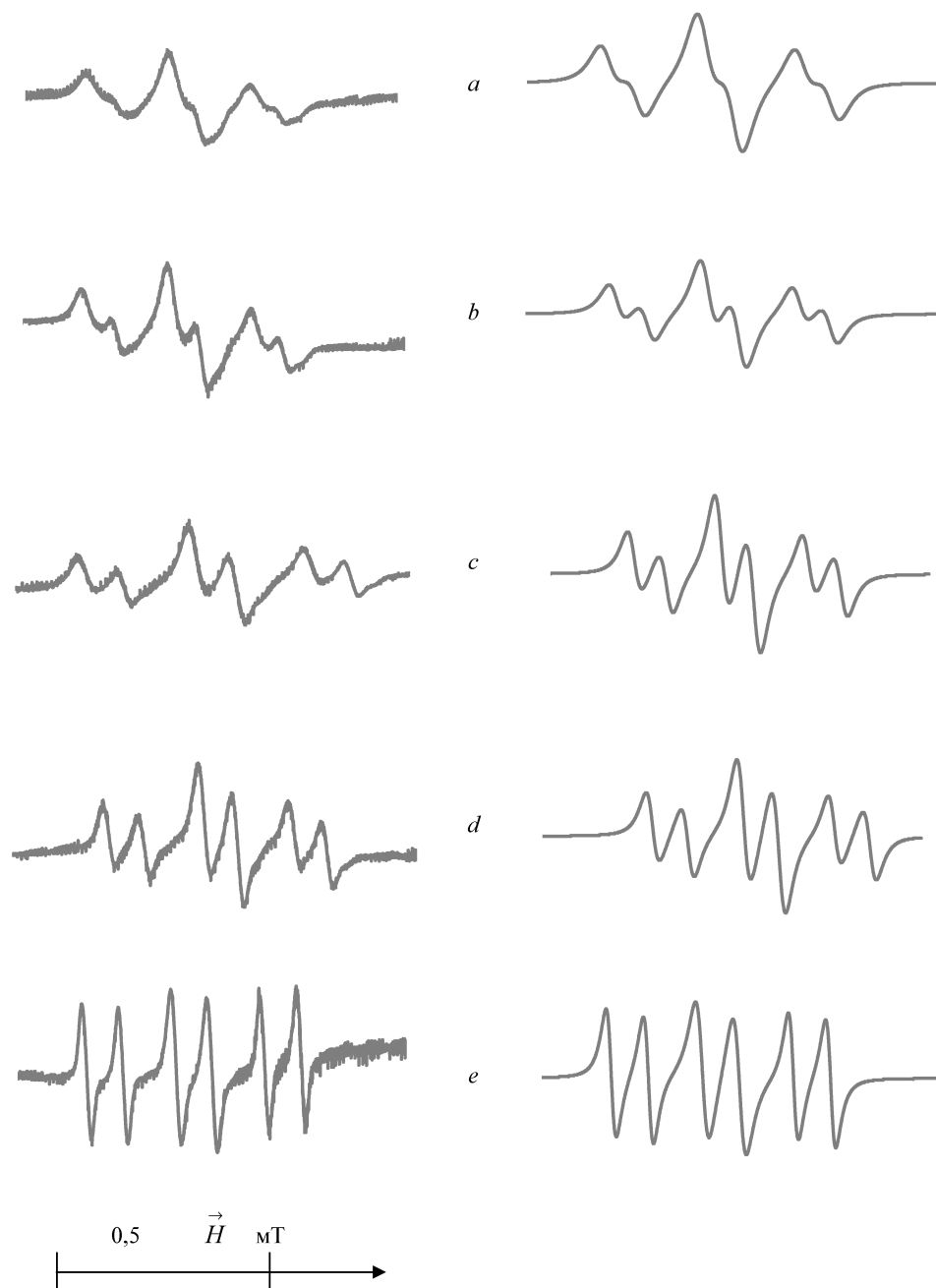
where A, B, C, D denote same forms of radical I differing spin of the hydrogen atom [8].

Studies were performed in a degassed, saturated solution of N-PhAA in toluene [11]. Figure 1 illustrates the ESR spectra of the radical I with N-phenylanthranilic acid to the solution of toluene (N-PhAA concentration 0.09 mol/l) as a function of the temperature.

The ESR spectra of the 3,6-di-tert-butyl-2-hydroxyphenoxy radical presented triplet of doublets with the hyperfine interaction constants (hfc) of aromatic protons equal to  $a_H = 0.392$  mT and with the hfc the proton of the hydroxyl group equal to  $a_H^{\text{OH}} = 0.162$  mT respectively. The broadening of the lines leading to a decrease in the hydroxyl proton constant indicates the presence of intermolecular proton exchange and the transformation of the radical spectrum from a triplet of doublets to a triplet. An analogous dependence is observed in the ESR spectra of the investigated radical and in the presence of others acids. In accord with the theory, such broadening of the lines in the ESR spectra is accompanied by a decrease in the hyperfine interaction. As can

be seen from Figure 1 the ESR spectrum of the radical undergoes a characteristic broadening of the lines corresponding to the intermolecular proton exchange, broadening increases with rising temperature.

The resulting complex due to the hydrogen bond between N-PhAA and the radical is quite strong. This effect slows down the rate of intramolecular tautomerism in the radical. This is evidenced by a decrease in the intensity of the central components of the triplet (Fig. 1 e).



*a* —  $k_{\text{exch}} = 3.56 \times 10^8 \text{ mol}^{-1}\text{s}^{-1}$  at 397 K; *b* —  $k_{\text{exch}} = 2.76 \times 10^8 \text{ mol}^{-1}\text{s}^{-1}$  at 382 K; *c* —  $k_{\text{exch}} = 2.44 \times 10^8 \text{ mol}^{-1}\text{s}^{-1}$  at 374 K;  
*d* —  $k_{\text{exch}} = 1.33 \times 10^8 \text{ mol}^{-1}\text{s}^{-1}$  at 351 K; *e* —  $k_{\text{exch}} = 3.11 \times 10^7 \text{ mol}^{-1}\text{s}^{-1}$  at 295 K.  
 Linewidth = 0.035 mT. Concentration of N-PhAA is 0.09 mol/l

Figure 1. Left: Temperature-dependent ESR spectra of 3,6-di-tert-butyl-2-oxyphenoxy + N-phenylanthranilic acid in toluene, 290–400 K; Right: the simulated spectra

Kinetic parameters of 3,6-di-tert-butyl-2-hydroxyphenoxy with N-phenylanthranilic acids intermolecular proton exchange were calculated using the program in the algorithmic language Fortran. The data obtained

are presented in Table 1. The kinetic parameters of some acids are also presented in Table 1 [12–13]. The Eyring plot gave a clear linear relationship between  $\ln k_{\text{exch}}$  and  $1/T$  with correlation coefficient  $r = 0.98$  (Fig. 2).

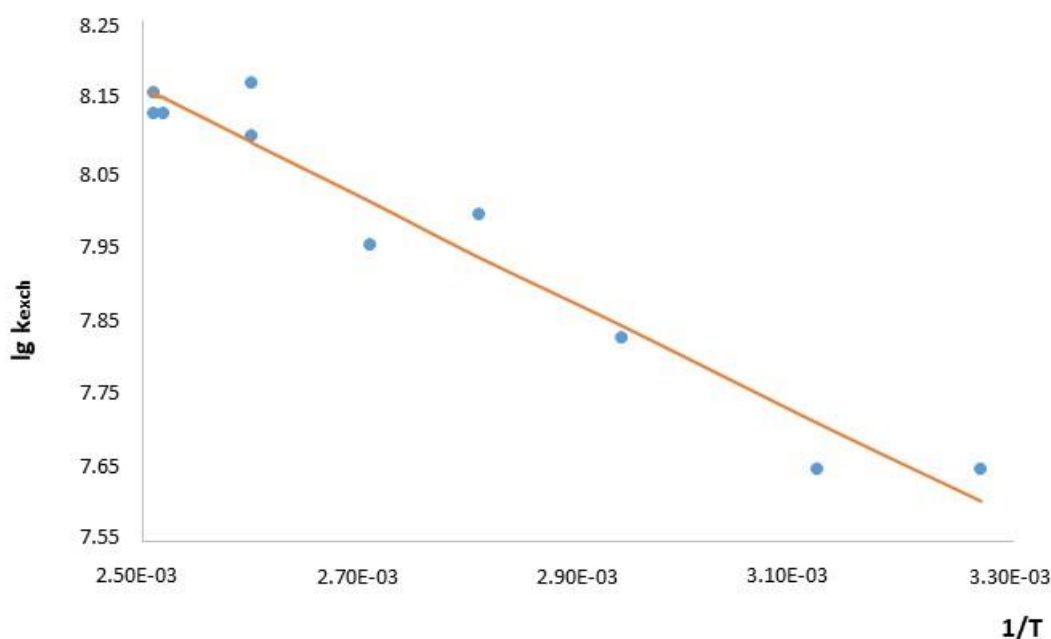


Figure 2. Eyring plot of the intermolecular rate constant ( $k_{\text{exch}}$ ) for 3,6-di-tert-butyl-2-oxyphenoxy + N-phenylanthranilic acid obtained from simulations of the ESR spectrum

Table 1

**Kinetic parameters of the fast intermolecular proton exchange reactions between radical I and various OH-acids in toluene**

Acid	$k_{\text{exch}}$ (293K), l/mol·s	$k^{\circ}_{\text{exch}}$ , l/mol·s	$E_a$ , kJ/mol	$pK_a$
Benzoic	$(1.32 \pm 0.11) \cdot 10^8$	$6.01 \cdot 10^9$	$9.3 \pm 0.9$	4.18
Salicylic	$(1.48 \pm 0.09) \cdot 10^7$	$8.57 \cdot 10^9$	$15.5 \pm 0.5$	3.00
Anthranilic 2-Aminobenzoic	$(1.76 \pm 0.21) \cdot 10^8$	$9.34 \cdot 10^9$	$9.7 \pm 0.2$	4.95
3-Aminobenzoic	$(2.55 \pm 0.19) \cdot 10^8$	$7.22 \cdot 10^9$	$8.2 \pm 0.9$	4.73
4-Aminobenzoic	$(2.93 \pm 0.15) \cdot 10^8$	$1.52 \cdot 10^{10}$	$9.6 \pm 0.9$	4.64
N-Phenylanthranilic 2-(Phenylamino)benzoic	$(3.15 \pm 0.20) \cdot 10^7$	$9.25 \cdot 10^9$	$13.8 \pm 1.1$	5.28

A comparison of the kinetic parameters of the proton exchange of N-phenylanthranilic acid with similar parameters anthranilic acid shows that the exchange rate is slightly lower, and the activation barrier is higher by 3 kJ / mol, as shown in Table 1. The decrease in the reaction rate is possibly associated with the formation of a stronger intramolecular complex between the carboxyl group and amino group acid. A second benzene ring conjugated to the nitrogen atom of the amino group acts on the complex being formed.

### Conclusions

Comparison of the protolytic properties of N-phenylanthranilic acid showed that the acid was the weakest acid submitted. The molecular structure of N-phenylanthranilic acid presents coplanarity between the carboxylic group and the nitrogen atom of the aromatic ring. In turn the lone pair on the nitrogen atom is in resonance with the aromatic rings. Perhaps that the molecular coplanarity is a consequence of the formation of a hydrogen bond between the oxygen of the carboxyl group and the hydrogen of the amino group. The

difference in the protolytic properties of anthranilic acid and N-phenylanthranilic acid is due to the influence of the second aromatic ring bound to the nitrogen atom.

In addition, interpretation of the obtained experimental data requires the use of corresponding quantum chemical calculations.

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### 3,6-ди-трет-бутил-2-оксифеноксидтің N-фенилантранил қышқылымен молекулааралық протон алмасуын ЭПР-спектроскопия әдісімен зерттеу

Мақалада 3,6-ди-трет-бутил-2-гидроксифеноксид (I) мен N-фенилантранил қышқылының спиндік зонд арасындағы молекулааралық протон алмасуының (МПА) реакциясы зерттелген. Динамикалық ЭПР спектроскопиясының көмегімен 3,6-ди-трет-бутил-2-гидроксифеноксид – N-фенилантранил қышқылы (N-ФАҚ) жүйесінің тәжірибелік спектрлері тіркелген. Зерттеу жұмыстары кең температуралық диапазондағы сусыз индифферентті толуол еріткішінде жүргізілген. ESR-EXCHANGE бағдарламасын қолдана отырып, әртүрлі технологиялық жылдамдықтарға сәйкес келетін I — N-ФАҚ радикалды жүйесінің теориялық ЭПР спектрлері сәтті түрде модельденді. Бағдарлама Fortran 90 алгоритмдік тілінің заманауи нұсқасында жазылған. Төрт секірмелі модельге арналған сызық формасының жалпы теңдеуі модифицирленген Блох теңдеулерінен алынған. Радикал I және N-ФАҚ арасындағы молекулааралық протон алмасу процесінің екінші ретті жылдамдық тұрақтылықтары тәжірибелік және модельденген ЭПР спектрлерін салыстыру арқылы анықталған. Ең аз квадраттардың итерациялық процедурасы молекулааралық протон алмасуының кинетикалық мәліметтерін компьютерлік талдау және реакцияның активтену параметрлерін алу үшін қолданылған. Кинетикалық мәліметтерден N-фенилантранил



кышкылы аминобензой кышкылдарымен салыстырғанда төмен протолиттік кабілеттілікке ие екендігі анықталған.

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## Исследование межмолекулярного протонного обмена 3,6-ди-трет-бутил-2-оксифеноксила с N-фенилантрилиновой кислотой методом ЭПР-спектроскопии

В статье исследована реакция межмолекулярного протонного обмена (МПО) между спиновым зондом 3,6-ди-трет-бутил-2-гидроксифеноксидом (I) и ароматической аминокислотой N-фенилантрилиновой кислотой (N-ФАК). Экспериментальные спектры системы 3,6-ди-трет-бутил-2-гидроксифеноксил – N-фенилантрилиновая кислота регистрировали с помощью динамической ЭПР-спектроскопии. Исследования проводились в неводном индифферентном растворителе — толуоле в широком температурном диапазоне. Теоретические спектры ЭПР системы радикал I — N-ФАК, соответствующие различным скоростям процесса, были успешно смоделированы с использованием программы ESR-EXCHANGE. Программа была написана на современной версии алгоритмического языка Фортран 90. Общее уравнение формы линии для четырехпрыжковой модели было получено из модифицированных уравнений Блоха. Константы скорости второго порядка для процесса межмолекулярного протонного обмена между радикалом I и N-ФАК были определены путем сравнения экспериментального и модельного спектров ЭПР. Итеративная процедура наименьших квадратов была использована для компьютерного анализа кинетических данных межмолекулярного протонного обмена и получения активационных параметров реакции. Из кинетических данных следует, что N-фенилантрилиновая кислота обладает наименьшим значением протолитической способности по сравнению с аминобензойными кислотами.

*Ключевые слова:* ЭПР-спектроскопия, спиновый зонд, семихиноновый радикал, антрилиновая кислота, N-фенилантрилиновая кислота, 3,6-ди-трет-бутил-2-оксифеноксил, ОН-кислоты, реакции протонного обмена, уравнение Блоха.

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## Thermal and electrochemical reduction of nickel (II) ferrite under the influence of polymer stabilizers

Nickel (II) ferrite samples have been prepared by co-precipitation of metal salts in an aqueous solution without and with the addition of polymer stabilizers (polyvinyl alcohol and polyvinylpyrrolidone) and further heat treatment at 500 °C, 700 °C and 900 °C. Their structural-phase changes before and after using as catalysts in the electrohydrogenation of acetophenone were revealed by X-ray phase analysis. Morphological features of the obtained NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> + polymer samples were studied by electron microscopy. It has been established that the addition of polymer stabilizer into the co-precipitation medium and its partial preservation in the composition of precursors (metal hydroxides and oxides) and in the formed nickel (II) ferrite have a noticeable effect on the structural-phase constitutions of the samples prepared. Differences in the phase constitutions are also depend on the heat treatment temperature of these samples. It was shown that, in contrast to nickel ferrite synthesized without stabilizers, NiFe<sub>2</sub>O<sub>4</sub> + polymer samples are partially reduced during heat treatment and additionally in an electrochemical system with the formation of Ni- and Fe-Ni-containing composites. The reduced samples of nickel (II) ferrite were tested for their ability to exhibit electrocatalytic properties in the electrohydrogenation of acetophenone. Their low electrocatalytic activity in this process was determined, which is presumably conditioned by the structure of Fe-Ni-alloy particles with iron content predominant, as well as by the presence of magnetite inhibited the activity of nickel particles.

*Keywords:* nickel (II) ferrite, co-precipitation method, heat treatment, electrochemical reduction, nickel and iron zero-valence particles, electrocatalytic hydrogenation, acetophenone.

### Introduction

Ferrites are magnetic oxide metal compounds with the general structural formula MFe<sub>2</sub>O<sub>4</sub> (M = doubly charged metal ion, for example, Cu, Ni, Co, Zn, Mn, Mg, etc.), in which magnetic and electrical properties are combined peculiarly. It should be noted the ecological safety of these materials due to their high thermal stability (melting and decomposition temperatures above 1500–1700 °C), lack of toxicity and insolubility in water.

Materials based on metal ferrites are widely used in instrument engineering, radio electronics, electro-technical industry, in catalysis and other branches of science and technology. In catalysis, ferrites of transition metals (Co, Ni, Cu, Zn) and their mixed compositions have been successfully applied. The particle size of such catalysts is varied from 2 nm to several micrometers. Moreover, their magnetic properties allow easy to remove them from the reaction system and repeatedly use them practically without loss of catalytic activity [1]. In the literature, examples of the application of transition metal ferrites in catalytic reaction have been described, such as decomposition of methanol into CO and methane or CO and H<sub>2</sub>, oxidation of various alkenes, alkylation, dehydration, synthesis of quinoxaline derivatives, 1,4-dihydropyridine, etc. [2–4].

Nickel ferrite has an inverse spinel structure, when half of the iron cations occupies tetrahedral positions in the crystal cell, while the other half and all Ni<sup>2+</sup> cations occupy octahedral positions. The location of nickel cations in the crystal structure of NiFe<sub>2</sub>O<sub>4</sub> is closely related to its magnetic properties. Nickel ferrite shows itself as a super-paramagnet and applies as gas-sensors, magnetic fluids, catalysts, magnetic storage systems, photomagnetic materials, site-specific drug delivery, microwave devices, etc. [5]. Recently the possibility of monodispersed NiFe<sub>2</sub>O<sub>4</sub> nanospheres using as a high-performance pseudo-capacitor [6] and electrode material for a super-capacitor has been established [7].

Transition metal ferrites are produced by various methods, including thermal decomposition, microemulsion method, co-precipitation, hydrothermal, solvothermal and biological methods [8–11]. Low temperature co-precipitation methods [12] and sol-gel processes [13], including the creation of complexes with the addition of surfactants, have such advantages as a lower calcining temperature as compared to solid-phase synthesis, simplicity of fulfilment, high chemical homogeneity and purity of the materials obtained. The incorporation of various type additives, which promote the formation of doped structures, into the base system composition

is considered as a one of the chemical methods for improving the structural and magnetic properties of the resulting ferrites. In research works [14–15], the effect of an organic stabilizer on crystallinity, phase constitution and morphological features of nickel ferrite nanoparticles has been studied.

The purpose of this work is to study the structural-phase transformations of nickel (II) ferrite samples synthesized without and in the presence of a polymer stabilizer during their heat treatment, as well as the possibility of their electrochemical reduction with the formation of Ni<sup>0</sup>-Fe<sup>0</sup>-containing composites and their electrocatalytic activity in electrohydrogenation of acetophenone (APh) as a model compound.

### Experimental

Dispersed nickel (II) ferrite (NiFe<sub>2</sub>O<sub>4</sub>) was synthesized by the co-precipitation method from aqueous solutions of metal salts according to the following procedure. A stoichiometric quantities of nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and iron chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) (in a ratio of 1:2) were dissolved in 300 ml of distilled water and the mixture was stirred for 30 min at 40 °C. Next 1M NaOH solution was poured dropwise to pH = 12 under constant stirring. The obtained brown precipitate was filtered and washed with distilled water heated up to 50 °C. It was dried at 80 °C. The resulting dark brown powder was divided into three equal parts and heat treated at 500 °C, 700 °C and 900 °C for 2 hours. It was crushed in a Tube Mill control at the same speed and duration of grinding.

Nickel (II) ferrite samples with the addition of water-soluble polymers (polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP)) were obtained by dissolving metal salts in a 3 % polymer solution and co-precipitating by sodium hydroxide. The filtered precipitates were washed with distilled water having room temperature. After drying the composites were also thermally treated at 500 °C, 700 °C and 900 °C during 2 hours. The NiFe<sub>2</sub>O<sub>4</sub> samples produced after heat treatment were crushed in a Tube Mill control.

The nickel and iron metals content in the filtrates after co-precipitation procedure was determined by a selective complexometric titration [16–17]. According to the results of titration the lack of metal cations in the obtained transparent filtrates was established, which indicate of their practically complete precipitation in the form of the corresponding hydroxides or oxides.

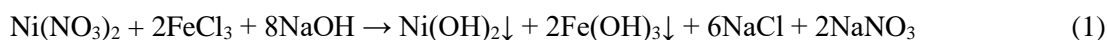
The structure and phase constitution of the synthesized nickel ferrite samples were studied by X-ray diffraction (XRD) analysis on a DRON-2 diffractometer. The morphological features of the nickel ferrite samples were scanned on the TESCAN MIRA 3 LMU electron microscope.

The ability of NiFe<sub>2</sub>O<sub>4</sub> samples prepared to electrochemical reduction and manifestation of electrocatalytic properties by the Fe-Ni-composites were tested in the electrochemical system. The electrocatalytic activity of Fe-Ni-composites was studied in the process of electrohydrogenation of acetophenone, the product of which is methyl phenyl carbinol (MPhC), a well-known fragrant substance with a wide range of applications. Experiments were carried out in an electrochemical diaphragm cell in alcohol-aqueous-alkaline catholyte at a current of 1.5 A, and a temperature of 30 °C. The cathode was a copper plate that was closely contacted the bottom of the cell and served as a substrate for the applied nickel ferrite particles (by a weight of 1 g), platinum gauze was used as an anode. The initial concentration of APh was 0.198M. The nickel ferrite samples deposited on the cathode were fixed on it by an inner magnet and saturated with hydrogen (stage I). During hydrogen saturation the electrochemical reduction of metal cations could be occur. The duration of this stage (until the ratio of the evolved gases is set to V(H<sub>2</sub>):V(O<sub>2</sub>) = 2:1) was varied from 10 to 200 minutes. Then organic compound was injected into the catholyte and its electrocatalytic hydrogenation carried out (stage II). The volume of hydrogen (V<sub>H<sub>2</sub></sub>) absorbed on the stage I, and also the hydrogenation rate (W), hydrogen utilization coefficient (η) and conversion of the hydrogenated compound (α) for the stage II were calculated from the volumes of gases evolved (oxygen and hydrogen). The hydrogenation products were extracted from the catholyte with chloroform, and the extracts were analyzed on a Kristall-5000.1 chromatograph.

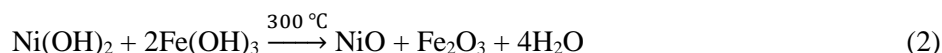
### Results and Discussion

Structural-phase changes of NiFe<sub>2</sub>O<sub>4</sub> samples after heat treatment, and after electrochemical reduction and use them in electrohydrogenation of APh are studied by X-ray phase analysis (XRD). The X-ray diffraction patterns of nickel ferrite samples prepared without and with addition of polymer stabilizers are shown in Figures 1–3.

At the co-precipitation of nickel nitrates and iron hydroxide in an aqueous solution the following reaction occurs:



Then the dried powder of co-precipitated hydroxides of both metals is subjected to heat treatment at 500 °C, 700 °C и 900 °C for 2 hours. Upon reaching a temperature of 300 °C metal oxides are formed from metal hydroxides:



At 500 °C nickel and iron oxides react with the formation of nickel (II) ferrite:



The formation of the above phases is confirmed by XRD patterns of nickel ferrite synthesized without addition of a polymer stabilizer (Figure 1, 1a). According to the XRD results, it was found that the samples of nickel ferrite heat treated contain crystalline phases of nickel (II) ferrite, as well as nickel oxide (NiO) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) with low intensity peaks, as shown in Figure 1.

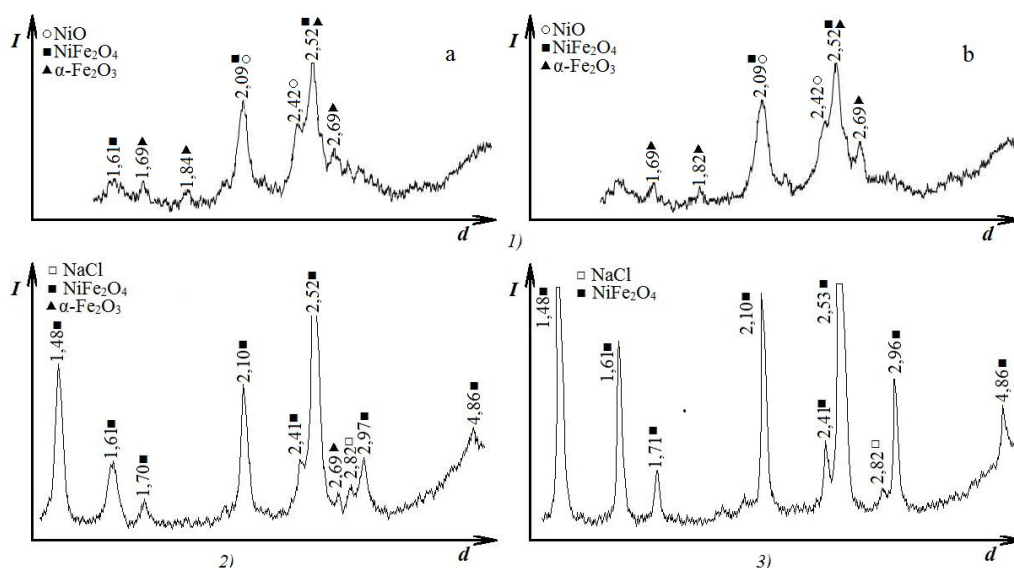
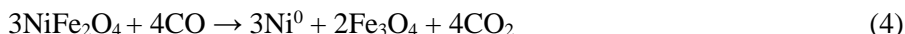


Figure 1. XRD patterns of  $\text{NiFe}_2\text{O}_4$  samples treated at 500 °C before (a) and after (b) electrohydrogenation of APh (1), at 700 °C (2) and 900 °C (3)

As follows from the given X-ray diffraction patterns, as the heat treatment temperature rises, the crystallinity of the present phases also increases. It has been established that in the compositions of all  $\text{NiFe}_2\text{O}_4$  samples after electrochemical reduction attempt and their use as electrocatalysts, the phase transformations do not occur (e.g. Figures 1, 1a and 1b). This indicates the inability of nickel (II) ferrite to electrochemical reduction under specified conditions and to manifestation of electrocatalytic properties in the studied process.

The addition of a polymer stabilizer into the co-precipitation reaction medium and its partial conservation in the composition of precipitated metal hydroxides and oxides have a noticeable effect on the structural phase constitution of nickel (II) ferrite samples heat treated (Fig. 2 and 3). Differences in phase constitution are also depended on the heat treatment temperature of these samples. Thus, the crystalline phases of metallic nickel ( $\text{Ni}^0$ ) reduced from nickel ferrite by the products of PVA thermal decomposition appear in the constitution of the  $\text{NiFe}_2\text{O}_4 + \text{PVA}$  sample treated at 500 °C (Figure 2, 1a):



In this case, the release of nickel from the  $\text{NiFe}_2\text{O}_4$  crystal lattice is accompanied by the formation of magnetite ( $\text{Fe}_3\text{O}_4$ ). The crystalline phases of nickel are saved in this sample after the electrochemical reduction (Fig. 2, 1b). The thermal treatment of a  $\text{NiFe}_2\text{O}_4 + \text{PVA}$  sample at 700°C leads to partial reduction of not only nickel, but also iron:



which form the Fe-Ni-alloy (Fig. 2, 2a).

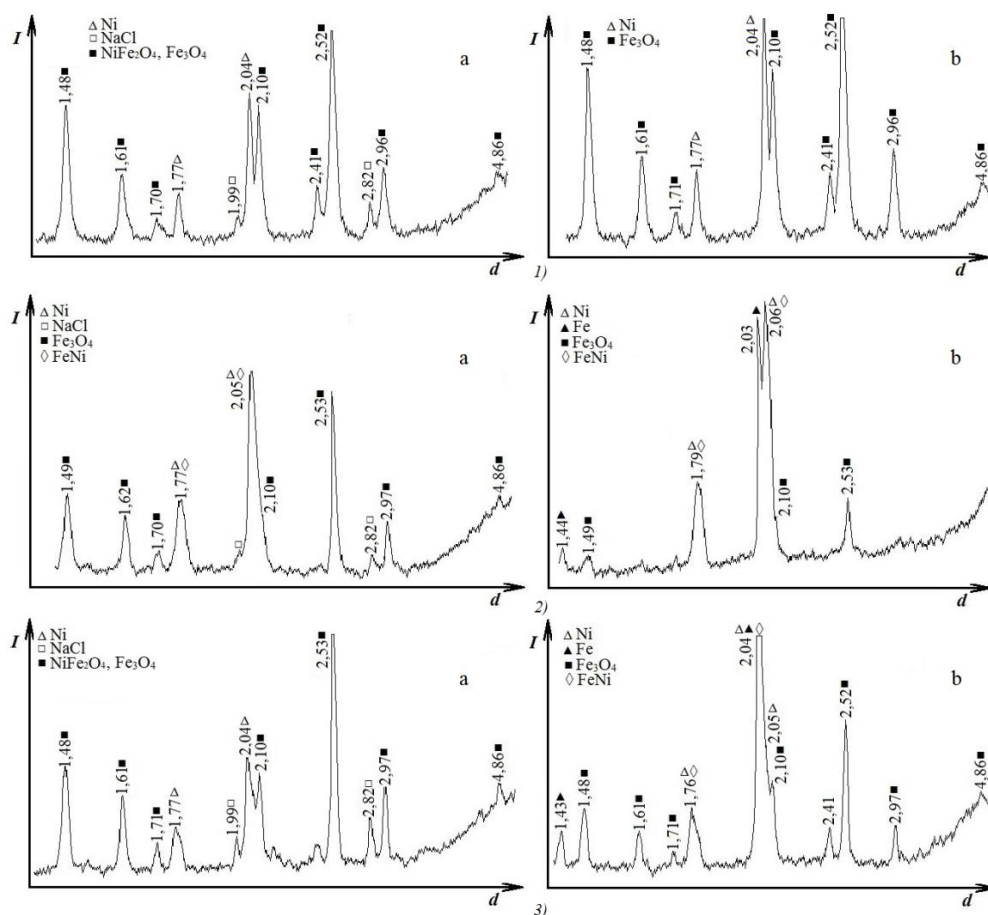


Figure 2. XRD patterns of  $\text{NiFe}_2\text{O}_4$  + PVA samples before (a) and after (b) electrohydrogenation of APh treated at 500 °C (1), 700 °C (2) and 900 °C (3)

After electrochemical reduction the amount of reduced iron and its alloy with nickel increases with a sharp decrease in the crystalline phases of magnetite. The constitution of the  $\text{NiFe}_2\text{O}_4$  + PVA (900 °C) sample after heat treatment (Fig. 2, 3a) is almost similar to the constitution of the  $\text{NiFe}_2\text{O}_4$  + PVA (500 °C) sample (Fig. 2, 1a), but crystalline phases of iron and Fe-Ni-alloy additionally appear during its electrochemical reduction. In so doing, magnetite also present in the composition of this sample.

Nickel (II) ferrite samples synthesized in the presence of PVP and thermally treated at the same temperatures ( $\text{NiFe}_2\text{O}_4$  + PVP) have similar phase constitutions (Fig. 3). The effect of this polymer stabilizer on the electrochemical reduction of both metals from  $\text{NiFe}_2\text{O}_4$  + PVP samples has a character similar to the PVA effect. The most full electrochemical reduction of nickel (II) ferrite is achieved in the case of its preliminary treatment at 700 °C (Fig. 3, 2a, 2b). As a result, the composite with Fe-Ni-alloy, metallic iron and  $\text{Fe}_3\text{O}_4$  residue in its constitution is formed.

The structure and morphological features of heat treated nickel (II) ferrite samples were studied by electron microscopy using two electron detectors (SE, BSE). Obviously, in the BSE images the light areas are metal formations ( $\text{Fe}^0$ ,  $\text{Ni}^0$ , Fe-Ni-alloys), the darker ones are oxygen-containing metal compounds and impurities in the sample (e.g. NaCl).

In the  $\text{NiFe}_2\text{O}_4$  + PVA (700 °C) sample after electrochemical reduction and electrohydrogenation of APh (Fig. 4, b), light areas are significantly more, than in the sample after heat treatment (Fig. 4, a), which confirms the passage of additional reduction of both metals from  $\text{NiFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  formation in the electrochemical system. Meanwhile the oxygen content significantly decreases and the iron content increases. If after heat treatment the particles of the resulting Fe-Ni-alloys had compositions with the ratio of metals Fe:Ni = 3:1, 1:1 and even 1:1.5 (i.e. with a high nickel content) according to the energy-dispersive X-ray spectroscopy (EDS) analysis, then after electrochemical reduction these ratios changed to 6:1 and 5:1. The distribution of metals in the surface layer of particles is also different (Fig. 5): iron is densely distributed over the entire surface and nickel is more often distributed along the particle edge and in separate coagulates.

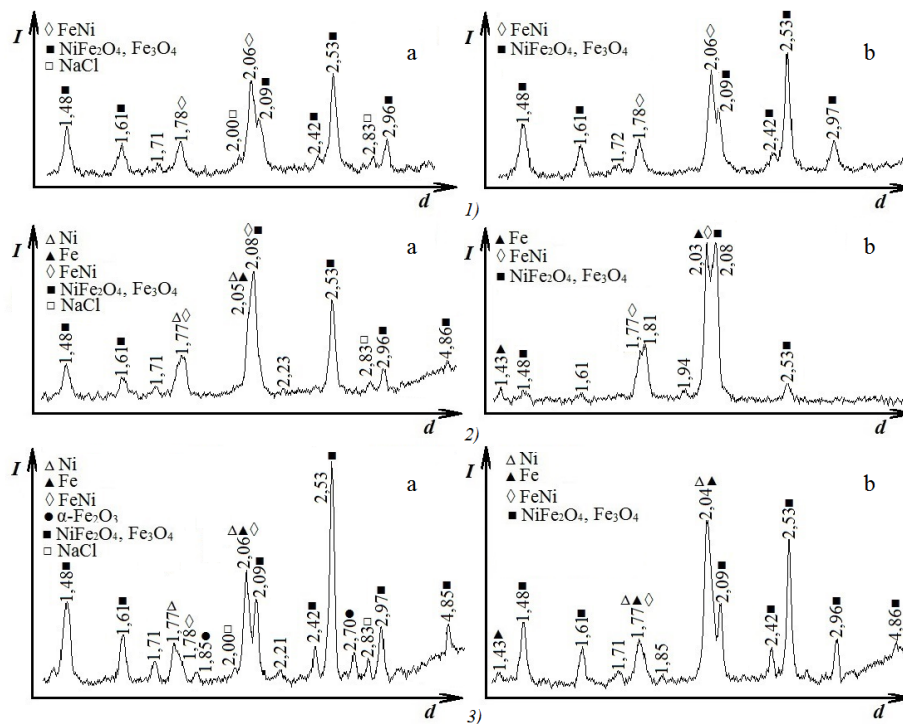


Figure 3. XRD patterns of  $\text{NiFe}_2\text{O}_4 + \text{PVP}$  samples before (a) and after (b) electrohydrogenation of APh treated at 500 °C (1), 700 °C (2) and 900 °C (3)

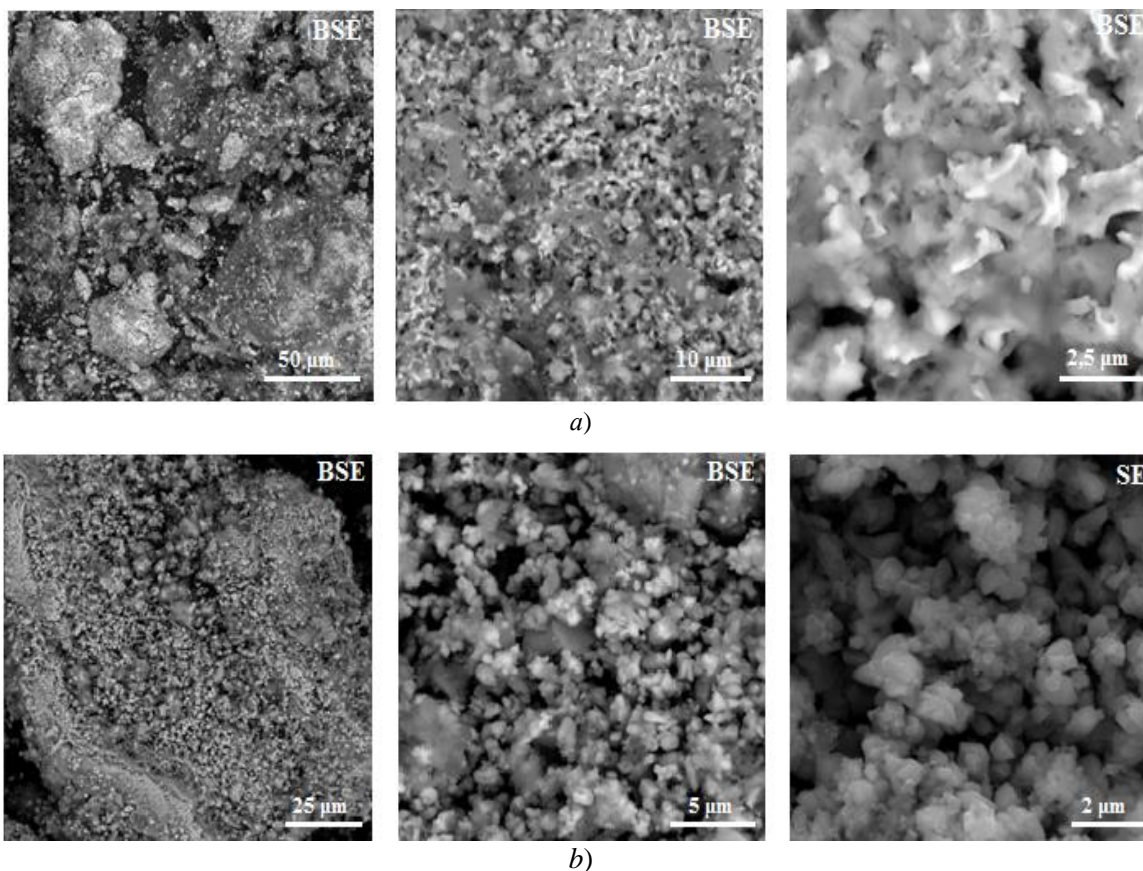


Figure 4. Micrographs of  $\text{NiFe}_2\text{O}_4 + \text{PVA}$  (700 °C) sample after heat treatment (a) and after electrocatalytic hydrogenation of APh (b)

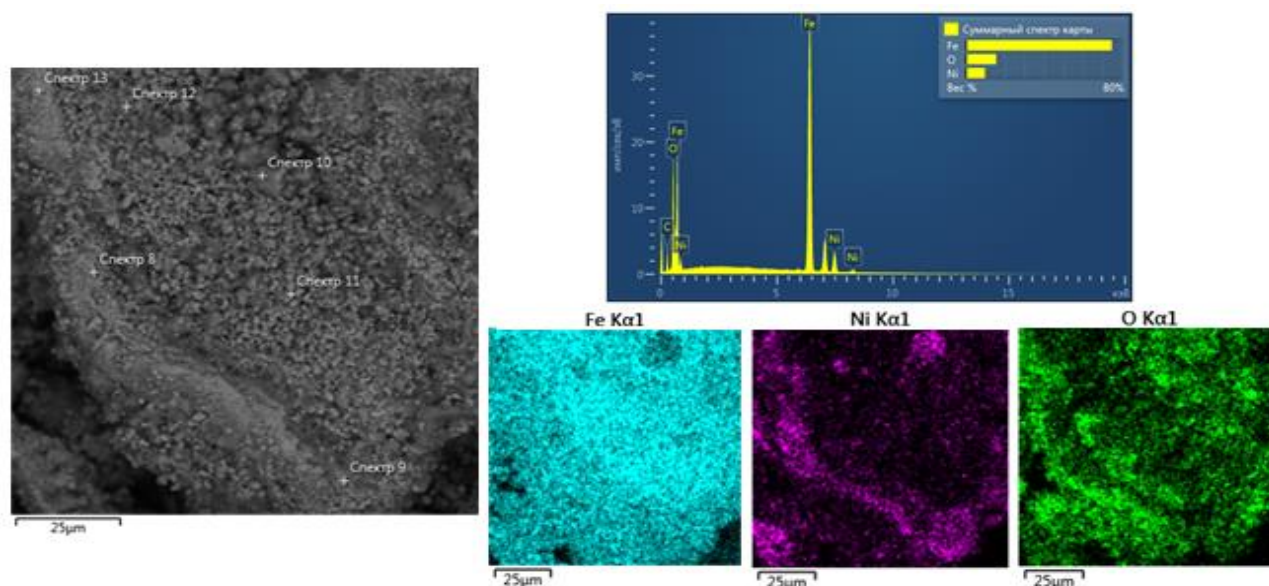


Figure 5. EDS analysis of  $\text{NiFe}_2\text{O}_4 + \text{PVA}$  (700 °C) sample particles after electrocatalytic hydrogenation of APh

All the nickel (II) ferrite samples synthesized without and with polymer stabilizers and heat treated were investigated for their ability to electrochemical reduction and manifestation of electrocatalytic properties in the electrohydrogenation of acetophenone:



The main resulting data of both stages of electrochemical experiments are given in Table 1. First the electrochemical reduction of  $\text{NiFe}_2\text{O}_4$  samples was carried out, then electrocatalytic hydrogenation of APh on forming Fe-Ni composites as electrocatalysts. For comparison, the results of electrochemical reduction of APh on a Cu cathode, which proceeds with a relatively low process rate and conversion of the hydrogenated substance, not exceeding 22,1 %, are also presented here. In addition to methyl phenyl carbinol (equation (1)), dimeric compounds were formed in the process.

Table 1

**Electrochemical reduction of synthesized nickel (II) ferrite samples and electrocatalytic hydrogenation of acetophenone in their presence**

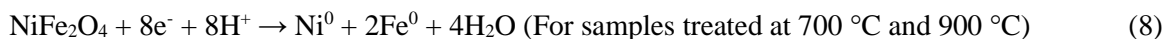
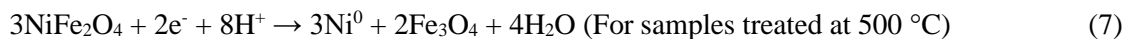
Nickel ferrite	Metal content in 1 g of a ferrite sample, g		Electrochemical reduction of ferrite		Electrocatalytic hydrogenation of acetophenone		
	Ni	Fe	$\tau$ , min	$V_{\text{H}_2}$ , ml	W, ml $\text{H}_2$ /min ( $\alpha = 0,25$ )	$\eta$ , %	$\alpha$ , %
Cu cathode	-	-	-	-	1,0	6,9	22,1
$\text{NiFe}_2\text{O}_4$ (500 °C)	0.245	0.467	40	13.0	0.0	0.0	0.0
$\text{NiFe}_2\text{O}_4$ (700 °C)	0.252	0.481	20	8.8	0.0	0.0	0.0
$\text{NiFe}_2\text{O}_4$ (900 °C)	0.256	0.488	20	8.9	0.0	0.0	0.0
$\text{NiFe}_2\text{O}_4 + \text{PVA}$ (500 °C)	0.224	0.426	20	8.6	0.0	0.0	8.7
$\text{NiFe}_2\text{O}_4 + \text{PVA}$ (700 °C)	0.245	0.467	140	108.1	0.0	0.0	8.7
$\text{NiFe}_2\text{O}_4 + \text{PVA}$ (900 °C)	0.265	0.506	160	90.4	0.9	7.9	48.2
$\text{NiFe}_2\text{O}_4 + \text{PVP}$ (500 °C)	0.236	0.450	50	13.3	0.0	0.0	0.0
$\text{NiFe}_2\text{O}_4 + \text{PVP}$ (700 °C)	0.288	0.549	200	114.7	1.0	8.8	47.7
$\text{NiFe}_2\text{O}_4 + \text{PVP}$ (900 °C)	0.285	0.544	110	52.5	1.1	10.0	63.5

The carrying out of the stage of electrochemical reduction of nickel (II) ferrite samples can be controlled by the volumes of absorbed hydrogen. According to data of Table 1,  $\text{NiFe}_2\text{O}_4$  samples prepared without the participation of polymers and thermally treated practically do not absorb hydrogen in the first stage, i.e. they are not reduced electrochemically. During the preliminary heat treatment these samples also were not reduced, and their constitutions were contained mainly crystalline phases of  $\text{NiFe}_2\text{O}_4$  (Fig. 1). The same crystalline



phases remain in their constitutions even after attempts to reduce them in the electrochemical system and, as can be seen from the data in Table 1, they do not exhibit electrocatalytic activity during the electrohydrogenation of APh – the second stage. The electrochemical reduction of APh does not pass in the presence of magnetic powder of nickel ferrite because it has not electrocatalytic properties, and covers the surface of the copper cathode holding onto it by an external magnet.

It has been established by the XRD analyzes that the  $\text{NiFe}_2\text{O}_4$  + polymer samples are partially reduced during heat treatment by the polymer decomposition products, and their additional reduction occurs in the electrochemical system (Fig. 2 and 3):



As can be seen from values of absorbed hydrogen volumes given in Table 1, the samples with heat treatment at 700 °C and 900 °C undergo additional electrochemical reduction. However, only one sample ( $\text{NiFe}_2\text{O}_4$  + PVA (900 °C)) among the samples prepared with PVA exhibits the electrocatalytic activity and only in relation to the APh conversion — it increases to 48 % (Table 1). The  $\text{NiFe}_2\text{O}_4$  + PVP samples partially reduced thermally are also reduced additionally in the electrochemical system (mainly, samples treated at 700 °C и 900 °C) and they show the electrocatalytic activity slightly higher than samples with PVA (Table 1).

The low electrocatalytic activity of nickel ferrite samples synthesized in the presence of polymers and partially reduced during heat treatment and additionally in an electrochemical system can be explained as follows. Firstly, in samples of  $\text{NiFe}_2\text{O}_4$  + polymer thermally treated at 500°C, the reduction of nickel (II) cations (Fig. 2, 1) is accompanied by the formation of magnetite (reaction equation (7)). It is possible that the magnetite completely closes the reduced nickel, which leads to the loss of its catalytic activity. Secondly, in the samples of  $\text{NiFe}_2\text{O}_4$  + polymer (700 °C) and (900 °C) after thermal and electrochemical reduction, the composites are formed consisting of reduced iron ( $\text{Fe}^0$ ), Fe-Ni-alloys, possibly reduced nickel and magnetite residues (Fig. 2 and 3). According to previously performed experiments, iron skeleton catalysts were practically inactive in the electrohydrogenation of APh. Therefore, the reduced iron should not exhibit high electrocatalytic activity in the studied process unless it interacts with other components of the composite as with carriers. Magnetite also did not catalyze the electrohydrogenation of APh. In this case, particles of Fe-Ni-alloys are formed with various compositions, but with a predominant iron content, as it was shown by X-ray spectral analyzes. And such Fe-Ni-particles exhibited low electrocatalytic activity in the electrohydrogenation of APh.

### Conclusions

Nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ) samples were obtained by co-precipitation method without and with the addition of polymer stabilizers (PVP, PVA) followed by heat treatment at 500 °C, 700 °C and 900 °C. XRD analysis shown that as a result of heat treatment of  $\text{NiFe}_2\text{O}_4$  + polymer samples, the nickel and iron partial reduction occurred due to the thermal decomposition products of polymer stabilizers of low content. The resulting Fe-Ni-composites possessed magnetic properties and exhibited low electrocatalytic activity in the electrohydrogenation of acetophenone, obviously caused by the structure of Fe-Ni-alloys particles with predominant iron content.

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## Полимерлік тұрақтандырғыштардың әсерімен никель ферритін (II) термиялық және электрохимиялық қалпына келтіру

Никель (II) ферритінің үлгілері сулы ерітіндіде полимерлі тұрақтандырғыштарды (поливинил спирт және поливинилпирролидон) қоспай және қосу арқылы металл тұздарын бірге тұндырумен және оларды одан әрі 500 °С, 700 °С және 900 °С кезінде термиялық өңдеуімен алынған. Олардың құрылымдық-фазалық өзгерістері ацетофенонды электрогидрлеуде оларды катализаторлар ретінде қолдануға дейін және қолданғаннан кейін рентгенофазалық талдау әдісімен анықталған. Алынған үлгілердің  $\text{NiFe}_2\text{O}_4$  және  $\text{NiFe}_2\text{O}_4$  + полимер морфологиялық ерекшеліктері электрондық микроскопия әдістерімен зерттелген. Полимерлі тұрақтандырғышты бірге тұндыру ортасына енгізу және оның прекурсорлар (металдар гидроксидтері және оксидтері) мен қалыптасатын никель (II) ферриті құрамында жартылай сақталуы алынған үлгілердің құрылымдық-фазалық құрамына айтарлықтай әсер ететіні анықталған. Фазалық құрамдардағы айырмашылықтар осы үлгілердің термиялық өңдеу температурасымен де анықталады. Тұрақтандырғыштарсыз синтезделген никель ферритіне қарағанда  $\text{NiFe}_2\text{O}_4$  + полимер үлгілері термиялық өңдеу барысында және құрамында Ni- және Fe-Ni-композиттерін қалыптастыра отырып электрохимиялық жүйеде жартылай тотықсыздады. Қалпына келтірілген никель (II) ферритінің үлгілері ацетофенонды электрогидрлеуде электрокаталикалық қасиеттердің пайда болу қабілетіне зерттелген. Өткізілген тәжірибелер арқылы осы үдерісте олардың әлсіз электрокаталикалық қасиеттері анықталды, ол құрамында басым бөлігі темір болатын Fe-Ni-балқыма бөлшектерінің құрылысымен, сондай-ақ никель бөлшектерінің белсенділігін тежейтін магнетиттің болуымен түсіндірілген.

*Клт сөздер:* никель ферриті (II), тұндыру әдісі, термиялық өңдеу, электрохимиялық қалпына келтіру, никель мен темірдің нуль-валентті бөлшектері, электрокаталикалық гидрлеу, ацетофенон.

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## Термическое и электрохимическое восстановление феррита никеля (II) под влиянием полимерных стабилизаторов

Образцы феррита никеля (II) получены совместным соосаждением солей металлов в водном растворе без и с добавлением полимерных стабилизаторов (поливинилового спирта и поливинилпирролидона) и дальнейшей термической обработкой при 500 °С, 700 °С и 900 °С. Методом рентгенофазового анализа выявлены их структурно-фазовые изменения до и после применения их в качестве катализаторов в электрогидрировании ацетофенона. Морфологические особенности полученных образцов NiFe<sub>2</sub>O<sub>4</sub> и NiFe<sub>2</sub>O<sub>4</sub> + полимер исследованы методом электронной микроскопии. Установлено, что введение полимерного стабилизатора в среду соосаждения и частичное сохранение его в составе прекурсоров (гидроксидов и оксидов металлов) и формирующегося феррита никеля (II) оказывают заметное влияние на структурно-фазовый состав полученных образцов. Отличия в фазовых составах определяются также температурой термической обработки этих образцов. Показано, что, в отличие от феррита никеля, синтезированного без стабилизаторов, образцы NiFe<sub>2</sub>O<sub>4</sub> + полимер частично восстанавливаются в ходе термической обработки и дополнительно в электрохимической системе с образованием Ni- и Fe-Ni-содержащих композитов. Восстановленные образцы феррита никеля (II) исследованы на способность к проявлению электрокаталитических свойств в электрогидрировании ацетофенона. Проведенными экспериментами установлены их слабые электрокаталитические свойства в этом процессе, предположительно обусловленные строением частиц Fe-Ni-сплавов с преобладающим содержанием железа, а также присутствием магнетита, ингибирующего активность частиц никеля.

*Ключевые слова:* феррит никеля (II), метод соосаждения, термическая обработка, электрохимическое восстановление, нуль-валентные частицы никеля и железа, электрокаталитическое гидрирование, ацетофенон.

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## **Research of the influence of external factors on copolymers based on unsaturated polyester resins**

The article is devoted to the research of the influence of external factors on copolymers based on poly(propylene fumarate phthalate) and acrylic acid. In this paper, the effect of organic solvents and pH of the medium on the rate of swelling of synthesized copolymers is studied. The rate of polymer swelling depends on many factors, including: the nature of the polymer and the solvent, the presence of electrolytes, changes in pH and ambient temperature, the molecular weight of the polymer, and so on. It is assumed that the polymer network of copolymers consists mostly of unsaturated polyester resin links. Research results show that the ratio of monomer units in the copolymer significantly affects the susceptibility of the polymer gel to the pH of the medium and the presence of organic solvents (DMSO, DMFA, ethanol). It is proved that changing the properties of the comonomer allows you to obtain hydrogels that can swell or collapse due to changes in the ionic strength or thermodynamic quality of the solution. By varying the ratio of comonomers of the links was adjusted by the intervals of the swelling and compression of the polymer networks. The molecular weight of poly(propylene fumarate phthalate) was determined by gel-penetrating chromatography. The identification and composition of copolymers were determined by IR spectroscopy and HPLC, respectively.

*Keywords:* polypropylene fumarate phthalate, acrylic acid, radical copolymerization, polar organic solvents, swelling, collapse, unsaturated polyester resin.

### *Introduction*

Hydrogels are one of great interest in high-molecular compound research area in the recent decades, because these polymers able to swell in water by a several values from the original volume. Ability to absorb large amounts of water and bind dissolved low-molecular substances is a distinctive feature of these polymers. The primary quality of these polymers is the possession of macromolecular segment chain having hydrophilic properties of ionic and non-ionic or ampholytic nature [1–3]. Since the main hydrogel feature is the absorption of extremely large amounts of water, this impacts its structure which has a three-dimensional grid form. These grids structure resembles a linear polymer with sparse cross-linking points. In case of swelling in water distance between adjacent cross-linking points increases while the amount of the points remains the same. Such behavior allows hydrogels to absorb large amounts of water with massive volume change.

Unsaturated polyesters are promising polymeric systems creation chemical agents which are obtained from polyatomic alcohols and carboxylic acids by polycondensation. The key feature of unsaturated polyesters is high copolymerization reaction ability (curing behavior) with vinyl monomers at room temperature without high pressure or volatiles or other byproducts emission [4–8]. Due to this, unsaturated polyesters can be used as chemical agents for synthesizing «intelligent» polymers widely used in medicine, pharmaceuticals, biotechnology and many other areas of the living environment.

Previously we have obtained and researched poly(propylene fumarate phtalate) based polymeric hydrogels with high absorbing abilities. Obtained results suggest prospects of their use as water sorbents in crop production [9] and efficient nanocatalysts [10]. However, it was interesting to continue researching in this area with a view to a comprehensive in-depth study of this unique and important group of materials.

This work is devoted to new polymers based on unsaturated polyester — poly(propylene fumarate phtalate) (p-PFP) with acrylic acid (AA) physical and chemical properties synthesis and research. Synthesized specimens have been analyzed for medium pH change, organic solvents and their concentration change, as well as initial composition of copolymers polymeric grid.

### Experimental

This article is a continuation of the work of the authors in this field (topic). The synthesis of an unsaturated polyester resin and the preparation of copolymers based on poly (propylene fumarate phthalate) are described in a previous article [13].

Cross-linked copolymer formation as result of p-PFP oligomeric molecule and AA radical copolymerization in presence of BP as initiating agent can be shown in the following diagram:

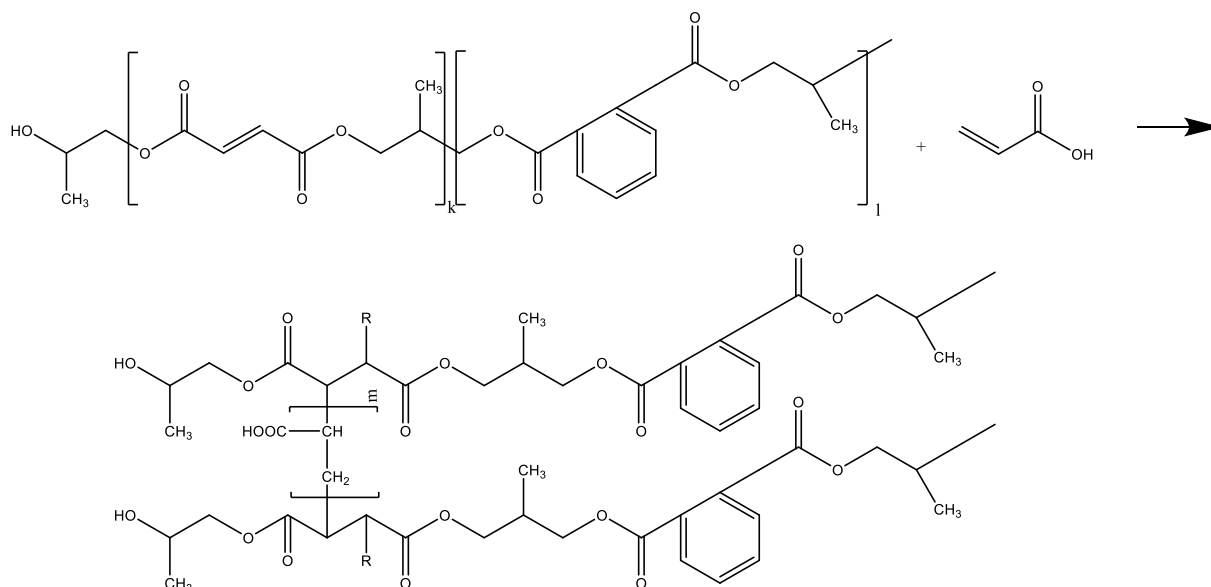


Figure 1. p-PFP and AA radical copolymerization

p-PFP molecular weight was defined by light scattering method at NACH 2100 AN nephelometer [14] and by gel-permeation chromatography, which is 2272 and 2394 atomic mass units.

Copolymers p-PFP and AA was identified by IR spectroscopy.

Contents of obtained copolymers were defined using high-efficient liquid chromatograph LC-20 Prominence by Shimadzu (Japan) [15, 16]. In order to find amount of copolymers unreacted double bonds (degree of unsaturation) bromide-bromate method was used.

Hydrogel swelling equilibrium degree was defined by gravimetric method. Sample swelling rate ( $\alpha$ ) was calculated as ratio of swollen hydrogel mass at swelling equilibrium degree point to its initial mass in dry condition [9, 10].

DMSO, DMF and ethanol were taken as solvents. The choice of solvents was based on the polarity of the solvents.

### Result and Discussion

The fundamental research related to radical copolymerization, which allows us to control the properties of polymers, their structure and molecular mass, and providing more ways to obtain the desired properties of polymers. As previously stated, the most desired products are unsaturated polyesters-based solidified with vinyl monomers; they have specific physical-chemical and physical-mechanical properties. The p-PFP molecules have unsaturated double bonds making which allows them to be used as a polymer matrix for obtaining cross-linked polymers during copolymerization with reactive acrylic acid.

p-PFP is obtained by fumaric acid, phthalic anhydride and propylene glycol polycondensation [11–13].

Cross-linked copolymer formation as result of p-PFP oligomeric molecule and AA radical copolymerization in presence of BP as initiating agent shown in the previous work of the authors [13]

p-PFP — AA copolymerization results are shown in Table 1. Copolymer yield ranges from 83 % to 62 %.

As seen in Table 1, copolymers are enriched with AA components throughout the range of initial mixtures; also, yield and swelling rate decrease at lower amounts of the latter.

Table 1

**Copolymer content dependence on initial mixture content in process of p-PFP ( $M_1$ ) and AA ( $M_2$ )**  
 $[BP] = 8 \cdot 10^{-3} \text{ mol/m}^3, T = 333 \text{ K}$

Initial monomer ratio, % by mass		Copolymer content, % by mass		Yield, %
$M_1$	$M_2$	$M_1$	$M_2$	
10.22	89.78	6.77	93.23	83.70
25.00	75.00	20.34	79.66	78.73
50.00	50.00	44.17	55.17	79.33
73.91	26.09	68.42	31.58	71.93
90.00	10.00	86.67	13.33	62.09

Copolymers were identified by IR spectrum data according to Figure 1. Bands describing the range of  $1450\sim 1640 \text{ cm}^{-1}$  are related to C=O bond. Meanwhile, p-PFP-AA copolymers IR spectrum absorption bands at  $1744 \text{ cm}^{-1}$  and  $2951 \text{ cm}^{-1}$  describe C=O and  $-\text{CH}_2$  bonds, respectively, and peaks at  $1107\sim 1172 \text{ cm}^{-1}$  are typical for C-O-C bond. Besides, absorption bands at  $1447 \text{ cm}^{-1}$  and  $1396 \text{ cm}^{-1}$  relate to  $-\text{CH}(\text{CH}_2)$  bond.

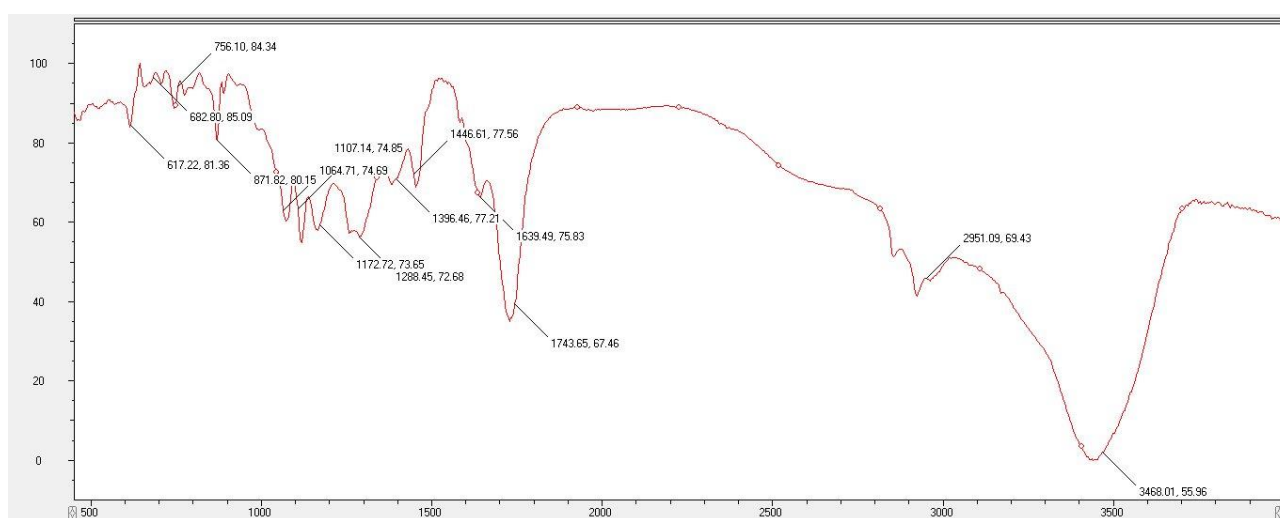


Figure 2. p-PFP-AA IR spectrum

Polymer swelling rate depends on number of factors: nature of polymer and solvent, presence of electrolytes, change of environment pH and temperature, molecular weight of the polymer, etc. Here, pH change influence on p-PFP and AA copolymer based hydrogel swelling is studied. Figure shows p-PFP-AA gels with various molar compositions swelling dependence on environment pH change. It can be seen on the figure that p-PFP and AA copolymer based hydrogels are highly sensitive to environment pH change (Fig. 2).

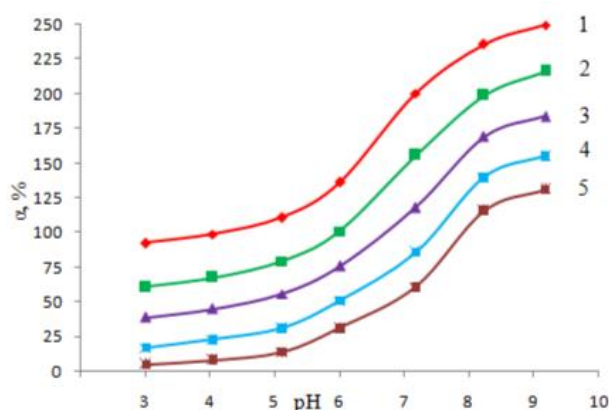


Figure 3. Impact of environment pH on pH p-PFP and AA copolymer based hydrogels volume

Provided experimental data show that when amount of p-PFP increases in copolymer, gel swelling ability decreases. This is explained by growth of p-PFP chains in initial monomer mixture and reduction of swelling ability due to increase of obtained copolymers cross-linking density. p-PFP-AA based gels dependence curves on figures can be example of hydrogels enriched by acid groups depending on change of medium pH.

Increase of solution pH leads to improvement of copolymer water-absorbing abilities, which causes rapid growth of hydrogel volume. Switching to medium solution pH alkaline area does not affect swollen cross-linked polymer conformation. Therefore, p-PFP-AA copolymer hydrogels also show properties of polyelectrolytes containing ionized acid groups with covalent compound in main chain. The main factor defining researched gel swelling is simple electrostatic repulsion of charge  $\text{COO}^-$  groups. Due to large amount of hydrogen ions carboxyl group dissociation can be traced in acid environment and compact subchain extremely close to each other, i.e. defining polymer gel collapse, is formed. Raise of precise saturated area environment pH leads to carboxyl groups hydrolysis, thus leading to similarly charged functional groups repulsion from each other.

In acid environment carboxyl group dissociation is suppressed, their dense conformation and, as a result, polymer gel collapse are formed. According to experimental data, increase of AA in copolymer leads to increase of gel swelling ability.

In the following research impact of organic solvents on p-PFP-AA 6,77:93,23 mol.% swelling rate was studied in order to obtain more information about impact of various environment factors on researched samples absorbing ability. As organic components dimethylformamide (DMF), dimethylsulfoxide (DMSO) and ethanol were used; their content in water solution ranged from 0.1 to 1.0 volume ratio ( $n_0$ ). Choice of these solvents was based on their polarity difference.

It was found that excessive content of DMSO, DMF and ethanol leads to polymer chains attraction and collapsing. Gel volume in this case depends on elements attraction; this is why volume difference between collapsed and swollen gels increases. Besides, it was found that p-PFP copolymers are also highly sensitive to thermodynamically weak solvents.

In described experiments testing was performed on copolymer samples selected in water and then gradually added into water-organic mixture with pre-set ratio of components. When the polymer swells and the concentration of organic solvent increases to a certain critical amount, the part of the solvent that provides relative stability of the hydrogel is reliably supported by the micromolecules in the form of a solvation layer. This allows to «shift» copolymer contraction to increase of organic components share in water-organic mixture.

As the research results suggest, in case of increasing clarifying tub volume hydrogel swelling ability reduces in water and organic solvent mixture, i.e. this is natural for charged polymer grids in subchains.

Polarity of solvents obtained in the researched work decreases from DMSO to ethanol. It should be noted that polymer swelling in pure organic solvents also follows this pattern.

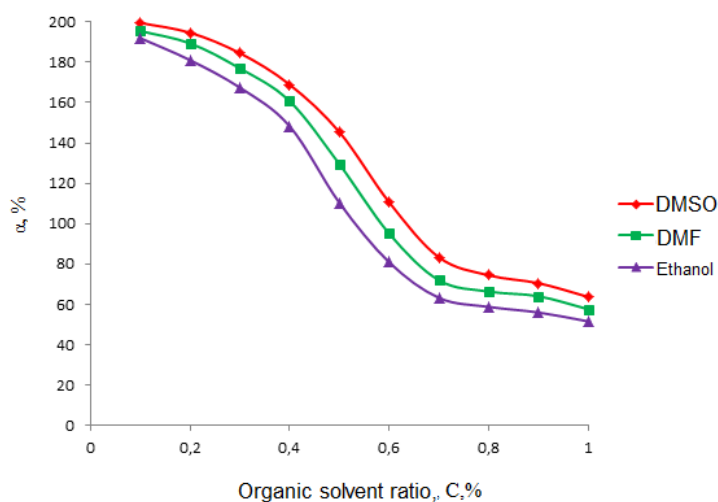


Figure 4. Impact of organic solvents volume ratio ( $n_0$ ) on p-PFP-AA copolymer based hydrogel swelling at molar ratio (20.34:79.66 mol.%)

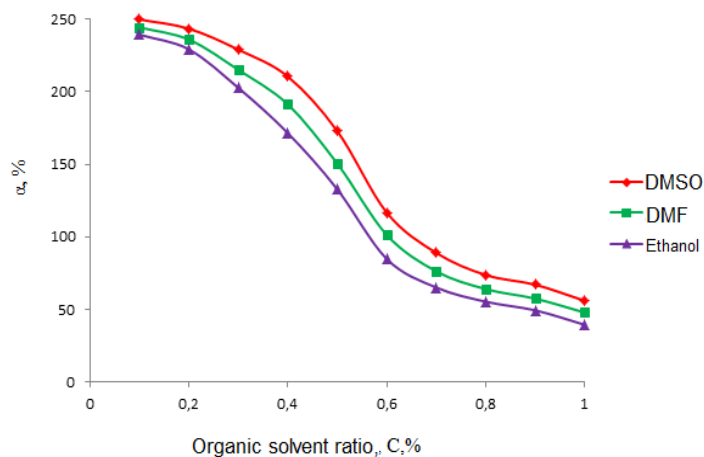


Figure 5. Impact of organic solvents volume ratio ( $n_0$ ) on p-PFP-AA copolymer based hydrogel swelling at molar ratio (6.77:93.23 mol. %)

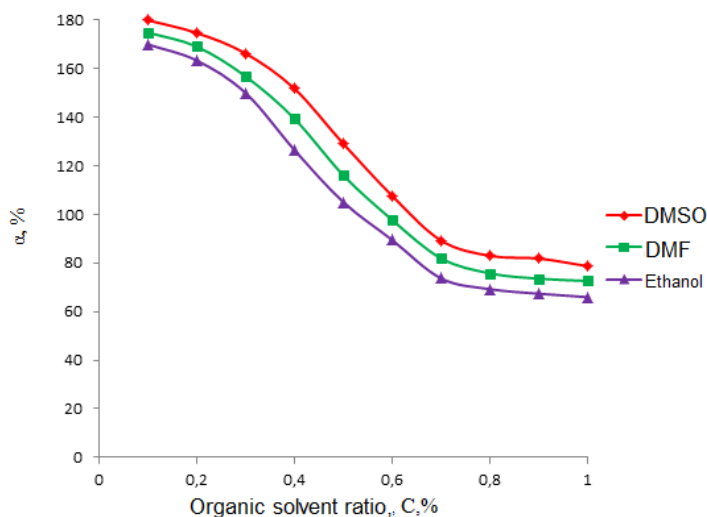


Figure 6. Impact of organic solvents volume ratio ( $n_0$ ) on p-PFP-AA copolymer based hydrogel swelling at molar ratio (68.42:31.58 mol. %)

It can be seen at graphs that nature of organic solvent has significant impact on copolymer swelling ability. Hydrogel collapse can be observed in ethanol, where its volume ratio is approximately 0.7 and DMF and DMSO volume ratio is 0.9. It means that in a low polarity solvent collapse happens immediately, while in a high polarity solvent contraction can be observed. Transition of gel particles from continuity to discreteness in case of organic solvent change corresponds to change of solvent polarity.

### Conclusion

Thus, the conclusion might be made that possibilities of control of physical and chemical properties of polymers based on p-PFP, demonstrated in the work, allow to develop new polymeric materials of polyfunctional destination. Copolymers of poly(propylene fumarate phthalate) and acrylic acid of various molar compositions have been obtained for the first time by radical copolymerization. Synthesized copolymers were identified by IR spectrum data and were defined using high-efficient liquid chromatograph. The results of the study, the influence of various factors (pH = 3–9, solvents DMSO, DMF, ethanol) on the swelling of the polymers showed that the polymers exhibit the properties of polyelectrolytes and can be used as a sorbent in purification and enrichment technologies.



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### **Қанықпаған полиэфирлі шайырлар негізіндегі сополимерлерге сыртқы факторлардың әсерін зерттеу**

Мақала поли(пропиленфумаратфталат) және акрил қышқылы негізіндегі сополимерлерге сыртқы факторлардың әсерін зерттеуге арналған. Ұсынылған жұмыста органикалық еріткіштер мен рН ортаның синтезделген сополимерлердің ісіну жылдамдығына әсері зерттелген. Полимердің ісіну жылдамдығы көптеген факторларға байланысты, олардың қатарына: полимердің және еріткіштің табиғаты, электролиттердің болуы, рН және қоршаған орта температурасының өзгеруі, полимердің молекулалық массасы және т. б. жатады. Жұмыста сополимерлердің полимерлік торының көп бөлігі қанықпаған полиэфирлі шайыр буындарынан тұрады деп болжанған. Зерттеу нәтижелері сополимердегі мономерлік буындардың ара қатынасы полимерлік гельдің ортаның рН-ға қабылдағыштығына және органикалық еріткіштердің (ДМСО, ДМФА, этанол) болуына айтарлықтай әсер ететінін көрсетті. Сополимер қасиеттерінің өзгеруі иондық күштің немесе ерітіндінің термодинамикалық сапасының өзгеруі салдарынан ісінуге немесе сығылуға қабілетті гидrogельдерді алуға мүмкіндік беретіні дәлелденген.

*Кілт сөздер:* полипропиленфумаратфталат, акрил қышқылы, радикалды сополимерлену, полярлы органикалық еріткіштер, ісіну, коллапс, қанықпаған полиэфирлі шайыр.

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## Исследование влияния внешних факторов на сополимеры на основе ненасыщенных полиэфирных смол

Статья посвящена исследованию влияния внешних факторов на сополимеры на основе поли(пропиленфумаратфталата) и акриловой кислоты. Авторами изучено воздействие органических растворителей и pH среды на скорость набухания синтезированных сополимеров. Скорость набухания полимера зависит от множества факторов, к числу которых относятся природа полимера и растворителя, наличие электролитов, изменение pH и температуры окружающей среды, молекулярная масса полимера и т.д. Предполагается, что полимерная сетка сополимеров по большей части состоит из звеньев ненасыщенной полиэфирной смолы. Результаты исследований показывают, что соотношение мономерных звеньев в сополимере существенно влияет на восприимчивость полимерного геля к pH среды и присутствию органических растворителей (ДМСО, ДМФА, этанол). Доказано, что изменение свойств сомономера позволяет получить гидрогели, способные набухать или разрушаться вследствие изменения ионной силы или термодинамического качества раствора. Путем варьирования соотношения сомономерных звеньев были отрегулированы интервалы набухания и сжатия полимерных сеток. Молекулярная масса поли(пропиленфумаратфталата) определена методом гель-проникающей хроматографии. Идентификация и состав сополимеров были установлены посредством ИК-спектроскопии и ВЭЖХ соответственно.

*Ключевые слова:* полипропиленфумаратфталат, акриловая кислота, радикальная сополимеризация, полярные органические растворители, набухание, коллапс, ненасыщенная полиэфирная смола.

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### **Features of sorption of rare-earth metals of cerium group by intergel systems based on polyacrylic acid, polymethacrylic acid and poly-4-vinylpyridine hydrogels**

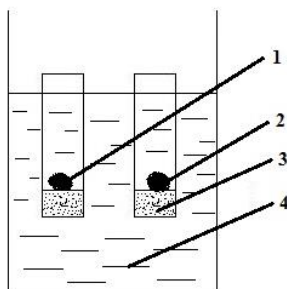
The work is devoted to study of sorption process of cerium and neodymium ions by individual hydrogels of polyacrylic acid (hPAA), polymethacrylic acid (hPMAA), poly-4-vinylpyridine (hP4VP) and intergel systems on their bases. Obtained results show that sorption properties (sorption degree, polymer chain binding degree, effective dynamic exchange capacity) of individual hydrogels of PAA, PMAA, P4VP are not sufficiently high: sorption degree is not high that 65 %; polymer chain binding degree is not high than 55 %; effective dynamic exchange capacity is not high than 4.5 mmol/g. Remote interaction of the polymer hydrogels in the intergel systems provides significant increase (over 30 %) of the sorption properties. Sorption degree increases up to 93.50 %; polymer chain binding degree increases up to 76.50 %; effective dynamic exchange capacity grows to 6.16 mmol/g. Such strong increase is a consequence of the mutual activation of the initial polymers in the intergel systems during their remote interaction. Macromolecules undergo ionization with further unfolding of the polymer globe with formation of optimal conformation for sorption of low-molecular ions.

*Keywords: Intergel systems, remote interaction, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, cerium ions, neodymium ions, sorption*

#### *Introduction*

At present technologies of rare earth metals concentration and extraction in hydrometallurgy are based on application of ion-exchangers [1–4]. However, ion-exchange resins do not have high extraction degree of metals and their regeneration is a rather complicated process. The major drawback of ion-exchangers is their regeneration, the process which is very complicated. It should be also noted that application of ion-exchangers is directed to selective extraction of one metal. As known, industrial solutions usually contain several valuable components. In this regard it is relevant to develop modern sorption technologies based on remote interaction of functional macromolecules, in other words creation of selective intergel systems seems to be concerned as the real alternative to the existing methods of sorption of rare-earth elements (mainly ion-exchangers) [5]. Remote interaction of functional polymers leads to significant changes of initial properties (conformational and electrochemical) of the macromolecules. Also, it should be noted that there is strong increase of sorption properties of the polymers in intergel systems due to transition into highly ionized state in result of mutual activation of the macromolecules during remote interaction [6]. There is a formation of optimal conformation during the process of remote interaction of rare-crosslinked polymer hydrogels in intergel systems. It was found earlier [7–10] that rare-crosslinked polymer hydrogels in intergel systems undergo additional ionization of the functional polymers during remote interaction. Such transfer provides significant changes in electrochemical, conformational and sorption properties of macromolecules [11–13].

Intergel system is a multicomponent system, which contains polybasis and polyacid. Intergel system is presented on figure. As seen from the figure, two polymers interact with each other on the distance. The glass filter has a pores, which are permeable for low-molecular ions and impermeable for hydrogels dispersion.



1 — polyacid; 2 — polybasis; 3 — glass filter; 4 — solution

Figure. Schematic illustration of typical intergel system

In this regard the aim of the paper is to study extraction properties (relatively to cerium and neodymium ions) of intergel systems based on polyacrylic acid, polymethacrylic acid and poly-4-vinylpyridine hydrogels.

### Experimental

*Equipment.* Rare-earth metals (REM) ions concentration in solutions was determined on spectrophotometers KFK-3KM (Russia).

*Materials.* Polyacrylic acid hydrogel (hPAA) and polymethacrylic acid hydrogel (hPMAA) were synthesized in presence of crosslinker (methylenebisacrylamide) and initiator (potassium peroxydisulphate — sodium tiosulphate) in water medium. Synthesized hydrogels were crushed into small dispersions and washed with distilled water until constant conductivity value of aqueous solutions was reached. Linear polymer of poly-4-vinylpyridine of Sigma-Aldrich company was initial reactant for further synthesis of the hydrogel (hP4VP) in presence of divinylbenzene, which was subsequently used as polybasis. Based on the obtained polymers the following intergel pairs: hPAA-hP4VP and hPMAA-hP4VP were made. The general experiments were carried out in the corresponding salts solutions of cerium and neodymium (nitrates hexahydrates, concentration 0.005 mol/L).

*Determination of the rare-earth metals.* Measurement of the cerium and neodymium concentration in the solution is based on application of the complexant arsenazo III [14].

Calculation of degree of sorption (extraction):

$$\eta = \frac{C_{ini} - C_{res}}{C_{ini}} \cdot 100\% ,$$

$C_{ini}$  — concentration before sorption of Ce or Nd, g/L;  $C_{res}$  — concentration after sorption of Ce or Nd, g/L.

Calculation of binding degree of the polymer chain:

$$\theta = \frac{v_{srb}}{v} \cdot 100\% ,$$

$v_{srb}$  — amount of links of the polymers, which participate in the sorption process of cerium or neodymium, mol;  $v$  — total amount of links of the polymers, mol.

Calculation of effective dynamic exchange capacity:

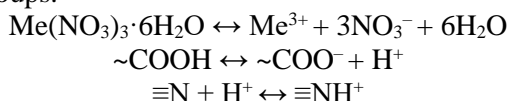
$$Q = \frac{v_{srb}}{m_{srbt}} ,$$

$v_{srb}$  — quantity of sorbed cerium or neodymium, mol;  $m_{srbt}$  — mass of the sorbent (polyacid or polybasis or intergel pair), g.

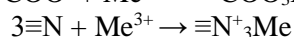
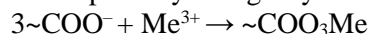
### Results and Discussion

Nitrates of cerium and neodymium present in solution in dissociated state. In presence of individual hydrogels and intergel systems the following processes take place:

1) REM (cerium or neodymium) nitrate dissociation, ionization of heteroatom (nitrogen) by binding of cleaved proton from carboxyl groups:



2) REM (cerium or neodymium) ions sorption by intergel system:



where Me — rare-earth metal (cerium or neodymium).

*Cerium ions sorption.*

Sorption degree (Table 1) of cerium ions of the intergel system hPAA-hP4VP and individual hydrogels of PAA and P4VP have different values (extraction degree of hPAA and hP4VP is not very high — no more than 65 %). It can be said, that in presence of the only polyacid or polybasis the equilibrium is almost reached at 24 hours of interaction, at this time sorption degree is 58.33 % for hPAA and 52.67 % for hP4VP. For the next 24 hours the parameter in this case increases very slightly and the final values (63.33 % and 56.67 %) are reached. In intergel pairs it can be seen that the phenomenon of mutual activation provides additional ionization of the internode links of the initial hydrogels. Maximum sorption occurs at ratio hPAA:hP4VP=17 %:83 % hydrogels ratio, at 48 hours of interaction 92.33 % of cerium is extracted by the intergel system.

Table 1

Sorption degree of cerium ions of intergel system hPAA-hP4VP

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\eta(\text{Ce})$ , %						
0	0	0	0	0	0	0	0
0.5	11.67	13.33	14.00	16.33	17.67	21.67	6.67
1	17.67	22.33	24.67	27.33	31.67	35.67	10.33
2	26.33	30.67	35.67	40.33	44.33	52.67	18.33
6	39.00	52.00	58.00	66.67	75.33	77.00	30.00
24	58.33	75.00	77.00	82.33	85.67	88.33	52.67
48	63.33	79.67	81.67	86.00	88.67	92.33	56.67

Polymer chain binding degree shows the amount of the active (which provides sorption of cerium) links of the individual polymer hydrogels and the intergel system. Polymer chain binding degree is presented in Table 2. Over the half of the links of the individual polymers of PAA and P4VP take part in sorption of cerium, binding degree at 48 hours is 52.53 and 47.00 % respectively. Formation of optimal conformation in intergel system for sorption of cerium occurs at ratio hPAA:hP4VP = 17 %:83 %. Binding degree is 76.59 % at 48 hours of remote interaction.

Table 2

Binding degree of polymer chain (relatively to  $\text{Ce}^{3+}$  ions) of the intergel system hPAA-hP4VP

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\theta(\text{Ce})$ , %						
0	0	0	0	0	0	0	0
0.5	9.68	11.06	11.61	13.55	14.65	17.97	5.53
1	14.65	18.53	20.46	22.67	26.27	29.59	8.57
2	21.84	25.44	29.59	33.46	36.77	43.69	15.21
6	32.35	43.13	48.11	55.30	62.49	63.87	24.88
24	48.39	62.21	63.87	68.29	71.06	73.27	43.69
48	52.53	66.08	67.74	71.34	73.55	76.59	47.00

Effective dynamic exchange capacity (relatively to  $\text{Ce}^{3+}$  ions) of the intergel system hPAA-hP4VP is presented in Table 3. The overwhelming majority of cerium is sorbed by hPAA and hP4VP during 24 hours, at this time exchange capacity is 3.89 mmol/g and 3.51 mmol/g respectively. The further increase is very slight, the final values can be seen at 48 hours of interaction, exchange capacity is 4.22 mmol/g and 3.78 mmol/g. The parameter's highest values are observed at ratio hPAA:hP4VP = 17 %:83 % after 2 days, effective dynamic exchange capacity is 6.16 mmol/g.

Table 3

**Effective dynamic exchange capacity (relatively to  $Ce^{3+}$  ions) of the intergel system hPAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q(Ce), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.78	0.89	0.93	1.09	1.18	1.44	0.44
1	1.18	1.49	1.64	1.82	2.11	2.38	0.69
2	1.76	2.04	2.38	2.69	2.96	3.51	1.22
6	2.60	3.47	3.87	4.44	5.02	5.13	2.00
24	3.89	5.00	5.13	5.49	5.71	5.89	3.51
48	4.22	5.31	5.44	5.73	5.91	6.16	3.78

Process of cerium ions sorption by the intergel system hPMAA-hP4VP occurs less intensive due to the fact that ionization of the initial polymers is complicated by the presence of bulky methyl substituent. Values of extraction degree of cerium ions are presented in Table 4. More than half of the sorbed metal is extracted during 6 hours after the beginning of the sorption process. The final values of the parameter in case with individual hPMAA and hP4VP are observed at 48 hours, the values are 60.33 % and 56.67 % respectively. The optimal conformation for cerium ions sorption is formed at ratio 50 % hPMAA-50 % hP4VP. At 48 hours of remote interaction at this ratio sorption degree is 89.33 %.

Table 4

**Sorption degree of cerium ions of intergel system hPMAA-hP4VP**

$\tau$ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\eta$ (Ce), %						
0	0	0	0	0	0	0	0
0.5	10.00	12.67	13.33	18.33	15.00	16.33	6.67
1	15.33	18.33	21.33	28.67	25.67	26.67	10.33
2	23.67	25.67	31.00	48.00	33.67	35.33	18.33
6	35.00	48.33	51.00	72.33	55.33	59.33	30.00
24	55.67	68.33	70.67	85.00	73.67	77.33	52.67
48	60.33	76.00	79.00	89.33	81.00	83.00	56.67

As can be seen from table 5, the part of active links of the individual hydrogels of PMAA and P4VP is over 50 %. Such low values are directly connected with the fact that equilibrium between the nitrates of the REM and the polymer hydrogels is reached rather fast. Additional activation of the internode links of the macromolecules leads to strong growth of binding degree. The area of maximum binding of cerium ions is ratio 50 % hPMAA – 50 % hP4VP, the share of active links is 74.10 %.

Table 5

**Polymer chain binding degree (in relation to cerium ions) of intergel system hPMAA-hP4VP**

$\tau$ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\theta$ (Ce), %						
0	0	0	0	0	0	0	0
0.5	8.29	10.51	11.06	15.21	12.44	13.55	5.53
1	12.72	15.21	17.70	23.78	21.29	22.12	8.57
2	19.63	21.29	25.71	39.82	27.93	29.31	15.21
6	29.03	40.09	42.30	60.00	45.90	49.22	24.88
24	46.18	56.68	58.62	70.51	61.11	64.15	43.69
48	50.05	63.04	65.53	74.10	67.19	68.85	47.00

Table 6 represents the difference in values of effective dynamic exchange capacity in presence and absence of the phenomenon of mutual activation. As was mentioned above, the equilibrium is almost reached at

24 hours of interaction of individual hPMAA and hP4VP with the salt solution. This is evidenced by the fact that the further increase is very low. As seen from the table, the significant increase in the intergel pair 50 % hPMAA – 50 % hP4VP points to the high ionization degree of the initial polymer structures. Maximum values of the exchange capacity are observed at this ratio at 48 hours of the remote interaction, exchange capacity is 5.96 mmol/g.

Table 6

**Effective dynamic exchange capacity (in relation to cerium ions) of intergel system hPMAA-hP4VP**

$\tau$ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
Q (Ce), mmol/g							
0	0	0	0	0	0	0	0
0.5	0.67	0.84	0.89	1.22	1.00	1.09	0.44
1	1.02	1.22	1.42	1.91	1.71	1.78	0.69
2	1.58	1.71	2.07	3.20	2.24	2.36	1.22
6	2.33	3.22	3.40	4.82	3.69	3.96	2.00
24	3.71	4.56	4.71	5.67	4.91	5.16	3.51
48	4.02	5.07	5.27	5.96	5.40	5.53	3.78

*Neodymium ions sorption.*

During the sorption process of neodymium ions there is an occurrence of the areas of minimum and maximum sorption (table 7). The lowest values of the sorption degree are observed in case when there is presence of only polyacid or polybasis in the salt solution, extraction degree is 61.60 % for hPAA and 54.67 for hP4VP. Significant increase of the parameter is seen at hPAA:hP4VP = 83 %:17 % and hPAA:hP4VP = 50 %:50 % ratios, sorption degree is 93.59 % and 91.74 % respectively.

Table 7

**Sorption degree of neodymium ions of intergel system hPAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
$\eta$ (Nd), %							
0	0	0	0	0	0	0	0
0.5	10.71	20.51	13.07	16.83	12.66	11.49	5.82
1	16.35	33.85	21.70	27.11	18.43	16.71	9.41
2	25.10	51.10	29.71	46.23	28.94	25.81	16.73
6	37.84	74.37	51.68	72.56	46.77	42.12	28.34
24	56.77	86.82	74.29	80.35	70.10	66.83	49.20
48	61.60	93.59	86.74	91.74	72.32	71.44	54.67

The part of active links (which take part in the sorption process of neodymium) of the individual macromolecules and the intergel pairs is presented in table 8. Obtained results show that the part of the active links of hydrogels (PAA and P4VP) is over 50 %, this is consequence of the absence of the high ionization process. The increase of the polymer chain binding degree in the intergel system occurs from 60 % to 73 %. It should be noted that maximum values of the parameter (73.24 %) are observed at ratio 83 % hPAA – 17 % hP4VP at 48 hours of remote interaction.

Table 8

**Polymer chain binding degree (in relation to neodymium ions) of intergel system hPAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
$\theta$ (Nd), %							
1	2	3	4	5	6	7	8
0	0	0	0	0	0	0	0
0.5	9.18	15.22	12.64	13.31	10.34	10.07	4.84
1	13.25	24.39	18.75	20.86	17.45	16.53	7.45

Continuation of Table 8

1	2	3	4	5	6	7	8
2	17.98	39.98	30.24	34.59	25.68	23.61	14.31
6	30.37	60.57	51.91	58.79	44.33	40.12	22.62
24	46.73	70.45	68.34	68.24	60.11	59.48	41.83
48	50.15	73.24	68.35	70.91	64.37	62.85	45.66

Table 9 represents the impact of mutual activation phenomenon on effective dynamic exchange capacity. The most of the metal is extracted by initial polymers (PAA and P4VP respectively) during 24 hours of interaction, exchange capacity is 3.81 mmol/g and 3.46 mmol/g. Further increase is not so strong and the final values (4.13 mmol/g and 3.67 mmol/g respectively) are reached at 48 hours. The significant increase (over 30 %) of the exchange capacity is due to formation of optimal conformation in the intergel pair 83 % hPAA – 17 % hP4VP for neodymium ions sorption, at 48 hours of remote interaction the parameter is 6.03 mmol/g.

Table 9

**Effective dynamic exchange capacity (in relation to neodymium ions) of intergel system hPAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
Q (Nd), mmol/g							
0	0	0	0	0	0	0	0
0.5	0.73	1.33	1.02	1.11	0.85	0.77	0.41
1	1.14	2.26	1.68	2.04	1.50	1.41	0.65
2	1.69	3.39	2.55	2.73	2.24	1.96	1.17
6	2.52	5.01	4.30	4.91	3.72	3.33	1.92
24	3.81	5.77	5.31	5.59	5.05	4.96	3.46
48	4.13	6.03	5.65	5.83	5.32	5.26	3.67

Sorption degree of neodymium ions of polymers (hPMAA, hP4VP) and intergel pairs (hPMAA:hP4VP) is presented in Table 10. Comparatively to intergel system hPAA-hP4VP (Table 7) the values of sorption degree are lower due to complication of the ionization process during unfolding of the macromolecular globe. The most intense sorption occurs during 6 hours of interaction with the salt solution as for the individual hydrogels of PMAA and P4VP as for the intergel system hPMAA-hP4VP. Sorption degree of neodymium ions of individual hPMAA and hP4VP is 57.91 % and 54.67 % respectively, while 92.41 % of the rare-earth metal is extracted at hPMAA:hP4VP = 67 %:33 % ratio.

Table 10

**Sorption degree of neodymium ions of intergel system hPMAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
$\eta$ (Nd), %							
0	0	0	0	0	0	0	0
0.5	8.33	15.72	19.89	11.71	9.60	9.13	5.82
1	12.18	25.61	31.46	19.83	15.12	14.32	9.41
2	18.56	42.40	47.71	27.34	23.61	23.05	16.73
6	31.25	70.86	73.05	46.76	38.85	38.41	28.34
24	51.71	78.10	83.90	70.29	60.11	58.23	49.20
48	57.91	90.63	92.41	84.33	70.72	69.45	54.67

The share of the active links of the following polymer structures: individual hPMAA and hP4VP and intergel pairs (hPMAA:hP4VP) is presented in Table 11. The part of active links in below 50 % for the individual hydrogels of PMAA and P4VP, polymer chain binding degree at 48 hours of interaction is 47.30 % and 45.66 % respectively. High ionization of the initial polyacid and polybasis at ratio 67 % hPMAA–33 % hP4VP provides strong increase of binding degree, it is 71.56 % after 48 hours.



Table 11

**Polymer chain binding degree (in relation to neodymium ions) of intergel system hPMAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\theta$ (Ce), %						
0	0	0	0	0	0	0	0
0.5	6.71	12.13	14.11	11.31	10.01	8.97	4.84
1	10.97	18.87	21.69	15.49	14.42	12.33	7.45
2	16.65	27.64	36.54	24.38	22.18	19.89	14.31
6	26.84	47.44	57.58	43.56	40.86	37.98	22.62
24	43.83	61.79	68.54	58.57	55.78	52.43	41.83
48	47.30	66.33	71.56	64.81	62.35	59.99	45.66

Comparison of the effective dynamic exchange capacities (Table 12) of the individual hydrogels of PMAA and P4VP and the intergel system hPMAA-hP4VP shows that the remote interaction provides significant increase of the parameter in the intergel pairs. The overwhelming majority of the neodymium ions is extracted during 24 hours of interaction, exchange capacity is 3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP, 5.55 mmol/g for ratio 67 % hPMAA – 33 % hP4VP. Further increase (up to 48 hours of interaction) is slight, the final values (3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP, 5.84 mmol/g for 67 % hPMAA – 33 % hP4VP) are observed at 48 hours of interaction.

Table 12

**Effective dynamic exchange capacity (in relation to neodymium ions) of intergel system hPMAA-hP4VP**

$\tau$ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q (Nd), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.56	1.03	1.17	0.91	0.79	0.73	0.41
1	0.87	1.67	1.86	1.58	1.35	1.1	0.65
2	1.43	2.19	3.14	2.07	1.98	1.56	1.17
6	2.22	3.87	4.79	3.51	3.33	3.07	1.92
24	3.59	5.03	5.56	4.75	4.62	4.43	3.46
48	3.86	5.39	5.84	5.25	5.11	5.01	3.67

As seen from the tables 1–12, the individual hydrogels (PMAA and P4VP respectively) do not have sufficiently high sorption properties (in relation to cerium and neodymium ions) due to the rather fast equilibrium reaching between them and the corresponding salt solution. As can be seen from the tables, high ionization degree and change of conformation of initial polymer structures during remote interaction with consequent mutual activation provides significant increase (over 30 %) of sorption degree, polymer chain binding degree and effective dynamic exchange capacity comparatively with individual hydrogels.

*Conclusions*

Based on obtained data on sorption of cerium and neodymium ions, the following conclusions can be made:

1. Individual hydrogels do not have high sorption properties relatively to cerium and neodymium ions. Sorption degree of cerium ions is 63.33 % for hPAA, 60.33 % for hPMAA, 56.67 % for hP4VP. Sorption degree of neodymium ions is 61.60 % for hPAA, 57.91 % for hPMAA, 54.67 % for hP4VP. Polymer chain binding degree (relatively to  $\text{Ce}^{3+}$  ions) is 52.53 % for hPAA, 50.05 % for hPMAA, 47.00 % for hP4VP; binding degree (relatively to  $\text{Nd}^{3+}$  ions) is 50.15 % for hPAA, 47.30 % for hPMAA, 45.66 % for hP4VP. Effective dynamic exchange capacity (relatively to  $\text{Ce}^{3+}$  ions) is 4.22 mmol/g for hPAA, 4.02 mmol/g for hPMAA, 3.78 mmol/g for hP4VP; exchange capacity (relatively to  $\text{Nd}^{3+}$  ions) is 4.13 mmol/g for hPAA, 3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP.

2. Mutual activation of the initial polymers provides their transition into highly ionized state in intergel pairs, this transition is accompanied with significant increase (up to 30 %) of the sorption properties

comparatively with individual hydrogels. The areas of maximum sorption are the following ratios: hPAA:hP4VP = 17 %:83 % ( $\eta = 92.33$  %;  $\theta = 76.59$  %;  $Q = 6.16$  mmol/g) and hPMAA:hP4VP=50 %:50 % ( $\eta = 89.33$  %;  $\theta = 74.10$  %;  $Q = 5.96$  mmol/g) for  $Ce^{3+}$  ions; hPAA:hP4VP=83 %:17 % ( $\eta = 93.59$  %;  $\theta = 73.24$  %;  $Q = 6.03$  mmol/g) and hPMAA: hP4VP=67 %:33 % ( $\eta = 92.41$  %;  $\theta = 71.56$  %;  $Q = 5.84$  mmol/g) for  $Nd^{3+}$  ions.

3. Presence of bulky methyl substituent complicates the process of ionization of hydrogel of PMAA in intergel system hPMAA-hP4VP, due to this fact the values of the sorption properties are lower comparatively with intergel system hPAA-hP4VP.

4. Differences of the values of the sorption parameters in dependence of the aimed ion (cerium or neodymium) are due to the differences of the main properties of these ions (atomic radius, polarizability, charge density).

5. Changing the polymer molar ratios in the developed intergel systems provides possibility to control «selectivity» in relation to each considered rare-earth metal. Developed intergel systems may be used at creation of innovative technologies for selective extraction of REM ions from industrial solutions.

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## Церий тобына жататын сирекжер металдарын полиакрил қышқылының, полиметакрил қышқылының және 4-винилпиридиннің гидрогельдеріне негізделген интергелдік жүйелермен сорбциялау ерекшеліктері

Мақала жекелеген гидрогелдер полиакрил қышқылы (ПАҚг), полиметакрил қышқылы (ПМАҚг), поли-4-винилпиридин (П4ВПг) және осы гелдердің негізінде құрылған интергелді жүйелер церий және неодим иондарын сорбциялау процесін зерттеуге бағытталған. Бұған дейін ПАҚ, ПМАҚ, П4ВП жекелеген гидрогелдерінің сорбциялық қасиеті (сорбция дәрежесі, полимерлік тізбектердің байланысу дәрежесі, әсерлі динамикалық көлемдік сиымдылық) аса жоғары емес екені анықталды: сорбциялық дәрежесі 65 % төмен; полимерлік тізбектердің байланысу дәрежесі 55 %-дан жоғары емес; әсерлі динамикалық көлемдік сиымдылығы 4,5 ммоль/г төмен). Интергелді жүйедегі полимерлік гидрогелдердің қашықтан әрекеттесуі гидрогелдердің сорбциялық қасиетінің анағұрлым жоғарылауына (30 %-ға жуық) ықпал етеді. Сорбциялық дәрежесі 93,5 %-ға дейін; полимерлік тізбектердің байланысу дәрежесі 76,5 %-ға дейін; әсерлі динамикалық көлемдік сиымдылығы 6,16 ммоль/г-ға дейін өседі. Интергелді жүйедегі полимерлік гидрогелдердің қашықтан әрекеттесу кезінде олардың өзара активтенуі салдарынан гидрогелдердің сорбциялық қасиеті жоғарылайды. Макромолекулалар ионизацияға ұшырайды, ары қарай полимерлік түйіндер айналып, төменмолекулалы иондарды сорбциялау үшін тиімді құрылымдар түзеді.

*Кілт сөздер:* интергелді жүйелер, өзара әрекеттесу, полиакрил қышқылы, полиметакрил қышқылы, поли-4-винилпиридин, церий иондары, неодим иондары, сорбция.

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## Особенности сорбции редкоземельных металлов цериевой группы интергелевыми системами на основе гидрогелей полиакриловой кислоты, полиметакриловой кислоты и поли-4-винилпиридина

Статья посвящена изучению процесса сорбции ионов церия и неодима индивидуальными гидрогелями полиакриловой кислоты (гПАК), полиметакриловой кислоты (гПМАК), поли-4-винилпиридина (гП4ВП) и интергелевыми системами на их основе. Полученные результаты показали, что сорбционные свойства (степень сорбции, степень связывания полимерной цепи, эффективная динамическая обменная емкость) индивидуальных гидрогелей ПАК, ПМАК, П4ВП недостаточно высоки: степень сорбции не выше 65 %; степень связывания полимерной цепи не выше 55 %; эффективная динамическая обменная емкость не выше 4,5 ммоль/г. Дистанционное взаимодействие полимерных гидрогелей в интергелевых системах приводит к существенному увеличению (около 30 %) сорбционных свойств. Степень сорбции возрастает до 93,5 %; степень связывания полимерной цепи — до 76,5 %; эффективная динамическая обменная емкость — до 6,16 ммоль/г. Такой существенный рост является следствием взаимной активации исходных полимеров в интергелевых системах во время их дистанционного взаимодействия. Макромолекулы подвергаются ионизации с последующим разворачиванием полимерного клубка с образованием оптимальной конформации для сорбции низкомолекулярных ионов.

*Ключевые слова:* интергелевые системы, дистанционное взаимодействие, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, ионы церия, ионы неодима, сорбция.

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## Application of cluster-associative model for calculation of kinematic viscosity of metal melts

Metal melts are often used in the national economy and industry. Therefore the study of the physicochemical properties of metals is given great attention. Especially researchers pay great attention to the study of viscosity, since viscosity is of great practical importance in metallurgy. Studying the viscosity of molten metal, at the same time, is essential scientific interest, since viscosity is the most structurally sensitive characteristic of the melt. The study of viscosity through experiment is somewhat difficult because many metals melt at very high temperatures. It is difficult to create such conditions without special equipment. Therefore many researchers are looking for additional development based on alternative approaches to understanding viscosity. The authors in their article consider a new concept of randomized particles and on this basis propose a cluster-associate model for calculating viscosity without conducting an experiment. The authors give examples of calculating the kinematic viscosity of some metals according to the model proposed in this paper. The results we received show that the proposed model allows us to calculate the viscosity even at very high temperatures. A comparison of the obtained results with experimental data shows the functionality of the proposed model. The proposed model can be used to calculate the viscosity of liquid metals in a wide temperature range. The article also shows the possibility of using this model for calculating the activation energy of a viscous melt flow.

*Keywords:* viscosity, chaotized particles, the degree of clusters association, cluster-associated model, liquid metals, reference point, crystal-moving particles, the temperature dependences of the viscosity.

### Introduction

The viscosity, which is the main characteristic of the liquid is unable to be strictly express in theoretical terms based on different calculations of binding forces of particles, i.e. structural factors. The staff of Chemical and Metallurgical Institute (Karaganda) has developed the concept of chaotized particles by applying the Boltzmann law [1].

According to this approach all three aggregate states of matter are considered from a unified point of view on its unstructured component, that is, in all three states of matter there are crystal-like, liquid-like and vapor-like particles.

Earlier in the article “Efficiency of applying cluster-associated model of viscosity of liquid metals” [2] 3 models of viscosity of liquid metals were given depending on the content of randomized particles.

Equation (1) represents the temperature dependence of viscosity with adjustment to crystal-mobile particles:

$$v_1 = v_r T_r / T, \quad (1)$$

where  $v_r$  and  $T_r$  — are kinematic viscosity and absolute temperature correspondingly for a certain reference point, in principle, arbitrarily chosen as the most reliable experimental determination.

Equation (2) represents the temperature dependence of viscosity with adjustment to crystal-mobile and liquid-mobile particles:

$$v_2 = \frac{v_r T_r [\exp(-T_m / T_r) - \exp(-T_b / T_r)]}{T [\exp(-T_m / T) - \exp(-T_b / T)]}, \quad (2)$$

where  $T_m$  and  $T_b$  — melting and boiling temperature correspondingly.

Equation (3) represents the temperature dependence of kinematic viscosity with adjustment to all three types of particles:

$$v_3 = \frac{v_r T_r}{T} \exp\left(\frac{T_m}{T} - \frac{T_m}{T_r}\right). \quad (3)$$

However, it is necessary to develop a generalized viscosity model taking into account the degree of association of clusters of crystal-moving particles.

These models have been tested on all the available reference material on the viscosity of metal melts.

The need to verify each of the three models of the viscosity and to select the most appropriate procedure complicates the data processing. This has prompted a closer look at the nature of the liquid state, while remaining within the concept of chaotized particles. It was found that the strong dependence on the temperature can be explained by the formation of aggregated or associated elementary cluster compounds. We propose a new model of viscosity:

$$\nu = \nu_r (T_r / T)^a. \quad (4)$$

Here the parameter  $a$  makes meaning of the association degree  $n$ -partial cluster compounds [2].

### Experimental

This section is devoted to the studies of the temperature dependence of the viscosity of the pure metals melts for which there are reference data. During the experimental data selection we rested upon the monograph [3] and reference books by M.E. Drits [4] in two parts about the properties of the elements. But there were no data about some elements viscosity.

The [3] with the reference to [5] provides data on the kinematic viscosity for cuprum at different temperatures. Melting and boiling points were taken from the reference book [4]. Their respective values are as follows:  $T_m = 1356$  K and  $T_b = 2846$  K. We applied the closer data to the melting point  $T_r = 1438$  K and  $\nu_r = 4.85 \cdot 10^{-7}$  m<sup>2</sup>/s as the fixed reference point. The viscosity calculation results for the four models are shown in Table 1 and Figure 1.

Table 1

Comparison of experimental data [3] with the values of the kinematic viscosity of cuprum, calculated by the models (1)–(4),  $\nu \cdot 10^7$ , m<sup>2</sup>/s

$T$	$\nu(\text{exp})$	$\nu(1)$	$\nu(2)$	$\nu(3)$	$a$	$\nu(4)$
$T_m = 1356$	–	5.14	5.27	5.44	–	5.34
1438	4.85	4.85	4.85	4.85	–	4.85
1568	4.05	4.45	4.33	4.11	2.08	4.20
1653	3.84	4.22	4.05	3.73	1.68	3.85
1738	3.72	4.01	3.82	3.41	1.40	3.55
1823	3.44	3.83	3.62	3.13	1.45	3.28
$T_b = 2846$	–	2.45	2.43	1.54	–	1.57
$R$	–	0.610	0.898	0.872	–	0.952

Table 1 and graphical comparison shows that the model (4) is more accurate to describe the temperature dependence.

The average value of  $\bar{a} = 1.65$ .

The average value must be checked for representativeness by the criterion of homogeneity of the set and then used in equation (4) to obtain the calculated values and compare with the experimental ones by the correlation coefficient.

The statistical homogeneity of the obtained set of values is evaluated by the Nalimov criterion:

$$r_{\min}^{\max} = \frac{|\bar{x} - x_{\min}^{\max}|}{S(x) \sqrt{\frac{n-1}{n}}} \leq r_{cr},$$

$$S(x) = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}},$$

where  $x_{\min}^{\max}$  — is the mini/max value of the set;  $\bar{x}$  — is the average value;  $S(x)$  — is the mean square error;

$n$  — is the volume of the set.

We have met the homogeneity of the obtained range for  $a$  under the Nalimov criterion:  $S(x) = 0.312$ ;

$r_{\min}^{\max} = 1.598 < r_{cr} = 1.688$ .

Model (4) can be used with a fixed reference point close to the melting temperature  $T_r = 1438$  K in the kinematic viscosity of cuprum during the consideration of the association degree of cluster compounds as a generalized model of melt viscosity in the full temperature range:

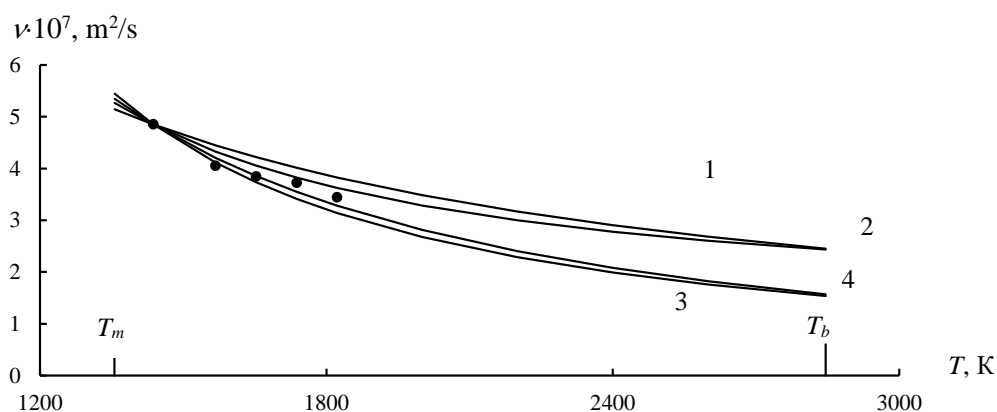
$$\nu = (0.080 / T^{1.65}) \pm 8.02 \cdot 10^{-9}, \text{ m}^2/\text{s}. \tag{5}$$

The correlation coefficient of model (3) is 0.898 and of model (4) is 0.952. The correlation coefficient of model (4) is higher; therefore it is advisable to use model (4) to calculate the viscosity. We can calculate the viscosity in the considered temperature range with the following equation:

$$\eta = A \exp\left(\frac{E_a}{RT}\right), \tag{6}$$

where  $E_a$  — is the activation energy;  $R$  — is the gas constant;  $T$  — is the temperature;  $A$  — is the constant proposed by Arrhenius.

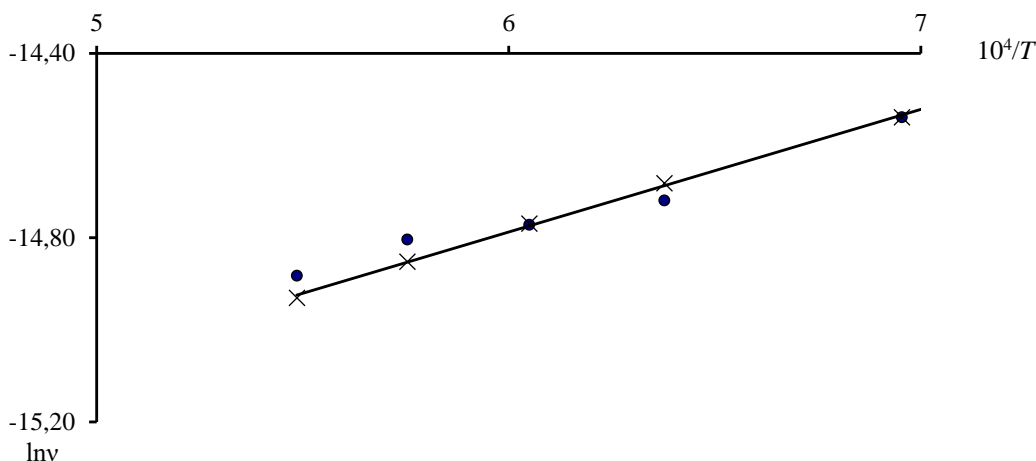
The activation energy for the estimated data equals to  $E_a = 18450$  J/mol, while the activation energy for the proposed model will be  $E_a' = 22133$  J/mol



$\nu$  — kinematic viscosity;  $T$  — temperature; points — experimental data [3],  
 1 — by the model (1); 2 — by (2); 3 — by (3); 4 — by (4)

Figure 1. The temperature dependence of the kinematic viscosity of cuprum

Figure 2 shows the dependence of the logarithm of the kinematic viscosity of cuprum on the inverse temperature.



$\nu$  — kinematic viscosity;  $T$  — temperature; points — experimental data, crosses — for model (5);  
 straight — according to the equation  $\ln \nu = \ln A' + E_a' / (RT)$

Figure 2. Logarithm dependence of the kinematic viscosity of cuprum on reverse temperature

## Results and Discussion

For magnesium the boiling and melting temperatures are known:  $T_m = 923$  K,  $T_b = 1380$  K. The values  $T_r = 973$  K and  $\nu_r = 7.01 \cdot 10^{-7}$  m<sup>2</sup>/s are taken as a fixed reference point. The viscosity calculation results for the four models are shown in Table 2 and Figure 3.

Table 2

Comparison of experimental data [3] with the values of the kinematic viscosity of magnesium, calculated by the models (1)–(4),  $\nu \cdot 10^7$ , m<sup>2</sup>/s

$T$	$\nu(\text{exp})$	$\nu(1)$	$\nu(2)$	$\nu(3)$	$a$	$\nu(4)$
$T_m = 923$	8.33	7.390	7.467	7.779	–	8.026
973	7.010	7.010	7.010	7.010	–	7.010
1073	5.420	6.357	6.288	5.819	2.629	5.453
1173	4.390	5.815	5.745	4.946	2.504	4.339
$T_b = 1380$	–	4.943	4.967	3.736	–	2.859
$R$	–	0.609	0.668	0.934	–	0.922

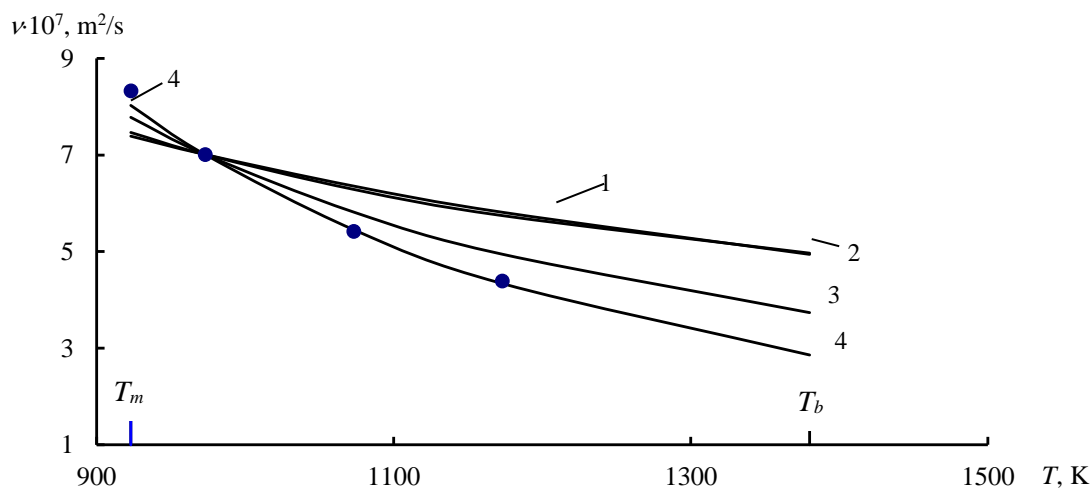
From the Table 2 and graphical comparison it can be seen that the model (4) is more accurate in describing the temperature dependence.

The average value of  $\bar{a} = 2.57$ . The increased degree of cluster association of metal atoms is a consequence of the fact that, against the background of the ionic structure of metal melts, it is possible to form molecular covalent bonds in them.

The uniformity of the obtained set for the Nalimov criterion is observed:  $S(x) = 2.568$ ;  $r_{\min}^{\max} = 0.035 < r_{cr} = 1.483$ .

Model (4) can be used with a fixed reference point close to the melting temperature  $T_r = 973$  K in the kinematic viscosity of magnesium during the consideration of the association degree of cluster compounds as a generalized model of melt viscosity in the full temperature range:

$$\nu = (0.337 \cdot 10^2 / T^{2.57}) \pm 4.47 \cdot 10^{-9}, \text{ m}^2/\text{s}. \quad (7)$$



$\nu$  — kinematic viscosity;  $T$  — temperature;  
points — experimental data [3]; 1 — by the model (1); 2 — by (2); 3 — by (3); 4 — by (4)

Figure 3. The temperature dependence of the kinematic viscosity of magnesium

According to equation (6), the activation energy is  $E_a = 22915$  J/mol, but it is  $E_a' = 22150$  J/mol for the proposed model. Figure 4 shows the logarithmic dependence of the magnesium viscosity on the inverse temperature.



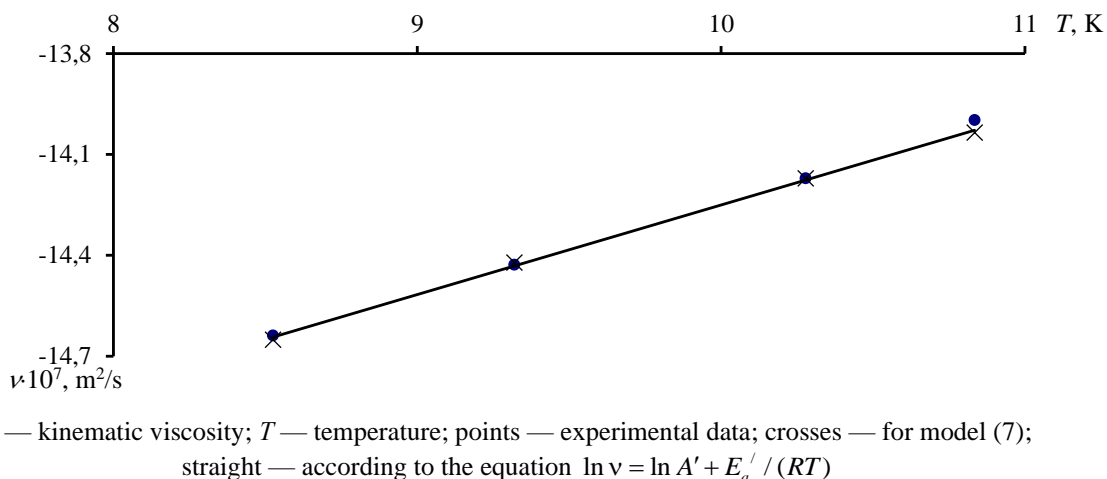


Figure 4. Logarithm dependence of the kinematic viscosity of magnesium on the inverse temperature

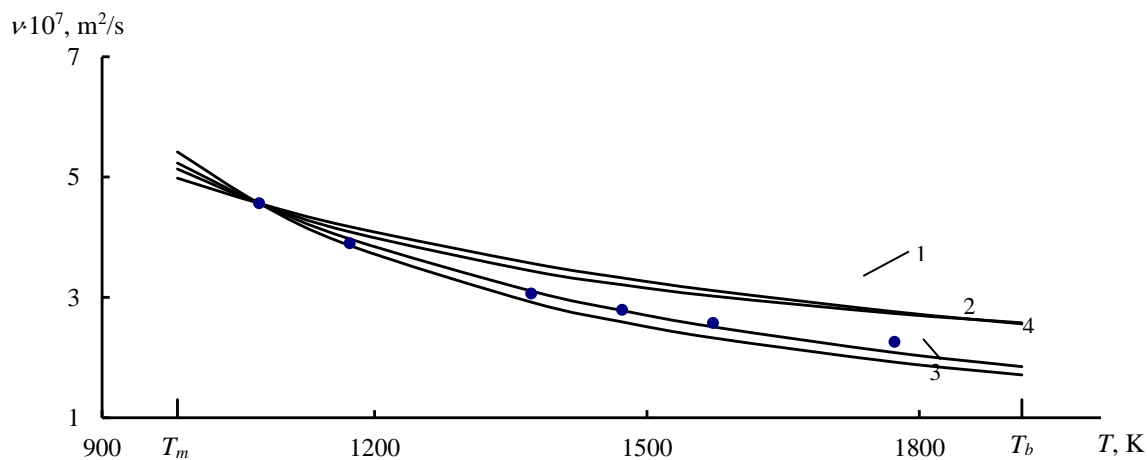
The melting and boiling temperatures of barium were taken from the reference book [4] and draw up  $T_m = 983$  K and  $T_b = 1913$  K. In the monograph [3] with reference to the source [6], smoothed experimental data on the kinematic viscosity of barium are presented.

The fixed reference points was taken under  $T_r = 1073$  K and  $\nu_r = 4.564 \cdot 10^{-7}$  m<sup>2</sup>/s. The calculation results for the four models are shown in Table 3 and Figure 5.

Table 3

Comparison of experimental data [3] with the values of the kinematic viscosity of barium, calculated by the models (1)–(4),  $\nu \cdot 10^7, \text{m}^2/\text{s}$

$T$	$\nu(\text{exp})$	$\nu(1)$	$\nu(2)$	$\nu(3)$	$a$	$\nu(4)$
$T_m = 983$	–	4.982	5.134	5.418	–	5.234
1073	4.564	4.564	4.564	4.564	–	4.564
1173	3.901	4.175	4.089	3.861	1.762	3.971
1373	3.067	3.567	3.440	2.920	1.612	3.105
1473	2.793	3.325	3.210	2.592	1.550	2.782
1573	2.577	3.113	3.022	2.327	1.494	2.510
1773	2.264	2.762	2.732	1.924	1.396	2.082
$T_b = 1913$	–	2.560	2.578	1.712	–	1.849
$R$	–	0.789	0.865	0.959	–	0.993



$\nu$  — kinematic viscosity;  $T$  — temperature; points — experimental data [4]; 1 — by the model (1); 2 — by (2); 3 — by (3); 4 — by (4)

Figure 5. Temperature dependence of the kinematic viscosity of barium

Table 3 shows that the experimental values and those calculated by model (4) are close. The Figure 6 also shows that the model (4) is more adequate in describing the temperature dependence of barium viscosity.

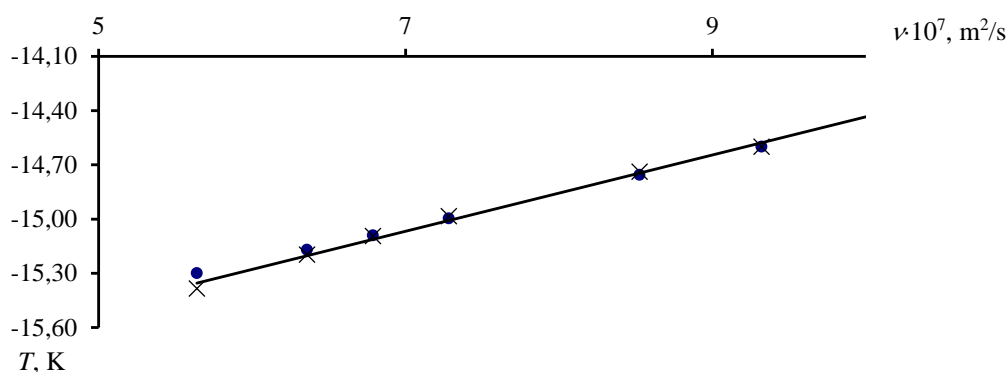
The average value  $\bar{a}=1.56$ .

We can see the uniformity of the obtained set for the Nalimov criterion as follows:  $S(x) = 0.137$ ;  $r_{\min}^{\max} = 1.365 < r_{cr} = 1.821$ .

Then considering the association degree of cluster compounds as a generalized model of melt viscosity in the full temperature range it is possible to use the model (4) with a fixed reference point close to the melting temperature  $T_r = 1073$  K in the kinematic viscosity of barium finding a confidence interval and rounding-off:

$$\nu = (0.0249 / T^{1.56}) \pm 1.68 \cdot 10^{-9}, \text{ m}^2/\text{s}. \quad (8)$$

At the temperature range under consideration, the activation energy was calculated as  $E_a = 15889$  J/mol, but it is  $E_a' = 17543$  J/mol for the generalized model. Logarithm dependence of barium viscosity on the inverse temperature is presented in Figure 6.



$\nu$  — kinematic viscosity;  $T$  — temperature; points — experimental data; crosses — for model (8); straight — according to the equation  $\ln \nu = \ln A' + E_a' / (RT)$

Figure 6. Logarithm dependence of the kinematic viscosity of barium on the inverse temperature

### Conclusions

If unstable solid nuclei — clusters consisting of a complex of crystal-mobile particles exist in the melt, they are the ones to prevent the fluidity of metals. Thus, the viscosity of a liquid and its dependence on temperature can be estimated through the clusters. This was the basis for generating a new semi-empirical generalized model of the temperature-dependant viscosity of liquid metals having regard to both the formation of clusters and the degree of their associativity, that is the stronger role of crystal-mobile particles.

Therefore, this model determines the viscosity over a wide temperature range.

The new semi-empirical model of viscosity has been tried out on 3 typical metals, for which the reference data on the temperature dependence of viscosity are available. In the majority of cases, the generalized model describes the temperature dependence of viscosity more adequately through the comparison with the experimental data.

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### **Кинематикалық тұтқыр сұйық металға кластерлі-ассоциативті модельді қолданудың тиімділігі**

Металл қорытпалары халық шаруашылығында және өнеркәсіпте жиі қолданылады. Сондықтан металдардың физика-химиялық қасиеттерін зерттеуге үлкен көңіл бөлінеді. Әсіресе зерттеушілер тұтқырлықты зерттеуге көп көңіл бөледі, себебі тұтқырлықтың металлургияда практикалық маңызы зор. Балқытылған металдың тұтқырлығын зерттеу үлкен ғылыми қызығушылық тудырады, сонымен қатар, тұтқырлық балқыманың құрылымдық-сезімталдық сипаттамасы болып табылады. Эксперимент арқылы тұтқырлықты зерттеу біршама қиын: көптеген металдар өте жоғары температураларда балқиды. Арнайы жабдықтарсыз мұндай жағдайларды жасау қиын. Сондықтан көптеген зерттеушілер тұтқырлықты түсінуге балама тәсілдер негізінде қосымша әзірлемелерді іздейді. Авторлар мақалада хаотизацияланған бөлшектердің жаңа концепциясын қарастырған және оның негізінде эксперимент жүргізбей, тұтқырлықты есептеу үшін кластерлік-ассоциаттық модель ұсынған. Олар ұсынылған үлгі бойынша кейбір металдардың кинематикалық тұтқырлығын есептеу мысалдарын келтірген. Алынған нәтижелерде ұсынылған модель өте жоғары температура кезінде де тұтқырлықты есептеуге мүмкіндік береді. Алынған нәтижелерді эксперименталды деректермен салыстыру ұсынылған модельдің функционалдығын көрсетеді. Ұсынылған модельді кең температуралық диапазонда сұйық металдардың тұтқырлығын есептеу үшін пайдалануға болады. Сонымен қатар, мақалада балқыманың тұтқыр ағынының белсендіру энергиясын есептеу үшін осы модельді қолдану мүмкіндігі көрсетілген.

*Кілт сөздер:* тұтқырлық, ретсізделген бөлшектер, ассоциирленген кластердің дәрежесі, кластерлі-ассоциативті моделі, сұйық металдар, реперлік нүкте, кристаллқозғалысты бөлшектер, тұтқырлықтың температураға тәуелділігі.

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### **Применение кластерно-ассоциатной модели для расчета кинематической вязкости расплавов металлов**

Расплавы металлов довольно часто используются в народном хозяйстве и промышленности. Поэтому исследованию физико-химических свойств металлов уделяется большое внимание. Особый интерес вызывает изучение вязкости, ввиду того, что она имеет большое практическое значение в металлургии. Изучение вязкости расплавленного металла в то же время представляет и научный интерес, так как является наиболее структурно-чувствительной характеристикой расплава. Изучение вязкости с помощью эксперимента несколько затруднено: многие металлы плавятся при очень высоких температурах. Создать такие условия без специального оборудования сложно. По этой причине многие исследователи ищут дополнительные разработки на основе альтернативных подходов к пониманию вязкости. Авторы данной статьи рассмотрели новую концепцию хаотизированных частиц и на ее основе предложили кластерно-ассоциатную модель для расчета вязкости без проведения эксперимента. Они привели примеры расчета кинематической вязкости некоторых металлов по предложенной модели. Полученные результаты показывают, что данная модель позволяет вычислить вязкость даже при очень высоких температурах. Сопоставление полученных результатов с экспериментальными данными указывает на функциональность предлагаемой модели, которую можно использовать для расчета вязкости жидких металлов в широком температурном диапазоне. Также в статье показана возможность применения данной модели для расчета энергии активации вязкого течения расплава.

*Ключевые слова:* вязкость, хаотизированные частицы, степень ассоциированности кластеров, кластерно-ассоциатная модель, жидкие металлы, реперная точка, кристаллоподвижные частицы, температурная зависимость вязкости.

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## **Low temperature gas-phase technology cladding powdered silicon carbide**

A technology for applying a metal coating to the surface of powdered silicon carbide has been developed. For this purpose, a film of copper phosphide is initially applied to the surface of the powder. The process consists in wetting the powdered carbide with a solution of copper sulfate and subsequent treatment with gaseous phosphine. The resulting film of metal-like copper phosphide has sufficient electrical conductivity, and is also a catalyst for the process of chemical nickel plating. This makes it possible to use chemical or electroplating methods for plating the surface of powders with the necessary metal. Testing this technology in the laboratory allowed obtaining a nickel coating that has the necessary adhesion to silicon carbide particles. All samples of powders at various stages of the process were examined using a scanning electron microscope ISM-6490-LV (JEOL, Japan), which allows to obtain electronic images (photos) of individual areas (spectra) of the surface at specified magnifications and chemical composition. The results of the scanning electron microscope study showed that the nickel coating contains 7 % phosphorus and covers about 90 % of the powder surface, and the estimated coating thickness is 0.8–1.0 microns. This makes it possible to use such silicon carbide powders in the preparation of composite products or coatings. If necessary, the degree of closure of the powder surface can be increased by re-performing the operation specified in this article. The article is intended for scientists and researchers, who are also interested in the problems of obtaining composite coatings.

*Keywords:* silicon carbide, copper sulfate, phosphine, copper phosphide film, chemical nickel plating, composite material.

### *Introduction*

Modern production requires the creation of new engineering materials that can be used as special materials in fillers for composites. Such materials can be metalized dielectric powders that have thin-film metal coatings on the surface. Combining the useful properties of dielectrics, such materials have unique properties: high strength, thermal and heat resistance, electrical conductivity and can be used as dual-use materials [1–5].

The main purpose of coating is to improve the retention of grain in the tool matrix, increase the thermal conductivity of the working layer, which allows intensifying cutting modes and thereby increasing the efficiency of the tool. This is especially important in the production of abrasive powders that can be used in the manufacture of various tools, as well as an independent product.

In addition, the metallization of particles can significantly improve the process of feeding the powder into the plasma jet, which has a positive effect on the uniformity of the formed coating, reduce the oxidation rate of sprayed powders (for example, carbides), reduce the porosity of coatings, increase the adhesion strength of coatings to the substrate and increase their wear resistance [6–8].

One used for this purpose is silicon carbide. Because of its increased hardness, silicon carbide is widely used in engineering. On the basis of silicon carbide, lining wear-resistant plates, o-rings and bushings, reaction-bonded ceramics are produced. Rings and bushings made of wear-resistant silicon carbide material are

designed for sealing shafts and sliding bearings in pumps that pump oil, petroleum products, liquefied hydrocarbon gases, organic solvents, neutral liquids, as well as acids (except fluoric acid) and salt solutions at temperatures from  $-100\text{ }^{\circ}\text{C}$  to  $+500\text{ }^{\circ}\text{C}$ . The products are suitable for use in any designs of friction pairs with the presence of lubrication or self-lubrication [9–11].

The literature describes many methods for applying metal films to dielectric materials that can be used for applying films to silicon carbide. The most commonly used of these are so-called physical and chemical methods. In the physical method, pre-molten metal particles are sprayed onto the coated surface with compressed air or gas. Liquid metal particles on the way to the surface are partially cooled and only melt the surface, sticking to it. A variation of this method is vacuum metallization [12].

For chemical deposition of metal coatings, reducing agents in the gas phase or compounds dissolved in an electrolyte solution are used [13–15].

When using hydrogen gas as a reducing agent, the reduction reaction is carried out at a high temperature of several hundred degrees. In this way, it is possible to obtain coatings from a fairly large number of metals, but the need to have special equipment for heating and dosing gas mixtures limits the wide application of the method.

Thermal decomposition reactions are often used for metallization in the gas phase. The most suitable compounds for this purpose are metal carbonyls. During the reaction, under certain conditions, they decompose, leaving a metal on the coated surface and releasing carbon monoxide, which can again be used to produce metal carbonyl. That is, CO plays the role of a metal carrier reagent. This is not only convenient in terms of production, but also minimizes the unproductive costs of auxiliary reagents, and eliminates environmental pollution. The relative high temperature of the process and the high cost of metal carbonyls prevent the widespread use of this method [9].

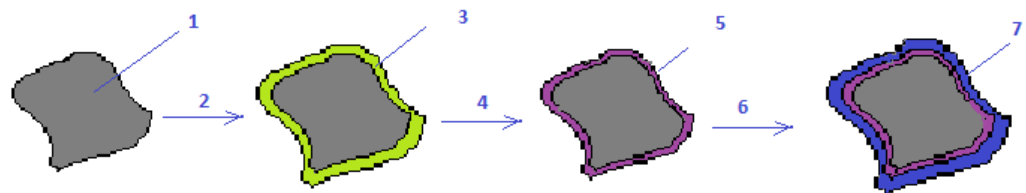
In chemical-electrolytic metallization [13–15], to create an electrically conductive layer, the dielectric surface is activated by creating catalytic centers, which are then coated chemically.

Chemical-electrolytic technology has limitations associated with the use of expensive substances, the use of high temperatures, and the inability to apply coatings on highly porous materials.

The above analysis shows that the task of developing effective methods for applying metal coatings to powdered silicon carbide is relevant.

### Experimental

In this paper, we consider the technology of metallization of silicon carbide powders by preliminary application of metal-like copper phosphide (Fig. 1). At the same time, the process of obtaining a copper-phosphorus film is based on the reaction of reducing divalent copper with gaseous phosphine. To do this, first a film of copper salt solution is obtained on the surface of the sample, and then this surface layer is treated with phosphine. In this case, the film of the copper salt solution is converted to copper phosphide. Sulfates, nitrates, and copper chlorides were investigated as copper salts. However, in most experiments we used the available and cheaper copper sulfate.



1 — separate particle of silicon carbide; 2 — wetting in a solution of copper sulfate;  
3 — sorption layer of copper sulfate; 4 — treatment with phosphine; 5 — a film of copper phosphide;  
6 — chemical nickel plating; 7 — nickel coating

Figure 1. Scheme of metallization of silicon carbide particles

The initial powders are degreased in a 15–20 % solution of hydroxide or sodium carbonate at a temperature of  $40\text{--}500\text{ }^{\circ}\text{C}$  until the surface of the particles is completely wetted, washed in hot running water. Then a layer of metal-like copper phosphide is applied to the surface of the powder particles. To do this, the powder

is immersed in a solution containing 100–200 g/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The ratio of the volume of the powder to the volume of the solution is 1:1.2–1.5 at concentrations of copper sulfate less than 100 g/l, the resulting copper phosphide film will have: a thickness insufficient to build up the metal with a chemical or galvanic metal. At concentrations of copper sulfate more than 200 g/l due to the formation of large crystals of copper sulfate in the subsequent drying of the powder increases the heterogeneity of the thickness of the resulting films. The remnants of the solution are not adsorbed by the surface of the powder is separated by filtration. After that, a sorption layer of the solution with a thickness of 50–70 microns is formed on the surface of the powder particles. The powder is dried for 40–50 minutes at a temperature of 18–25 °C to create gas permeability between the individual particles. The dried powder is placed in a sealed chamber and treated with phosphine gas. Phosphine for research was obtained by acid decomposition of powdered technical zinc phosphide. This phosphide contains about 22 mass % of phosphorus and therefore it can be considered that the main component is zinc phosphide with a small amount of free zinc.

When treated with phosphine in the metallization chamber a reaction occurs between phosphine and the adsorption film of the copper sulfate solution leading to the formation of copper phosphide by reaction:



A small amount of phosphine remains in the gas environment after its reuse, so this gas must be purified. For this purpose, the residual gas was passed sequentially through a layer of copper carbonate and an oxidizing solution (500 g/l of potassium permanganate). After this treatment, phosphine is not detected in the waste gas.

During the experiments, 10 g of skimmed silicon carbide powder was filled with 10 ml of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (200 g/l). After stirring for 5 minutes, the excess solution was filtered out. The powder was transferred to a Petri dish and dried at room temperature until moist state (40–50 minutes).

A Petri dish with dried powder was placed in a sealed chamber. The air was forced out of the free space of the chamber with nitrogen. Then phosphine was fed into this chamber by forcing it out of the bottle with water. At the same time, phosphine was absorbed by the surface film of copper sulfate.

The phosphine treatment process took place at room temperature for several minutes.

Further build-up of the metal film was carried out by chemical Nickel plating in a solution of the following composition:  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  — 30 g/l;  $\text{NaH}_2\text{PO}_2$  — 10 g/l;  $\text{CH}_3\text{COONa}$  — 10 g/l, at an electrolyte temperature of 90 °C for 30 minutes.

Samples of powders at various stages of the process were examined using a raster electron microscope ISM-6490-LV (JEOL, Japan), which allows obtaining electronic images (photos) of individual sections (spectra) of the surface at specified magnifications. The microscope made it possible to simultaneously obtain the elemental compositions of the spectra in the form of a table.

### Results and Discussion

Figure 2 shows an electronic image of carborundum powder after applying a film of copper phosphide. The spectral analysis in Table 1 shows that the content of this phosphide (Cu+P) is about 44 %. However, the entire surface of the powder has a light gray tone characteristic of metal-like copper phosphide and the presence of silicon is due to the fact that due to the small thickness of the copper phosphide film in some areas, the scanning probe partially captures the signals of the lower layer of silicon carbide. If this is the case, then after the deposition of a sufficiently thick layer of chemical nickel, the signals of the lower layer should disappear. In addition, the phosphide film has good adhesion to the carbide particles. This is due to the fact that the copper salt solution penetrates all the pores of silicon carbide, which become gas-permeable as the solution dries. Therefore, the course of the reduction reaction in the pores also provides good adhesion of the film with silicon carbide.

Table 1

#### Elemental composition of carborundum powder

Element	Weight, %
C	12.68
O	13.79
Al	0.92
Si	25.76
P	7.69
Cu	36.75

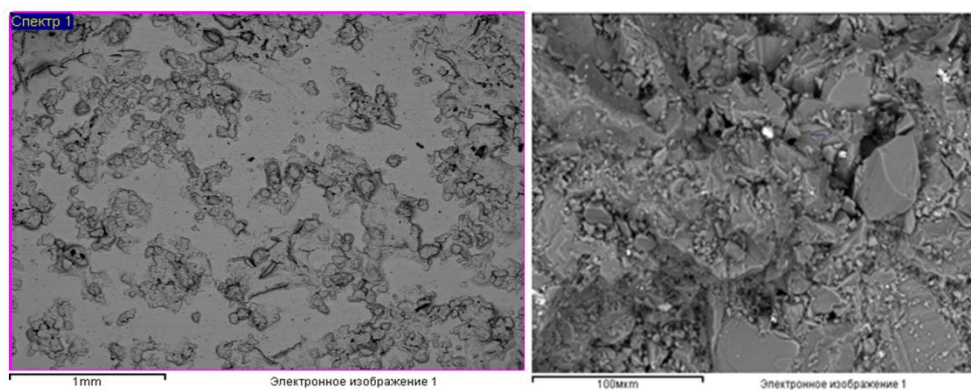
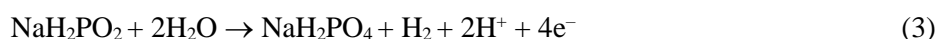
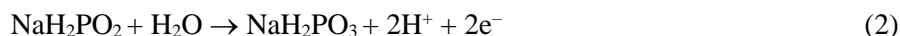


Figure 2. An electronic image of the silicon carbide powder after application of a film of copper phosphide

Copper phosphide is a catalyst for the chemical Nickel plating process, so nickel deposition occurs on the surface of silicon carbide particles covered with a phosphide film, including in the pores. This should also provide the necessary adhesion of the coating to the base. In addition, the process of chemical nickel plating on the surface of copper phosphide is characterized by increased gas release [16, 17]. This leads to some fluctuations of the powder particles and contributes to the formation of a nickel coating over the entire surface of the powder particles. Therefore, such a coating will provide the necessary adhesion between the carborundum particles and the matrix in the preparation of the composite product or coatings.

The reaction occurring in this case is described by the following chemical equations:



As can be seen from these equations, the process of chemical nickel plating is accompanied by the release of hydrogen. In addition, elemental phosphorus is also released, which gives the coating additional hardness.

Figure 3 shows the electronic image and the elemental composition (Table 2) of the powder after applying a layer of chemical nickel. The estimated coating thickness is 0.8–1.0 microns.

This data shows that the nickel coating contains 7 % phosphorus and covers about 90 % of the powder surface. This makes it possible to use such silicon carbide powders in the preparation of composite products or coatings. If necessary, the degree of closure of the powder surface can be increased by repeated conduct of the above operations.

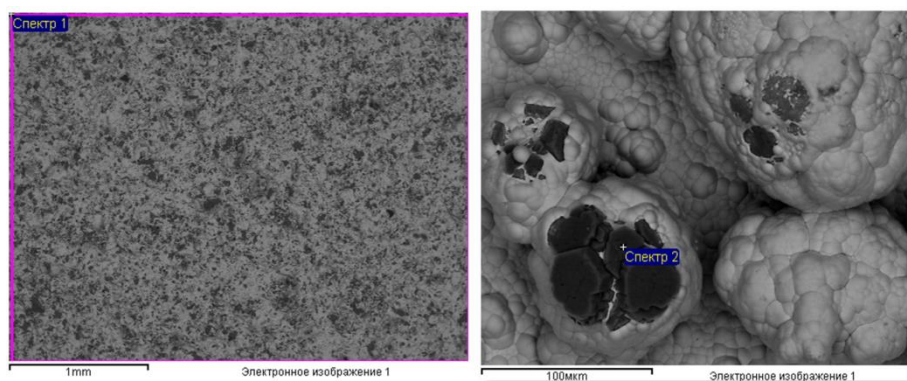


Figure 3. An electronic image of silicon carbide powder after application of chemical nickel



**Elemental composition of silicon carbide powder after application of chemical nickel**

Element	Weight, %
C	7.18
O	2.38
Al	0.39
Si	13.22
P	5.48
Ni	71.35

In a similar work [18], a nickel coating was obtained by electrodeposition. This method is very well known, but has its drawbacks. The main disadvantage is the reduced hardness and complexity of production.

### Conclusions

Phosphine gas is used for applying metal coatings to powdered materials. Thus, for metallization of silicon carbide powder, an adsorption layer of copper sulfate solution is first created by wetting on its surface, which is then transformed by phosphine treatment into a metal-like copper phosphide. Copper phosphide is a catalyst for the chemical nickel plating process. This allows you to apply a layer of chemical nickel. Although the thickness of the copper phosphide film is insignificant, it catalyzes the chemical nickel plating process well. This allows you to apply a coating of the desired thickness to the surface of the silicon carbide powder.

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### Ұнтақ тәрізді кремний карбидін қаптаудың газофазды төментемпературалы технологиясы

Ұнтақ тәрізді кремний карбидінің бетіне металл қаптамасын төсеудің технологиясы әзірленген. Бұл мақсат үшін ұнтақ бетіне бастапқыда мыс фосфидінің қаптамасын қолданады. Үрдіс ұнтақ тәрізді карбидті мыс сульфаты ерітіндісімен сулап, газ тәрізді фосфинмен өңдеуден тұрады. Бұл ретте түзілетін металл тәрізді мыс фосфидінің қаптамасы жеткілікті электр өткізгішіне ие, сондай-ақ химиялық никельдеу процесінің катализаторы болып табылады. Бұл ұнтақтың бетін қажетті металмен қаптауға арналған химиялық немесе гальваникалық әдістерді пайдалануға мүмкіндік береді. Осы технологияны зертханалық жағдайда тексеру кремний карбидінің бөлшектерімен қажетті ұстасуы бар никель қаптамасын алуға мүмкіндік берді. Процестің әртүрлі сатыларында ұнтақтардың барлық үлгілері ISM-6490-LV (JEOL, Жапония) растрлық электрондық микроскоп көмегімен зерттелген. Растрлық электрондық микроскоп әдісімен жүргізілген зерттеу нәтижелері никельді қаптаманың құрамында 7 % фосфор бар және ұнтақ бетінің шамамен 90 % жабатынын көрсетті, ал қаптаманың қалыңдығы 0,8–1,0 мкм құрайды. Бұл композициялық бұйымдарды немесе қаптамаларды алу кезінде кремний карбидінің осындай ұнтақтарын қолдануға мүмкіндік береді. Қажет болған жағдайда ұнтақ бетін қаптау дәрежесін осы мақалада көрсетілген операцияны қайта жүргізу арқылы іске асыруға болады. Мақала ғалымдар мен зерттеушілерге, сондай-ақ композициялық қаптамаларды алу мәселелеріне қызығушылық танытатын тұлғаларға арналған.

*Кілт сөздер:* кремний карбиді, мыс сульфаты, фосфин, мыс фосфидінің қаптамасы, химиялық никельдеу, композициялық материал.

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### Низкотемпературная газофазная технология плакирования порошкообразного карбида кремния

Разработана технология нанесения металлического покрытия на поверхность порошкообразного карбида кремния. Для этой цели на поверхность порошка первоначально наносят пленку фосфида меди. Процесс заключается в смачивании порошкообразного карбида раствором сульфата меди и последующей обработке газообразным фосфином. Образующаяся при этом пленка металлообразного фосфида меди обладает достаточной электропроводностью, а также является катализатором процесса химического никелирования. Это дает возможность использования химических или гальванических методов для плакирования поверхности порошков необходимым металлом. Проверка данной технологии в лабораторных условиях позволила получить никелевое покрытие, имеющее необходимое сцепление с частицами карбида кремния. Все образцы порошков на различных стадиях процесса исследовались при помощи растрового электронного микроскопа ISM-6490-LV (JEOL, Япония), позволяющего получать электронные изображения (фотографии) отдельных участков (спектров) поверхности при задаваемых увеличениях и химический состав. Результаты исследования методом растрового электронного микроскопа показали, что никелевое покрытие содержит 7 % фосфора и закрывает около 90 % поверхности порошка, а расчетная толщина покрытия составляет 0,8–1,0 мкм. Это дает возможность применения таких порошков карбида кремния при получении композиционных изделий или покрытий. При необходимости степень закрытия поверхности порошка можно увеличить повторным проведением операции, указанной в данной статье. Статья предназначена ученым и исследователям, а также лицам, интересующимся проблемами получения композиционных покрытий.

*Ключевые слова:* карбид кремния, сульфат меди, фосфин, пленка фосфида меди, химическое никелирование, композиционный материал.

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## Baromembrane technologies for purification of industrial wastes, using pulse water treatment

In this article the data of the purification of water steam condensate of the LLP «Pavlodar Petrochemical Plant» is considered. In the course of research multifunctional ion exchangers for pre-filters synthesized and were studied. A pilot reverse osmosis unit was produced with a capacity of 600 L per hours, and had been tested to clean steam condensate using a «Unit of Electromagnetic Treatment» (UET) and without it. The optimal treatment mode of purification was selected to the separation of the concentrate 0.1 m<sup>3</sup> per hour. It was found that after desalination of water acidity value of pH changed to acidic medium (permeate) or to the basic medium in the concentrate tract, which associated by decreasing or increasing hydrocarbonate ions, accordingly, in permeate and concentrate. It was noted that the using of the UET at the inlet, led to a slight decreasing of the operating pressure inside the reverse osmosis unit, while on the reverse osmosis unit without UET it corresponded to the calculated value. It was established that the membranes used in testing by using the UET practically have no deposits on themselves, and without it they have a noticeable amount of contamination on their surface. Thus, using the UET in the process of reverse osmosis desalination can significantly increase the service life of membranes and maintain their selectivity, and the proposed method allows to achieve the required water purification standards set by the plant.

*Keywords:* anion exchanger, static exchange capacity, process flow, membrane elements, selectivity, pilot reverse osmosis unit, electromagnetic water treatment device, water sample, test protocol, antiscalant.

### Introduction

Rapid industrialization and economic growth have significantly contributed to human welfare in the recent decades in contributing to industrial pollution and eradication of the natural resources around the world. In particular, the generation of large amounts of industrial effluents has considerably stressed the available water resources, thus raising a great concern not only in developing countries, but also worldwide. There are a number of pieces of evidence for subsequent toxic effects on aquatic organisms when industrial effluents are discharged into the environment without an effective treatment [1, 2].

The environmentally friendly methods recently used for obtaining water are ion exchange and reverse osmosis. These technologies can assure an obtainment of deeply purified water, with content of impurities much below the maximum permissible values according to hygienic standards and even below the limits of detection [3, 4].

Nowadays the membrane and sorption technologies are one of the most progressive and developing branches in chemical engineering [5, 6]. High efficiency of the using membrane processes in various industrial technologies, and their environmental compatibility contribute to rapid growth of the scientific and applied research. Also, the number and range of manufactured membranes and units are increased, as well as it associated in the funding allocated for these purposes in all economically developed countries. Membrane technology in its modern form has been entering in our life since the 70s of the 20<sup>th</sup> century.

One of the reasons for the intensive development of the membrane technology is its relatively low energy costs of separation processes [7,8]. In the forecasts of the world economy development, the membrane technologies are characterized as technologies of the future. The volume of their utilization in the economically developed countries increases annually by 20–25 % [9]. Thus, membranes in reverse osmosis and ultra-filtration, as compared with the other methods (evaporation, freezing, distillation), make it possible to carry out dehydration and concentration of the product, dispose of impurities, isolate the necessary substances and purify solutions. Herewith, the energy consumption is significantly reduced.

Among the membrane processes, which have been intensively developing in the recent years, baromembrane processes, such as reverse osmosis, ultra-, micro- and nano-filtration, hold a special place, which is connected with related to their universality and a wide range of application [10, 11]. They are characterized by

such features as low energy consumption, simplicity of the equipment design, an ability to work at the ambient temperature.

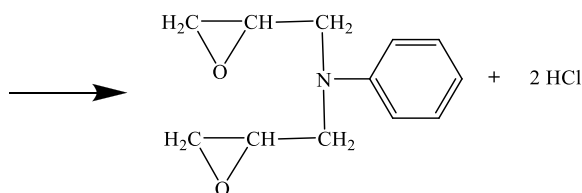
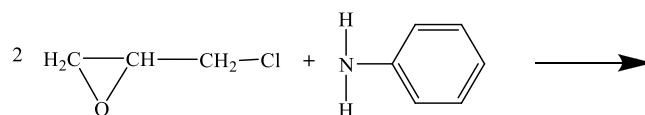
The Republic of Kazakhstan has the largest mineral and raw material resources and does not have sufficient sources of fresh water. At the same time, a number of regions of our country have large reserves of underground waters, which are not used for the needs of water supply due to the high content of salts, dissolved in water. These waters can become sources of water supply only in case of their further desalination.

That is why, the development of methods for producing new membranes, which are the basis of the desalination equipment, is of a big practical importance [12].

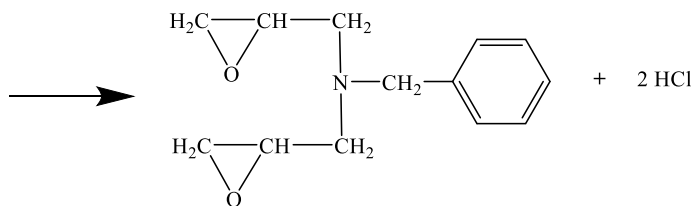
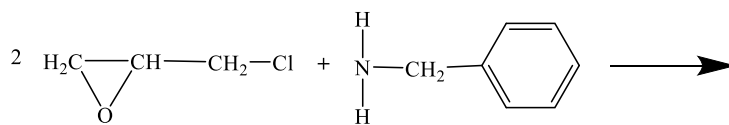
This work aims at the purification of the water steam condensate of Pavlodar Petrochemical Plant LLP (PPCP LLP), using the reverse osmosis method, combined with an electromagnetic water treatment device (EWTD) for ensuring a minimum volume of the concentrate (no more than 10 %), and preventing an intense salt deposition on the reverse osmosis membranes.

### Experimental

Polyfunctional anion exchangers, based on aniline (A), benzylamine (BA) and polyethyleneimine (PEI) were obtained by the condensation with PEI of epoxyamines, synthesized from A or BA, and ECH. First, glycidyl derivatives of amines (epoxyamines) were synthesized from aniline (A) or benzylamine (BA), and epichlorohydrin (ECH) in the presence of NaOH at the temperature of 50 °C for 6 hours:

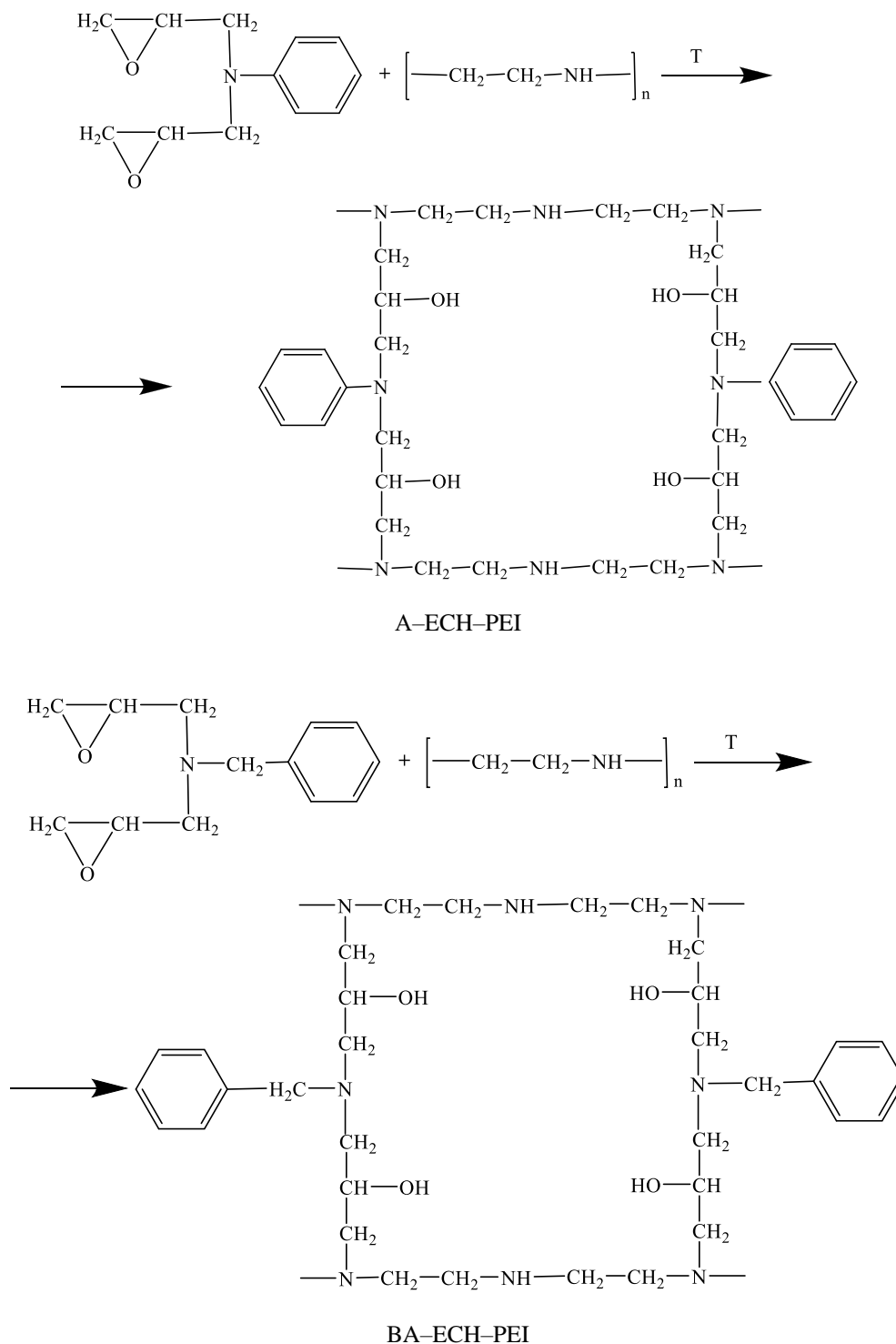


A-ECH



BA-ECH

The polycondensation with PEI was carried out in a solution of dimethylformamide (DMF) at different mass ratios, at the temperature of 60–65 °C for 5–6 hours, after which the reaction mass was baked at the temperature of 100 °C for 16–24 hours.



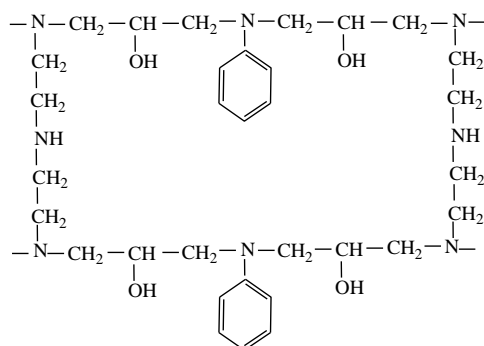
The elemental composition of anion exchangers (found/calculated), % for A-ECH-PEI: C — 73,32/73,86; H — 17,60/17,34; N — 5,89/5,60; O — 3,19/3,20 and BA-ECH-PEI: C — 70,72/70,92; H — 17,61/17,48; N — 7,81/8,09; O — 3,86/3,51.

The study of the main physical and chemical characteristics of ion exchangers, based on A-ECH-PEI and BA-ECH-PEI has been carried out according to the GOSTs 19180-73, 10898.1-74 and GOST 10898.5-74 on the enlarged batches, obtained under the optimal conditions.

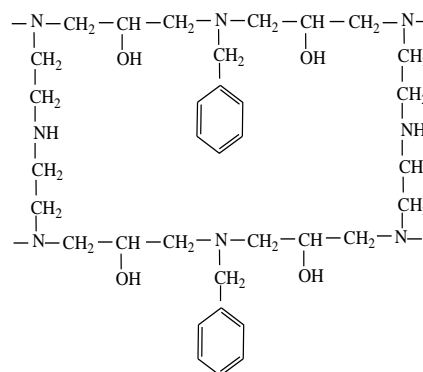
### Results and Discussion

In the course of our studies, we have synthesized and investigated polyfunctional ion exchangers for pre-filters.

On the basis of the chemical analysis, the structure of the synthesized polymers may be represented as follows:



A-ECH-PEI



BA-ECH-PEI

Table 1 shows the main physicochemical characteristics of the synthesized anion exchangers A-ECH-PEI and BA-ECH-PEI.

Table 1

**Main physicochemical characteristics of the synthesized anion exchangers**

Anion exchangers based on	COE <sub>HCl</sub> , mg-equ/g	V <sub>sp</sub> , ml/g	Chemical stability in solutions, %			Thermal stability in water, %
			5 n H <sub>2</sub> SO <sub>4</sub>	5 n NaOH	10 % H <sub>2</sub> O <sub>2</sub>	
A-ECH-PEI	4.83	4.5	92.5	94.9	70.1	95.0
BA-ECH-PEI	8.95	5.7	97.9	98.7	72.0	94.1

*Note.* COE<sub>HCl</sub> — static exchange capacity of an anion exchanger by 0.1 n solution of HCl; V<sub>sp</sub> — specific volume of an ion exchanger.

Tests of efficiency of applying the electromagnetic water treatment technology have been carried out in the process of the reverse osmosis desalination of the water steam condensate of PPCP LLP. It has been found that with a decrease in the volume of the concentrate, the concentration of all salts in it increases, namely, the hardness salts in the concentrate form microcrystals with their isolation on the surface of a membrane element. As a result the productivity of the unit sharply decreases and the membrane elements should be «chemically» washed or replaced. This problem may be solved either with the help of reagents, introduced into the initial water, or with the help of magnetic pulse treatment of water in the process of reverse osmosis. To solve this problem it is necessary to create the conditions, when only the emerging microcrystals of the hardness salts will be in water, as if on a «magnetic pad», without isolating them on the membrane surface.

An electromagnetic transducer is designed for cleaning and protection against the deposits of the hardness salts. It can be used both independently and as an addition to the existing water treatment systems. The control unit has a printed board with a powerful electromagnet and a microprocessor, which generates electromagnetic pulses and controls the change in the frequency range from 1 kHz to 25–50 kHz. Electromagnetic waves of various lengths, amplitude and frequency, which vary over time, are transmitted through the wire-transmitters. An electromagnetic pulse is concentrated in the volume of water flowing in the pipeline where the coil is installed. Under the effect of electromagnetic waves, divalent cations of calcium and magnesium lose an ability to interact with anions and form insoluble compounds. The converted calcium and magnesium cations lose an ability to crystallize and precipitate. Herewith, the chemical and mineral composition of water does not change.

According to the goal to be sought, a set of documents for the test bench has been developed, including two reverse osmosis units, one of which is equipped with an electromagnetic water treatment device. A process flow has been developed, according to the fact that the initial water enters the tank, where from the water is

supplied to the two reverse osmosis units with a capacity of 600 l/h. In front of a high pressure pump — after the tie-in point of the recirculation line — an electromagnetic water treatment device is installed on the pipeline of one unit. The test bench operates in a closed circuit, i.e. permeate and brine return to their initial capacity. The controlled parameters of the test bench are: the capacity of permeate, concentrate, recirculation line, differential pressure at each circuit, TDS in the water steam condensate before the treatment, in permeate and concentrate thrice a day.

During the next researches, tests have been conducted for the purification of the steam condensate, taken from PPCP LLP, using EWTD and without it. An assembled pilot reverse osmosis unit with a capacity of 600 l/h is shown in Figure 1.

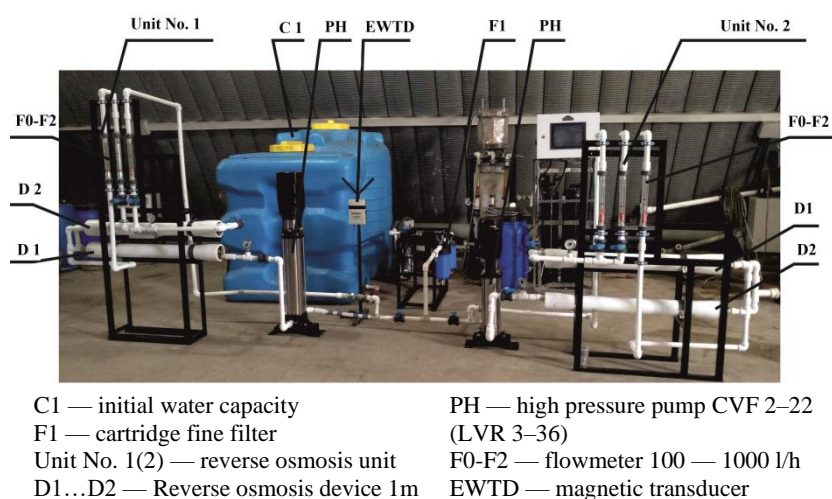


Figure 1. General view of a pilot reverse osmosis unit with a capacity of 600 l/h

Sampling of the steam condensate from PPCP LLP, amounting to 2500 L has been carried out. The obtained samples have been submitted for a complete chemical analysis to an independent certified testing laboratory of «Kazecologiya» Scientific Research and Production Center LLP (Almaty). According to the test protocol, the composition of the obtained water samples is as follows (Table 2).

Table 2

#### Data of the chemical analysis of the steam condensate samples from PPCP LLP

Parameters	Content
Salt content, mg/dm <sup>3</sup>	238
Total hardness, mg-equ/dm <sup>3</sup>	3.0
Iron, mg/dm <sup>3</sup>	50
Oil products, mg/dm <sup>3</sup>	0.8
pH — value	7.24

The required standards for the purified steam condensate requested by PPCP LLP are presented in Table 3.

Table 3

#### Required standards for the purified water steam condensate

Product	Parameters	Standard
Water steam condensate	Salt content, mg/dm <sup>3</sup>	No more than 40
	Total hardness, mg-equ/dm <sup>3</sup>	No more than 5
	Iron, mg/dm <sup>3</sup>	No more than 0.5
	Oil products, mg/dm <sup>3</sup>	No more than 0.3
	pH — value	6.8–7.5



Tables 4, 5 show the results of the tests, carried out on the reverse osmosis unit, combined with EWTD and without it.

During the tests at the pilot units, the optimal mode for desalinating the water steam concentrate has been selected, whose gist is as follows: a water flow with a capacity of  $0.7 \text{ m}^3/\text{h}$  has been supplied to the inlet of the high-pressure pump of the reverse osmosis units, the permeate output has been  $0.6 \text{ m}^3/\text{h}$ , the discharge into the concentrate circuit has been  $0.5 \text{ m}^3/\text{h}$ , of which  $0.4 \text{ m}^3/\text{h}$  has been fed back to the inlet to the high pressure pump via the recirculation circuit. Thus, the concentrate discharge has been equal to  $0.1 \text{ m}^3/\text{h}$ . Also, in the course of the repeated tests, the optimal volume of water flow in the recirculation circuit of the reverse osmosis units ( $0.4 \text{ m}^3/\text{h}$ ) has been chosen.

It should be noted, that pH of the initial water has been equal to 7.24, after desalination of the water, pH has shifted to the acidic medium (permeate) and to the alkaline medium on the concentrate circuit, which is connected with a decrease and, respectively, an increase of hydrocarbonate ions in permeate and concentrate. It has been noted, that the use of EWTD at the inlet leads to a slight decrease in the working pressure inside the reverse osmosis unit, while at the reverse osmosis unit without EWTD, the working pressure corresponds to the calculated one. This effect is explained by the effect of electromagnetic waves on the ability of divalent calcium and magnesium cations to interact with anions to form insoluble compounds and their subsequent precipitation on the working surface of the reverse osmosis membranes (which, as a rule, leads to an increase in the working pressure as the membrane surface becomes polluted).

It has been found, that a pressure decrease is connected with a change in the salt content of the tested water. The water temperature also has an indirect effect. With a temperature increase of the water for osmosis, the medium becomes less viscous and dense, as a result, more mobile. This leads to the increase of the filtration rate, which negatively affects the membrane life. To ensure the maximum possible mode of operation of the membranes, it is necessary to have a temperature range between  $15\text{--}20 \text{ }^\circ\text{C}$ .

The following statement is actual for expressing the dependence of the diffusion rate of water molecules through the membrane walls, upon changing of the water temperature before osmosis: when the solution temperature changes by one degree (decreases or increases), the specific flow rate of the medium reaches 3 % of the set value. This change causes a negative effect on the filtration processes on the industrial scale, as the osmosis treatment units require constant capacity. The osmosis capacity is temperature dependent as follows: a decrease in the temperature reduces the capacity, and when it reaches  $4 \text{ }^\circ\text{C}$ , the rate drops approximately twice.

Upon the completion, the membrane elements have been removed for visual inspection and determination of the degree of microcrystal contamination. Figures 2–3 present the photographs of the membrane samples, using EWTD and without it.



Figure 2. Photo of the membrane samples after the tests, using EWTD



Figure 3. Photo of the membrane samples after the tests, without using EWTD

Table 4

**Results of the tests of the steam condensate samples on the reverse osmosis unit, combined with EWTD**

Date	Time	$\Delta P_{in}$ , bar	$\Delta P_{out}$ , bar	$Q_{perm}$ , m <sup>3</sup> /h	$Q_{conc}$ , m <sup>3</sup> /h	$Q_{rec}$ , m <sup>3</sup> /h	TDS, (mg/l)			T, °C			pH		
							initial	perm.	conc.	initial	perm.	conc.	initial	perm.	conc.
09.12.19	9.00	6.8	6.8	0.5	0.07	0.3	20.2	12.0	143.7	7	7	7	7.24	6.31	6.93
09.12.19	12.00	6.8	6.8	0.5	0.07	0.3	20.2	11.9	143.7	7	8	8	7.24	6.34	6.93
09.12.19	15.00	6.7	6.7	0.5	0.07	0.3	20.2	11.9	143.7	8	8	8	7.24	6.32	6.93
10.12.19	9.00	6.8	6.7	0.5	0.07	0.3	20.2	12.2	144.0	6	6	6	7.24	6.31	6.92
10.12.19	12.00	6.8	6.8	0.5	0.07	0.3	20.2	11.7	144.2	6	7	7	7.24	6.34	6.96
10.12.19	15.00	6.7	6.7	0.5	0.07	0.3	20.2	12.0	143.7	8	8	8	7.24	6.34	6.93
11.12.19	9.00	6.8	6.7	0.5	0.07	0.3	20.2	12.0	143.7	8	8	8	7.24	6.34	6.93
11.12.19	12.00	6.7	6.7	0.5	0.07	0.3	20.2	11.9	143.7	8	8	8	7.24	6.32	6.94
11.12.19	15.00	6.8	6.7	0.5	0.07	0.3	20.2	11.7	144.0	8	8	8	7.24	6.32	6.92
12.12.19	9.00	6.8	6.8	0.5	0.07	0.3	20.2	12.0	144.2	7	7	7	7.24	6.34	6.96
12.12.19	12.00	6.7	6.7	0.5	0.07	0.3	20.2	11.7	143.7	7	7	7	7.24	6.34	6.93
12.12.19	15.00	6.8	6.8	0.5	0.07	0.3	20.2	12.0	144.1	7	8	8	7.24	6.31	6.93
13.12.19	9.00	6.8	6.8	0.5	0.07	0.3	20.2	11.7	143.7	8	8	8	7.24	6.34	6.93
13.12.19	12.00	6.7	6.7	0.5	0.07	0.3	20.2	11.9	143.7	8	8	8	7.24	6.31	6.93
13.12.19	15.00	6.7	6.7	0.5	0.07	0.3	20.2	12.2	144.2	8	8	8	7.24	6.31	6.93

Table 5

**Results of the tests of the steam condensate samples on the reverse osmosis unit**

Date	Time	$\Delta P_{in}$ , bar	$\Delta P_{out}$ , bar	$Q_{perm}$ , m <sup>3</sup> /h	$Q_{conc}$ , m <sup>3</sup> /h	$Q_{rec}$ , m <sup>3</sup> /h	TDS, (mg/l)			T, °C			pH		
							initial	perm.	conc.	initial	perm.	conc.	initial	perm.	conc.
09.12.19	9.00	7.0	7.0	0.5	0.07	0.3	20.2	12.0	142.4	7	7	7	7.24	6.40	6.98
09.12.19	12.00	7.0	7.0	0.5	0.07	0.3	20.2	12.0	142.4	7	8	8	7.24	6.37	6.98
09.12.19	15.00	6.9	6.9	0.5	0.07	0.3	20.2	12.0	142.4	8	8	8	7.24	6.39	6.98
10.12.19	9.00	7.0	6.9	0.5	0.07	0.3	20.2	12.3	142.1	6	6	6	7.24	6.40	6.99
10.12.19	12.00	7.0	7.0	0.5	0.07	0.3	20.2	11.8	142.0	6	7	7	7.24	6.37	7.1
10.12.19	15.00	6.9	6.9	0.5	0.07	0.3	20.2	12.0	142.4	8	8	8	7.24	6.37	6.98
11.12.19	9.00	7.0	6.9	0.5	0.07	0.3	20.2	12.0	142.4	8	8	8	7.24	6.37	6.98
11.12.19	12.00	6.9	6.9	0.5	0.07	0.3	20.2	12.0	142.4	8	8	8	7.24	6.39	7.2
11.12.19	15.00	7.0	6.9	0.5	0.07	0.3	20.2	11.8	142.1	8	8	8	7.24	6.39	6.99
12.12.19	9.00	7.0	7.0	0.5	0.07	0.3	20.2	12.0	142.0	7	7	7	7.24	6.37	7.1
12.12.19	12.00	6.9	6.9	0.5	0.07	0.3	20.2	11.8	142.4	7	7	7	7.24	6.37	6.98
12.12.19	15.00	7.0	7.0	0.5	0.07	0.3	20.2	12.0	142.1	7	8	8	7.24	6.40	6.98
13.12.19	9.00	7.0	7.0	0.5	0.07	0.3	20.2	11.8	142.4	8	8	8	7.24	6.37	6.98
13.12.19	12.00	6.9	6.9	0.5	0.07	0.3	20.2	12.0	142.4	8	8	8	7.24	6.40	6.98
13.12.19	15.00	6.9	6.9	0.5	0.07	0.3	20.2	12.3	142.0	8	8	8	7.24	6.40	6.98

It is seen in the above photographs, that the membranes, which have been tested, using EWTD, practically have no deposits thereon, and those, tested without using EWTD, have a noticeable contamination on their surface. Hence it follows, that the use of EWTD in the process of the reverse osmosis desalination can significantly increase the service life of the membranes, and maintain their selectivity.

*Conclusions*

Thus, a highly effective technology for purifying the water steam condensate of Pavlodar Petrochemical Plant LLP has been developed on the basis of the reverse osmosis method, combined with the electromagnetic water treatment device. During the tests at the pilot units, the optimal mode for desalinating the water steam concentrate has been selected. It has been established, that the use of this technology, which is based on pulsed water treatment technique, makes it possible to minimize the volume of the concentrate and contributes to preventing an intense salt deposition on the reverse osmosis membranes. Herewith, a high efficiency of water purification and an increase in the concentration coefficient are achieved and therefore service life of these membranes is increased with preservation of their highly selective properties.

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Е.Е. Ерғожин, Т.К. Чалов, Т.В. Ковригина, Е.А. Мельников, Б.Е. Бегенова

## Суды импульстік өңдеуде қолдана отырып, өнеркәсіптік ағындарды тазартудың баромембранды технологиялары

Мақалада «Павлодар мұнай-химия зауыты» ЖШС су бу конденсатын тазарту бойынша деректер келтірілген. Жүргізілген зерттеулер барысында алдын-ала тазалау сүзгілеріне арналған полифункционалды иониттер синтезделген және зерттелген. Өнімділігі 600 л/с пилоттық керіосмостық кондырғы дайындалды, онда электромагнитті өңдеу құралын (ЭӨҚ) қолдана отырып және онсыз бу конденсатын тазалау бойынша сынақтар жүргізілген. Тазалаудың оңтайлы режимі таңдап алынған, ол бойынша концентратты шығару 0,1 м<sup>3</sup>/сағ. құрайды. Суды тұщыландырылғаннан кейін рН қышқыл ортаға (пермеат) және концентратты жолда сілтілі ортаға ығысуы орын алды, бұл пермеат пен концентраттағы гидрокарбонат-иондардың азаюымен және тиісінше ұлғаюымен байланысты. ЭӨҚ-ны кіреберісте пайдалану керіосмос кондырғысының ішіндегі жұмыс қысымының аздап төмендеуіне әкелді, ал ЭӨҚ-сыз керіосмос кондырғысында ол есептелгенге сәйкес келді. ЭӨҚ-ны қолдану арқылы сынау процесінде пайдаланылатын мембраналардың іс жүзінде шөгінділері жоқ, ал ЭӨҚ-ны пайдаланбаса олардың бетінде ластанудың елеулі мөлшері бар екені анықталған. Сонымен, керіосмос тұзсыздандыру процесінде ЭӨҚ-ны қолдану мембраналардың қызмет ету мерзімін едәуір арттырып, олардың селективтілігін сақтауға мүмкіндік береді, ал ұсынылған әдіс зауыт орнатқан суды тазарту стандарттарына қол жеткізуге көмектеседі.

*Кілт сөздер:* анионит, статикалық алмасу сыйымдылығы, технологиялық схема, мембрандық элементтер, селективтілік, пилоттық керіосмос кондырғысы, электромагниттік су тазарту құрылғысы, сынақ есебі, антискалант.

Е.Е. Ергожин, Т.К. Чалов, Т.В. Ковригина, Е.А. Мельников, Б.Е. Бегенова

## Баромембранные технологии очистки промышленных стоков с применением импульсной обработки воды

В статье приведены данные по очистке водяного парового конденсата ТОО «Павлодарский нефтехимический завод». В ходе проведенных исследований синтезированы и исследованы полифункциональные иониты для фильтров предварительной очистки. Изготовлена пилотная обратноосмотическая установка, производительностью 600 л/ч, на которой проведены испытания по очистке парового конденсата с применением прибора электромагнитной обработки (ПЭО) и без него. Подобран оптимальный режим очистки, по которому сброс концентрата составлял 0,1 м<sup>3</sup>/ч. Найдено, что после опреснения воды происходил сдвиг pH в кислотную среду (пермеат) и в щелочную среду на концентратном тракте, что связано с уменьшением и, соответственно, увеличением гидрокарбонат-ионов в пермеате и концентрате. Отмечено, что использование ПЭО на входе привело к незначительному уменьшению рабочего давления внутри обратноосмотической установки, в то время, как на обратноосмотической установке без ПЭО, оно соответствовало расчетному. Установлено, что мембраны, используемые в процессе испытаний с применением ПЭО, практически не имеют на себе отложений, а без использования ПЭО обладают заметным количеством загрязнений на их поверхности. Таким образом, использование ПЭО в процессе обратноосмотического опреснения позволяет значительно увеличить срок службы мембран и сохранить их селективность, а предложенный способ помогает достичь требуемых норм очистки воды, выведенных заводом.

*Ключевые слова:* анионит, статическая обменная емкость, технологическая схема, мембранные элементы, селективность, пилотная обратноосмотическая установка, прибор электромагнитной обработки воды, проба воды, протокол испытаний, антискалант.

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## Review of methods for enrichment of phosphate raw materials in the world

With the development of the global economy, the consumer market for phosphorus-containing products is growing. All existing deposits of rich phosphorites are being depleted. In this regard, there is a need to involve in the production of low-grade phosphorites and substandard phosphate raw materials, which are currently little studied and are not used. For the processing of substandard phosphorites, there is a need for new methods for improving and enriching low-grade ores and removing impurities as much as possible in order to increase the content of the target components and improve the suitability for processing. The article provides modern information about the processes of enrichment of phosphorites in different countries. This information is fundamental for further research on the enrichment of Karatau phosphorites. The review is made mainly of two methods: flotation (applicable for silicate phosphates) and the use of organic acids (for carbonate substances). The mechanisms of separation of substances during flotation enrichment and decomposition of carbonate minerals using organic acids are described. The advantages and disadvantages of each method are considered. It is established that the choice of a certain method is determined by the mineralogical structure and chemical composition of phosphorites.

*Keywords:* phosphorite, deposit, chemical industry, production, enrichment, flotation, substandard raw materials, low-grade ores.

### *Introduction*

Phosphorites are sedimentary rocks with a content of  $P_2O_5$  — from 5 % to 30 %, a significant part of which consists of phosphates close in composition to the Apatite group and are represented by hidden or microcrystalline formations. Natural phosphates serve as raw materials for obtaining elemental phosphorus and its various compounds. More than 90 % of all extracted phosphorus is used for the production of mineral fertilizers.

The world raw material potential of natural phosphates-apatites and phosphorites is estimated at about 30 billion t  $P_2O_5$ . Structurally, it is almost 95 % represented by phosphorites and only 5 % is accounted for by apatites, and in Russia apatites are sharply predominant (80 %). Africa (Morocco, Tunisia, Western Sahara, South Africa) holds the leading position in terms of reserves of phosphate ores, and America (USA, Peru, Mexico, Brazil) is in second place. The Asian continent is characterized by the largest reserves of phosphorites in China, Jordan, Mongolia, and Saudi Arabia. Australia has significant reserves of phosphorites. About 80 % of the total world production (130 million tons of commodity ore) is accounted for by the United States, Morocco, Russia, Kazakhstan, and China. The leading producers of phosphorus concentrate are the United States (36 million tons) and Morocco (20 million tons). The leading positions in the production of apatite concentrate are occupied by Russia (4.5 million tons), Brazil (3 million tons), and South Africa (2.5 million tons) [1].

The Republic of Kazakhstan occupies the fourth place in the world in terms of reserves of phosphate raw materials and is the largest phosphate raw material base in Eurasia. Today, about 45 deposits of phosphorites have been explored. Among them, the resources of Karatau phosphorite ores are more than 15 billion tons of  $P_2O_5$ , where the largest deposits are Zhanatas, Kokzhon, Koksou, Aksai and Akzhar. However, all the above-mentioned countries of the world, including Kazakhstan, have depleted the resources of the rich in  $P_2O_5$  content. In this regard, the use of low-grade phosphorites is required, but their processing requires an enrichment process [2].

### *Discussion*

Usually, flotation, thermal (calcination) and mechanical methods are used for ore phosphorite enrichment in practice. Flotation is of great importance as a secondary method of enrichment, and is used in the enrichment of phosphorites. The method is based on the different ability of minerals to wetting with water. Through an aqueous suspension of crushed solid ore, air is blown from below with small bubbles. Hydrophobic particles of raw materials (apatite) adhere to air bubbles and are carried out with their help to the surface. The formed

foam is collected in special receivers. The flotation concentrate is obtained after the destruction of the foam solid residue. There are difficulties in the enrichment of sedimentary rocks (phosphorites) with carbonate impurities, since they are resistant to flotation.

For example, the enrichment of Karatau phosphorites occurs at the processing plants in Zhanatas and Karatau city in the Zhambyl region. In many cases, these processing plants are enriched with phosphorites of siliceous-carbonate composition and use a combined method-chemical-flotation and suspension-flotation. The essence of the combined method is that at the first stage, after crushing the ore and screening the fraction, suspension enrichment is carried out. In this case, a mixture of acidic sodium salts of aliphatic polyphosphoric acids with the name «Flotol-7.9» is used as a flotation reagent. At the second stage, carbonate flotation of the heavy fraction is carried out. Increasing the content of  $P_2O_5$  is achieved by the fact that the enrichment is partially removed siliceous rock (with a light fraction and slime) and reduces the volume of slime, clay particles. This method was used for the phosphorites of the Aksai deposit, where the initial ore contained  $P_2O_5$  21.6 %,  $MgO$  3.48 %, and an insoluble residue 21.9 %. The overall results of the combined scheme were:  $P_2O_5$  30.2 %,  $MgO$  1.75 %, insoluble residue 13.46 %. The obtained indicators of the content of basic substances indicate the suitability of the enriched product for further processing [2].

It is known that various collectors and depressants are used for flotation. Fatty acids [3], amphoteric derivatives of amines [4] and others are considered as collectors and depressants. In Brazil, natural flotation reagents such as coconut oil and starch were used to enrich low-grade phosphorites in the Itataya field, Ceara state with a content of 17.34 %  $P_2O_5$ , 20.78 %  $CaCO_3$  and 24.14 %  $SiO_2$  for flotation [5]. As a result, the content of  $P_2O_5$  in the concentrate at 80.8 % extraction reached 30.5 %.

In the same country, scientists [6] conducted a laboratory study using a collector in the form of soy bran oil, Flotanol D25 (polyalkylene glycol ether foamer), sodium hydroxide, phosphoric acid, citric acid and carbon dioxide. The initial composition of phosphorites: 17.73 %  $P_2O_5$ , 34.00 %  $CaCO_3$  and 24.14 %  $SiO_2$ . In the first stage, soy bran oil and Flotanol D25 were used to separate the insoluble residue. In the second stage, the effectiveness of phosphoric and citric acid for the extraction of carbonates was investigated. When using citric acid, the  $P_2O_5$  content reached 32.46 % (product yield 87.3 %), and when using phosphoric acid  $P_2O_5$  27.86 % (product yield 87.6 %).

A study of two-stage calcite flotation followed by phosphorite flotation was also conducted. For flotation of calcite are used the same collectors — soybean bran oil, Flotanol D25 and carbon dioxide. The addition of carbon dioxide is explained by the fact that it reduces the strength of hydrogen bonds and facilitates the adsorption of the reservoir. For flotation of phosphorite used sodium hydroxide and soybean bran oil. As a result, the flotation concentrate had 32.48 % of  $P_2O_5$ . The presence of carbon dioxide increased the selectivity of calcite flotation in relation to phosphorite even when using a low collector dosage by suppressing the electrostatic barrier for adsorption of the anion collector [6].

The phosphorites of the Guizhou deposit (China) are classified by scientists as low-grade phosphorites according to the content of  $P_2O_5$  23.56 %, while this content belongs to ordinary ones. But nevertheless, regarding the phosphorites of this Deposit, research was undertaken on enrichment by the method of reverse flotation, where rapeseed oil was used as flotation reagents in combination with the de-magnesium collector EM-LS-01. By studying the flotation characteristics of various fatty acids, scientists obtained the flotation agent EM-LS-01 by saponification, amidation and addition of surfactants. The effectiveness of the flotation agent was proved on Guizhou phosphorites, where the results obtained flotation concentrate with  $P_2O_5$  30.25 % with a product yield of 90.63 %. The authors argue that it is necessary to study the composition and nature of fatty acids, and deduce the hypothesis that the higher the content of linoleic acid in vegetable oils, the better the performance of flotation [7].

The economic component of the flotation process is touched in the investigations of Chinese scientists. They conducted research to reduce the dosage of flotation reagents using the gravity-flotation method for the phosphorites of the Yichang deposit in Hubei province. In the first stage, using gravitational separation, it was possible to obtain a gravitational concentrate with  $P_2O_5$  of 28.95 %. In the future, flotation was performed with the resulting concentrate, where liquid glass, sodium oleate and sodium dodecyl sulfate were used as flotation reagents for comparison. Because of its mineralogical structure, the main mineral in these phosphorites is dolomite. In this regard, sodium dodecyl sulfate is a collector of dolomite. The study resulted in a flotation concentrate with  $P_2O_5$  of 30.36 % with a product yield of 75.36 %. The improved gravity-flotation combined process has proven to be effective in reducing the flow rate of flotation reagents from 6.1 kg/t to 3.9 kg/t with similar separation results [8].

Promising research on phosphorite enrichment is also being conducted in Africa. For example, in Zimbabwe, The Mumbwa phosphorite deposit is 22.7 % in terms of the main component  $P_2O_5$ . In laboratory conditions, flotation was performed using petroleum sulfonate as a collector. The results of the study allowed to obtain a flotation concentrate with  $P_2O_5$  content of about 37 % at the optimal dosage of the flotation agent 1100 g/t [9].

Of the African countries in terms of phosphorite reserves, Tunisia stands out, where deposits of phosphorites are located in the Gafsa-Metlaoui basin in the South of the country. The Tozeur-Nefta field is a very important resource for the economy of this country, where according to data there are 410 million tons of phosphates. But it was not previously used in industrial scale because of the low content of  $P_2O_5$  (about 12–16 %). Before flotation, the raw material underwent mechanical treatment, which resulted in raw materials with  $P_2O_5$  15.5 %. Phosphoric acid was used as an anion collector to remove carbonate impurities. According to the results of the study, the  $P_2O_5$  of the flotation concentrate was 27.1 %, but the CaO/  $P_2O_5$  ratio of 1.71 is high and makes the product unsuitable for industrial use [10]. In addition, use as a flotation agent is economically unprofitable due to the high cost.

In this regard, the following work is a study of the enrichment of phosphorites in Egypt, where phosphoric acid was completely replaced by oleic acid mixed with kerosene (in a ratio of 1:1) as a collector. High-grade sodium carbonate, hydrochloric acid, and bromoform were used as pH regulators for comparison. For laboratory research, crushed ore was used  $0.25 \text{ mm} \pm 0.074 \text{ mm}$ . The  $P_2O_5$  content was 19.59 %. When using bromoform, the  $P_2O_5$  content increased to 33.43 %. But due to its toxicity, it is forbidden to use bromoform in industry. Studies with a mixture of oleic acid with kerosene allowed increasing  $P_2O_5$  up to 30 %. The mechanism of interaction of this mixture with phosphorite is explained by the fact that at low pH oleic acid is essentially present in the form of neutral molecules. Consequently, these neutral molecules physically bind to the calcite surface, which is slightly positively charged, by hydrogen bonding with  $H_2CO_3$ , improving the selective flotation of calcite [11].

Also in Egypt the method of enrichment of phosphorites by acid leaching with the use of inorganic and organic acids has been studied. Inorganic acids are strong in comparison with organic ones, and in the leaching process carry away a part of the phosphorites, which are subjected to the action of a strong acid. For example, the phosphorites of the Abu Tartour deposit (Egypt) have a  $P_2O_5$  of 21.8 %. 4 organic acids were selected for leaching, namely acetic acid, tartaric acid, citric acid and oxalic acid. The authors note the cost-effectiveness of using organic acids to remove carbonate impurities and the solubility/digestibility of phosphates in the final product. The process of leaching with organic acids is carried out at relatively low temperatures and concentrations, since with an increase in the temperature of the process and the concentration of the acid, the transition of phosphates to the solution is possible. The studies were conducted in laboratory conditions at room temperature and reaction time equal to 30 min. The ratio of S:L, is respectively, 1:2. The concentration of the acid is 0.2, 0.8 and 1.4 M in terms of leaching efficiency, tartaric acid was the weakest, followed by citric and acetic acid. The use of oxalic acid increased the  $P_2O_5$  content to 28 % [12].

Similar studies on the use of organic acids have been conducted in China. Phosphorites from the Xinhua deposit with a  $P_2O_5$  content of 17.45 % were selected for study. The organic acids selected for leaching were diluted, thereby reducing the concentration. This is due to the fact when water is diluted with organic acid, the contact surface between the dolomite and the acid increases. Meanwhile, acids with high concentrations do not react with calcium and magnesium carbonate due to the high polarity of the O-H-bond of the acid molecules. In comparison with the previous work, the reaction time was increased to 40–60 minutes and the temperature to 40 °C. At 30 minutes of reaction and at 40 °C,  $P_2O_5$  is reached 33.78 %. When increasing the time already at 40 minutes revealed a slight entrainment of phosphates in the solution, but the removal of the carbonate component improved. The results of the study are confirmed by thermodynamic methods of analysis, the data of which indicate the primary leaching of carbonates than phosphates [13].

Leaching with organic acids was also studied in Uzbekistan of Kyzylkum phosphorites of the Zheroy-Sardar deposit with a  $P_2O_5$  content of 16.2 %. Acetic and formic acids were used as leachable reagents. As a result of the conducted laboratory research, the optimal stoichiometric norm of acetic and formic acids was established in the limit of 110 %, the time of 240 min and the temperature of 25 °C. The content of  $P_2O_5$  in the final enriched product was 23.27 %, which is suitable for obtaining phosphorus and phosphoric acid. In this case, the regeneration of waste acid, as stated here and in previous works is carried out with sulfuric acid [14]. The process of regeneration has not studied yet been fully, since the process of leaching with organic acids has not introduced yet been into production anywhere in the world.

### Conclusions

The use of organic acids is characterized by high efficiency, low cost, simple operating conditions (room temperature and atmospheric pressure), the possibility of organic acid regeneration, preservation of the surface properties of the resulting phosphate. In addition, it does not cause any special environmental hazards due to the produced by-product in the form of pure calcium sulfate (gypsum) in comparison with phosphogypsum obtained by sulfuric acid decomposition. In industrial applications, organic acids have a weakly pronounced corrosive effect.

In conclusion, the identification of new, technologically optimal, cost-effective, environmentally safe opportunities for enrichment of substandard phosphorous raw materials and the implementation of the results in production is an urgent task for researchers.

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### Әлемдегі фосфат шикізатын байыту әдістеріне шолу

Жаһандық экономиканың дамуымен фосфорлы өнімдерді тұтыну нарығы өсуде. Қазіргі кездегі бай фосфориттердің кен орындары сарқылуда. Осыған байланысты кедей фосфориттер мен кондициялық емес фосфат шикізатын өндіріске тарту қажеттілігі туындайды, олар қазіргі уақытта аз зерттелген және қолданусыз жатыр. Жарамдылығы төмен фосфориттерді қайта өңдеу үшін төмен сұрыпты кендерді байытудың және мақсатты компоненттердің құрамын ұлғайту мен қайта өңдеуге жарамдылығын жақсарту мақсатында қоспаларды барынша жоюдың жаңа әдістеріне қажеттілігі туындайды. Мақалада түрлі елдердің фосфорит байыту процестері туралы заманауи мәліметтер берілген. Бұл мәліметтер Қаратау фосфориттерін одан әрі байытуды зерттеу үшін негізге алынатын ақпарат болып табылады. Негізінен екі әдіс — флотация (силикатты фосфаттар үшін қолданылады) және органикалық қышқылдарды пайдалану (карбонатты заттар үшін). Флотациялық байыту және органикалық қышқылдарды қолданудағы карбонатты минералдардың ыдырауы кезінде заттардың бөліну механизмдері сипатталған. Әр



тәсілдің артықшылықтары мен кемшіліктері қарастырылған. Белгілі бір әдісті таңдау фосфориттердің минералогиялық құрылымымен және химиялық құрамымен байланысты екені анықталған.

*Кілт сөздер:* фосфорит, кен орны, химия өнеркәсібі, өндіріс, байыту, флотация, жарамдылығы төмен шикізат, төмен сұрыпты кендер.

Е.Б. Райымбеков, У. Бестереков, П.А. Абдуразова

## Обзор методов обогащения фосфатного сырья в мире

С развитием глобальной экономики возрастает потребительский рынок в фосфорсодержащих продуктах. Все ныне существующие месторождения богатых фосфоритов истощаются. В связи с этим возникает необходимость вовлечь в производство бедные фосфориты и некондиционное фосфатное сырье, которые в данное время мало изучены и не используются. Для переработки некондиционных фосфоритов возникает необходимость в новых методах улучшения и обогащения низкосортных руд и максимально возможного удаления примесей в целях увеличения содержания целевых компонентов и улучшения пригодности к переработке. В статье приведены современные сведения о процессах обогащения фосфоритов разных стран. Эти сведения являются основополагающими для дальнейших исследований обогащения фосфоритов Каратау. Сделан обзор преимущественно двух методов — флотации (применительно для силикатных фосфатов) и использование органических кислот (для карбонатных веществ). Описаны механизмы разделения веществ при флотационном обогащении и разложении карбонатных минералов при применении органических кислот. Рассмотрены преимущества и недостатки каждого способа. Установлено, что выбор определенного метода обуславливается минералогическим строением и химическим составом фосфоритов.

*Ключевые слова:* фосфорит, месторождение, химическая промышленность, производство, обогащение, флотация, некондиционное сырье, низкосортные руды.

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## **Synthesis and investigation of PLGA-based nanoparticles as a modern tool for the drug delivery**

The possibility of immobilization of the «Tamoxifen» antitumor drug in polylactide glycolide nanoparticles was shown in this study. Nanoparticles based on a biodegradable and biocompatible polylactide glycolide polymer were prepared by the simple emulsion method. Various concentrations of the drug substance and stabilizer were studied to obtain nanoparticles with the best physico-chemical parameters (particle size, polydispersity, degree of binding and release, biodegradation). Polyvinyl alcohol was used as a stabilizer in the present work. The sizes of polymer nanoparticles determined by dynamic light scattering vary from 226.7 nm to 397.2 nm with a narrow size distribution (the polydispersity (PDI) values were 0.01–0.2). The degree of «Tamoxifen» binding to the polymer calculated by the UV spectrophotometric method ( $\lambda = 275.5$  nm) was about 82 %, which makes it promising for application in drug delivery. The shape and morphology of nanoparticles were studied with the help of scanning electron microscopy. The kinetics of drug release from polylactide glycolide nanoparticles was studied under conditions simulating a biological medium. The general character of the biodegradation of polylactide glycolide nanoparticles immobilized by «Tamoxifen» was also studied by a viscometric method at different pH values and at 310 K.

*Keywords:* nanoparticles, polymer nanoparticles, polylactide glycolide, tamoxifen, simple emulsion method, immobilization, drug delivery, polymers.

### *Introduction*

At present modern pharmacotherapy is known to have many powerful drugs, but the results of treatment often remain unsatisfactory. One of the factors that reduce the effectiveness of drugs is unfavorable biodistribution, which can be due to difficulties in penetrating the focus of the pathology; which in turn leads to low therapeutic effect. The relevance of this problem served as an incentive for the development of approaches to the creation of various systems of targeted delivery of drugs. Polymer nanoparticles are of particular interest among such systems. These are particles ranging in size from 10 to 1000 nm, combining qualities important for carriers, such as stability and high capacity in relation to a wide range of drug substances.

Treatment of cancer based on nanotechnology has become one of the promising areas of biomedicine that has been widely studied over the past few decades for providing effective and targeted delivery of chemotherapeutic agents which allows to reduce the dose of the drug and minimize non-specific side effects. Nanomedicine in the field of cancer treatment overcomes the shortcomings of traditional drug delivery systems, such as nonspecific biodistribution and targeting, lack of solubility in water, low oral bioavailability and low therapeutic parameters [1–3].

Various drug carriers (e.g., micelles, liposomes, and polymer-drug conjugates) have been developed to enhance tumor targeting, drug delivery and controlled release in the past few decades. In particular, polymer particles are of great interest in targeting a tumor site for application in cancer therapy. Nanoparticles can be attached to small molecules of drugs and serve as drug carriers for delivering molecules to the targeted region in the human body [4].

Polymers based on natural hydroxy acids such as glycolic, lactic, malic acid, etc. capable of degrading in human body into harmless substances, are widely used as drug delivery systems [5]. Micro and nanoparticles based on polyglycolic, polylactic acids, their copolymers and esters are used for targeted delivery of drugs for a wide variety of purposes. It was established that the ratio of lactide and glycolide units in the polymer affected the release of the drug [6]. The release rate of hydrophilic preparations increases with an increase in the content of glycolide units and decreases for lipophilic ones, if the release occurs before the polymer degradation process.

An important feature of polylactides and polyglycolides is biocompatibility with human body tissues which is due to enzymatic degradation of ester bonds based on derivatives of lactic and glycolic acids.

It has been established that polylactides with hydrophobic end groups degraded 2.7 times faster *in vitro* and 4 times faster *in vivo* than polymers with hydrophilic groups [7]. A copolymer based on lactic and glycolic acids [50/50 poly-(*d,l*-lactide-*co*-glycolide) (nominal)] is non-toxic and undergoes biodegradation in the human body with the formation of lactic and glycolic acids, the catabolism of which ends with the formation of carbon dioxide and water [8].

In this regard, the purpose of this work was to study the possibility of binding nanoparticles of poly-(*d,l*-lactide-*co*-glycolide) with the «Tamoxifen» antitumor drug in order to prolong its therapeutic efficacy and reduce undesirable toxic effects.

### *Experimental*

#### *Preparation of poly-(d,l-lactide-co-glycolide) nanoparticles loaded with Tamoxifen drug substance by the simple emulsion method*

The poly-(*d,l*-lactide-*co*-glycolide) copolymer (PLGA) nanoparticles loaded with Tamoxifen drug were prepared by the emulsion method, followed by solvent evaporation according to the following procedure. The calculated amount of polymer was dissolved in an organic solvent, namely chloroform. The drug substance was also dissolved in a mixture of ethyl alcohol and chloroform. The solvent mixture was combined to form a diffusion phase. Then, the diffusion phase was added dropwise to the dispersing phase for ten minutes by emulsification using an Ultra-Turrax T-10 homogenizer (IKA, Germany) with a syringe located directly in the medium. The resulting oil-water emulsion was analyzed for particle size by photon correlation spectroscopy (PCS). Then it was stirred on a magnetic stirrer for several hours at room temperature until all of the organic solvent evaporated, leaving the cured nanocapsules in an aqueous medium.

Newly formed nanoparticles were centrifuged 2 times for 30 minutes at 14100 rpm (miniSpinplus 14500 centrifuge, Eppendorf, Germany) and washed with distilled water to remove all unbound drug.

#### *Determination of particle size and polydispersity*

The average nanoparticle size and their polydispersity were determined by the PCS method on a Malvern Zetasizer Nano S90 instrument (Malvern Instruments Ltd., UK) at 298 K and 90° scattering angle. Each nanoparticles sample was properly diluted immediately after preparation with a non-solvent. The average size and polydispersity were measured three times for each series.

#### *Determination of the binding degree and drug release of Tamoxifen from PLGA nanoparticles.*

The binding of tamoxifen with nanoparticles was determined by the concentration of the drug in the solution of the centrate. An analysis of the solution of the centrate was performed on UV-1800 SHIMADZU using UV spectrophotometry ( $\lambda = 275.5$  nm). The solutions were diluted with water before measurement. An *in vitro* drug release study was carried out in phosphate-buffered saline (pH = 5.4; pH = 7.4) at 310 K for 3 days. Samples were removed from a thermostat and analyzed using UV spectrophotometry.

### *Results and Discussion*

The emulsion method is used for polymers having hydrophobic properties. It is based on the dissolution of the amphiphilic polymer in an organic solvent followed by the addition of water to form the primary emulsion, after which it is homogenized or sonicated to obtain a finely dispersed emulsion. The formation of an emulsion is one of the key aspects of this method, due to the fact that the size of the droplets of the emulsion is directly related to the size of the particles. It is connected with the curing of the particles after evaporation of the organic solvent. Drug loading into nanoparticles of a PLGA copolymer was carried out as described above.

Different concentrations of drugs (5 and 10 mg/ml) and surfactants (0.5 %; 1 % and 2 %) were used to obtain polymer nanoparticles with satisfactory physico-chemical characteristics. As a result of encapsulation of Tamoxifen in PLGA nanoparticles, the obtained emulsion had a white tint without visible delamination. The particles were analyzed for particle size by the PCS method directly after homogenization. The results of the study of physico-chemical parameters of polymer nanoparticles are presented in Table 1.

The experimental results show that an increase in the concentration of the stabilizer leads to a shift in the distribution towards large diameters. This is due to an excess of surfactants. Large particles and agglomerates are formed when encapsulating the drug with a concentration of 5 mg/ml in the polymer matrix in the presence of 1 % and 2 % surfactant. A decrease in the concentration of PVA (0.5 %) and an increase in the concentration

of drugs (10 mg/ml) lead to positive results, namely nanosized particles (200–300 nm) were formed. The PDI polydispersity index for all particles stabilized by PVA did not exceed 0.2.

Table 1

**Physico-chemical characteristics of PLGA nanoparticles immobilized by «Tamoxifen»**

PVA, %	DS, mg/ml	Average particle size, d, nm	NPs Polydispersity (PDI)	Degree of binding, %	NPs yield, %	Degree of release, %	
						pH = 5.4	pH = 7.4
0.5	10	226.7	0.215	69.0	52	25.3	34.1
		225.4	0.189				
		226.2	0.206				
		226.1±0.66	0.203±0.013				
1	5	485.2	0.054	82.6	73	–	90.4
		486.3	0.125				
		483.8	0.153				
		485.1±1.25	0.111±0.051				
	10	397.2	0.011	62.0	68	21.4	30.2
		396.5	0.121				
	395.8	0.136					
	396.5±0.70	0.089±0.068					
2	5	779.2	0.244	78.0	61	-	38.0
		778.3	0.298				
		780.1	0.321				
		779.2±0.90	0.288±0.040				

Figure 1 shows the distribution curves of PLGA nanoparticles over diameters obtained by dynamic light scattering. It can be seen from the above figures that PLGA nanoparticles have satisfactory physico-chemical characteristics. The average particle size when using a PVA concentration of 0.5 % is 226.1±0.66 nm, for a PVA concentration of 1 % is 396.5±0.70 nm, the polydispersity value is 0.215 and 0.011, respectively.

A monomodal particle size distribution was observed in both cases. The uniformity of sizes is an important problem in the preparation of nanoparticles, since the size affects the chemical and biological properties of the nanoparticles. The formation of particles less than 300 nm in size is preferable due to a more favorable pharmacological profile, prolonged kinetics in the circulatory system, and delayed release at the sites of action [9, 10].

Given the effectiveness of encapsulation of tamoxifen in nanoparticles (NPs), their size and polydispersity, PVA concentrations of 0.5 % and 1 % were selected for *in vitro* analysis of drug release and drug characteristics.

The determination of the degree of drug binding to polymer nanoparticles is an important indicator characterizing the quantitative volume of drug immobilization in polymer nanoparticles. The degree of binding of PLGA and tamoxifen nanoparticles was determined spectrophotometrically and calculated by the formula 1:

$$\text{Degree of binding} = (\text{mass of drug substance in nanoparticles}) / (\text{total mass of drug}) \times 100 \%. \quad (1)$$

The results presented above in Table 1 indicate a significant effect of the concentration of PVA on the most important characteristics of the system. The greatest values of encapsulation efficiency which were equal to 82.6 % and 78.0 % were observed at 1 % and 2 % concentrations of PVA respectively. But, despite the high degree of binding and release, these PVA concentrations were not considered, since the average particle size does not meet the requirements allowed for nanoparticles. Therefore, polymer NPs with the concentration of PVA equal to 0.5 % and 10 mg of the drug were selected as the most effective one. Moreover, the degree of binding was 69 % for a 0.5 % PVA concentration and the degree of binding was 62 % for a 1 % PVA concentration.

The PCS method allows one to establish the distribution of NPs by their hydrodynamic diameters in an aqueous suspension, while all particles are considered spherical. The method does not provide information on the shape of the particles. It is necessary to use a set of experimental methods for a more complete characterization of low frequencies.

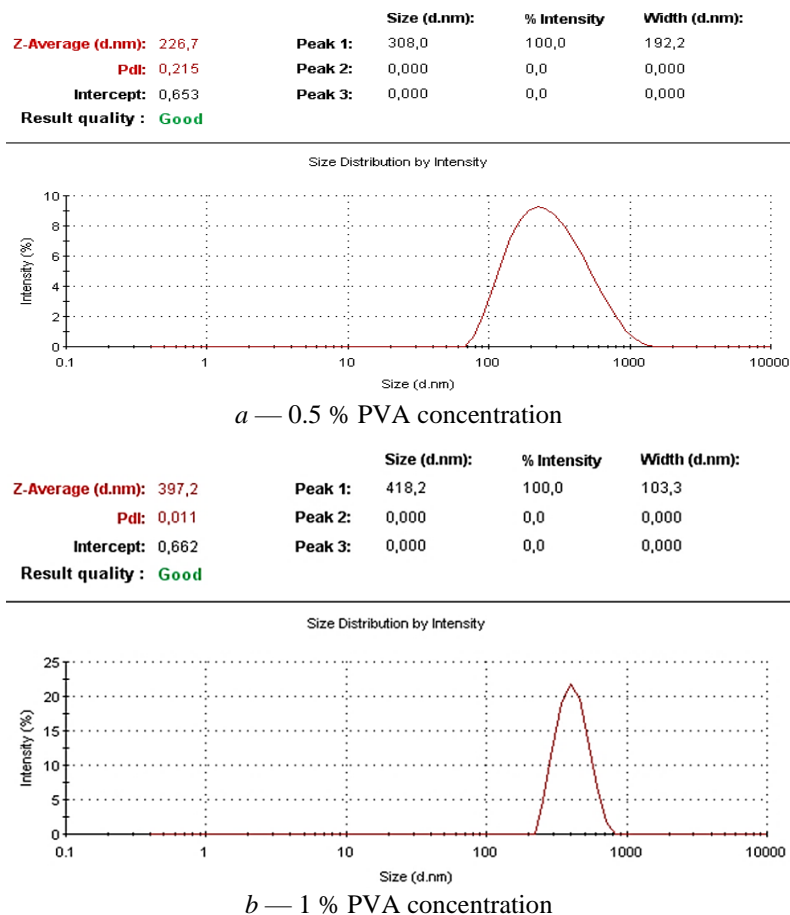


Figure 1. Particle size distribution of PLGA NPs immobilized by Tamoxifen stabilized with PVA

For this purpose a number of nanoparticles samples were additionally investigated by scanning electron microscopy. Morphological analysis of the samples was carried out with the help of a scanning electron microscope MIRA 3 LM TESCAN (Czech Republic) in the Laboratory of Electron Microscopy in collaboration with the staff of the Physico-Technical Faculty of the E.A. Buketov Karaganda State University. Electron-microscopic images were taken to confirm the data obtained by the PCS method, which are presented in Figure 2(*a*) and (*b*). Microphotographs of nanoparticles samples show both single particles and their agglomerates. Systems mainly consist of particles of the same size in the range of 200–400 nm, however, larger particles (larger than 500 nm) are also present in the system. We assume that they are formed in the process of aggregation of NPs upon evaporation of an organic solvent.

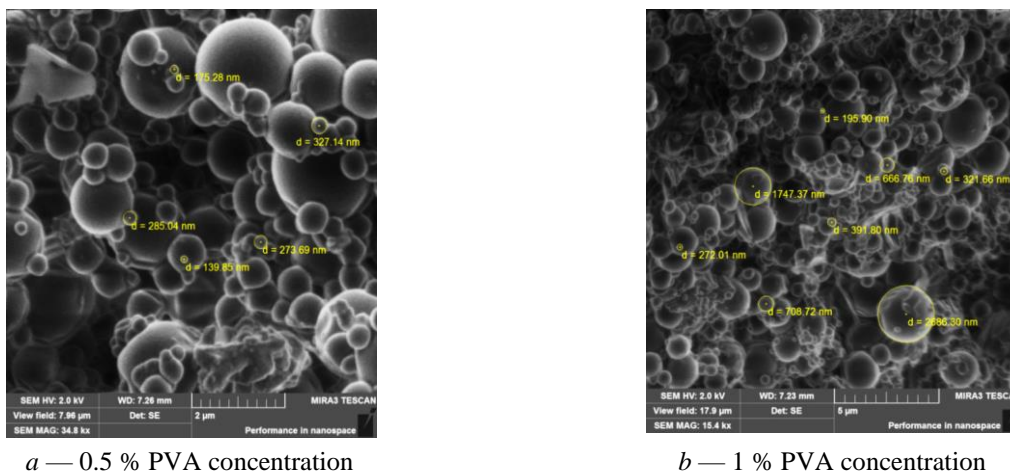


Figure 2. Microphotographs of PLGA-based NPs samples stabilized by PVA

Decomposition of polymer-immobilized complexes in a biological environment is an important condition for their use. This is a prerequisite for the release of the drug from the polymer matrix as a result of the decomposition of polymer nanoparticles. In general, the mechanism of drug release from polymer nanoparticles may vary depending on the nature of the polymer. Decomposition of polymers can occur as a result of chemical destruction of the chain and mechanical destruction of polymer nanoparticles.

In this work, the destructive nature of PLGA nanoparticles was carried out by the viscometric method at 310 K temperature and various pH values (5.4 and 7.4). The results of the study of PLGA nanoparticles are presented in Figure 3.

The destruction of polymers occurs faster *in vivo* than *in vitro*, which is associated with biological effects, as well as with the formation of an immune response. Chemical bonds in the macromolecules are broke down in the process of destruction, and the degree of polymerization and the molecular weight of the polymer are reduced. As can be seen from the figures, the destruction of polymer nanoparticles occurs very slowly depending on time. As a result of the destruction of polylactide glycolide the glycolic and lactic acids are formed [5]. It is seen that the viscosity of the medium decreases depending on the pH of the medium as a result of the destruction of polylactide glycolide. And in the second system, that is, in a system with 1 % PVA concentration (Fig. 3b), the destruction occurs very slowly, which is explained by a higher concentration of PVA and a larger particle size compared to the first concentration.

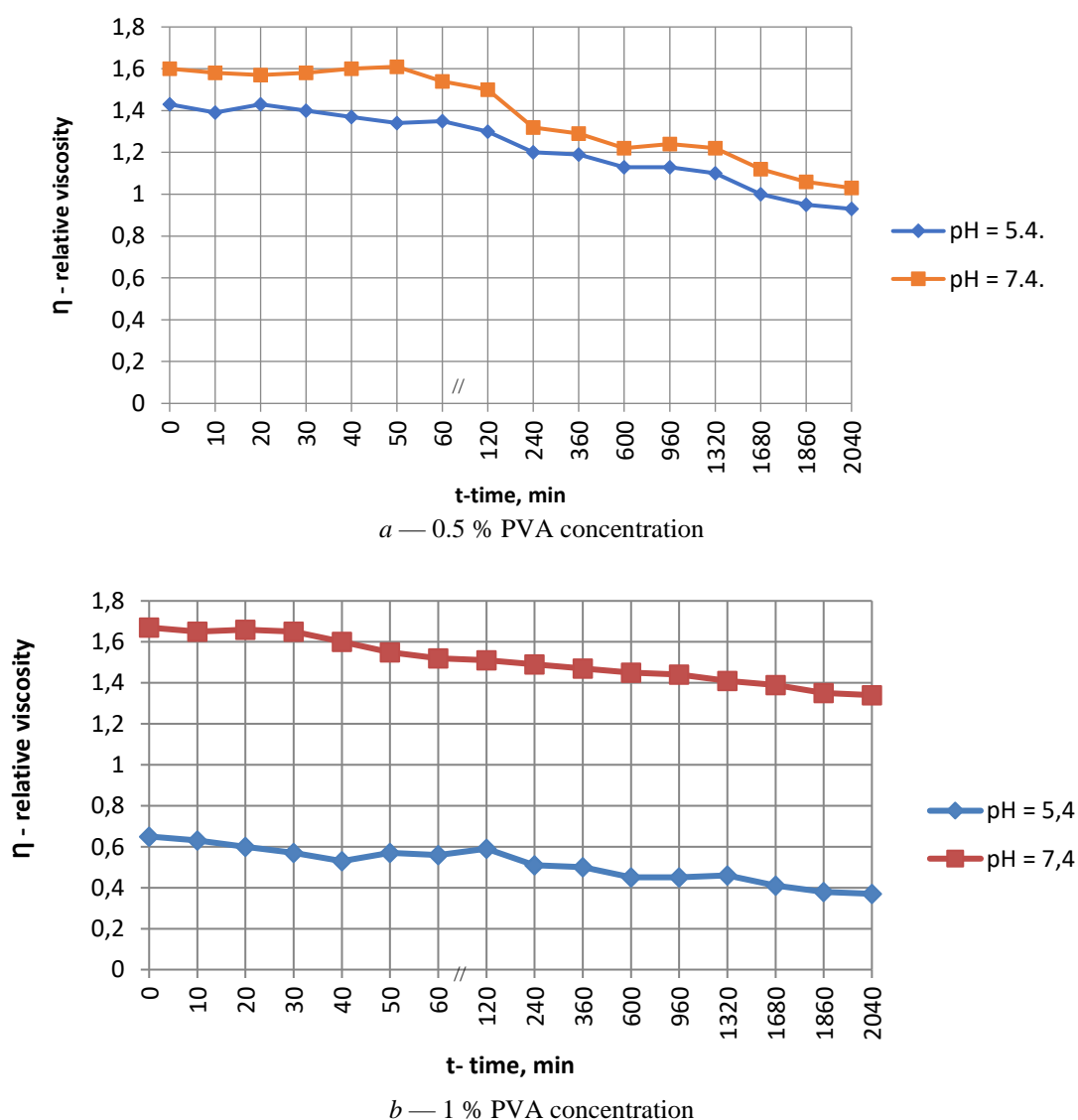


Figure 3. Viscometric study of the destruction of PLGA nanoparticles stabilized with PVA

After studying the destruction by UV spectrophotometry, we analyzed the release profiles of tamoxifen from polymer nanoparticles for two samples, over 3 days, under conditions simulating a biological state, i.e., in a phosphate-buffered solution (pH = 5.4; pH = 7.4) at 310 K temperature. The results are presented in Figure 4 (a) and (b).

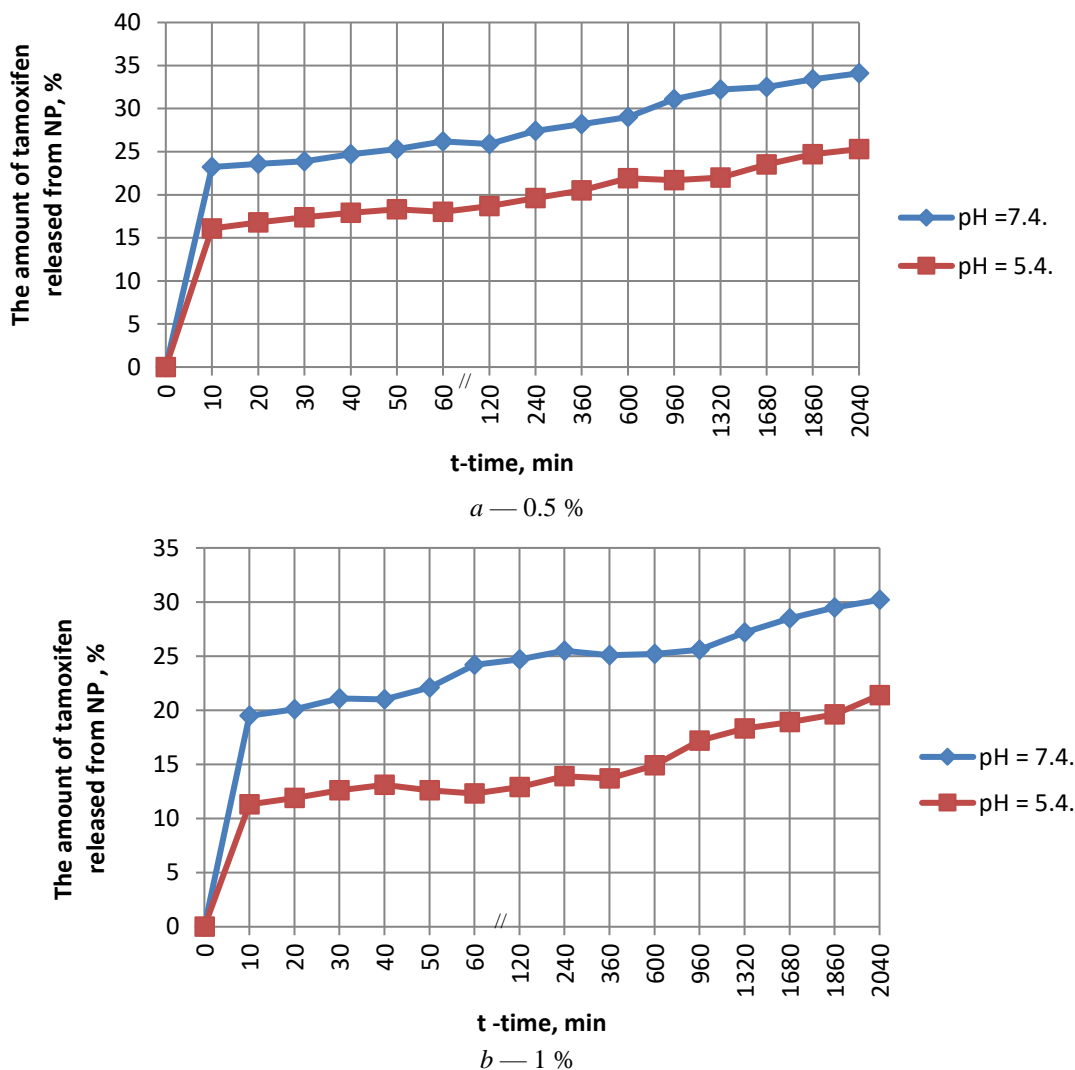


Figure 4. Dependence of the amount of Tamoxifen released from the PLGA NPs matrix obtained in the presence of PVA

It is seen from the presented data that approximately 20–30 % of the drug was released within 72 hours from PLGA. In this case, the kinetics of drug release in the medium pH = 7.4 is higher than at pH = 5.4. A similar dependence was observed when studying the destruction of polymers. Studies have shown that drug release became much slower after 74 hours for all samples. An emergency release of the drug of about 10–20 % was observed for 10 minutes at the initial stage. Subsequently, the total yield of the drug reached 20–30 % within 3 days.

### Conclusions

Thus, PLGA nanoparticles immobilized by the anti-tumor drug «Tamoxifen» were obtained by the simple emulsion method. The nanoparticles synthesized have satisfactory physico-chemical characteristics, which makes them promising systems for drug delivery. The binding degree of polylactide-co-glycolide with anti-tumor drug «Tamoxifen» was 60–80 %. Kinetics of release of the drug has prolonged profile which gave opportunity to work out less toxic forms of «Tamoxifen» with longer period of action.

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### Дәрілік заттарды тасымалдаудың заманауи құрал ретінде PLGA негізіндегі нанобөлшектерді синтездеу және зерттеу

Мақалада қатерлісікке қарсы «Тамоксифен» препаратын полилактидгликолид негізіндегі нанобөлшектерге иммобилизациялау мүмкіндігі көрсетілген. Биобдырамалы және биоүйлесімді полимер негізіндегі нанобөлшектер эмульсия әдісімен алынған. Жақсартылған физико-химиялық көрсеткіштермен (бөлшектердің өлшемі, полидисперстілігі, байланысу және босап шығу дәрежесі, биодegradациясы) нанобөлшектерді алу үшін дәрілік заттың және тұрақтандырғыштың әртүрлі концентрациялары қолданылған. Аталған жұмыста тұрақтандырғыш ретінде поливинил спирті пайдаланылған. Динамикалық жарық шашу әдісімен алынған полимерлі нанобөлшектердің өлшемдері 226,7–397,2 нм аралығында және өлшем бойынша таралуы тар (полидисперстілік мәнделері (PDI) 0,01–0,2) болды. УК-спектрофотометрлік әдіспен ( $\lambda = 275,5$  нм) анықталған тамоксифеннің полимермен байланысу дәрежесі шамамен 82 % құрады және ол оның дәрілік заттардың тасымалдаушылары ретінде қолдануда болашағы зор екендігі көрсетілген. Электронды микроскопия әдісімен нанобөлшектердің формасы мен морфологиясы және биологиялық органы модельдейтін жағдайда полилактидгликолид нанобөлшектерінен дәрілік заттың босап шығу кинетикасы зерттелген. Сонымен қатар, әртүрлі рН мәнделерінде 310 К температурада тамоксифенмен иммобилизацияланған полилактидгликолид нанобөлшектерінің биодegradациясының жалпы сипаттамалары вискозиметрлік әдіспен анықталған.

*Кілт сөздер:* нанобөлшектер, полимерлі нанобөлшектер, полилактидгликолид, тамоксифен, эмульсия әдісі, иммобилизация, дәріні тасымалдау, полимерлер.

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### Синтез и исследование наночастиц на основе PLGA как современного инструмента транспорта лекарств

В статье показана возможность иммобилизации противоопухолевого препарата «Тамоксифен» в наночастицы полилактидгликолида. Наночастицы на основе биодegradируемого и биосовместимого полимера полилактидгликолида были получены методом простой эмульсии. Для получения наночастиц с наилучшими физико-химическими показателями (размера частиц, полидисперсности, степени связывания и высвобождения, биодegradации) были исследованы различные концентрации лекарственного



вещества и стабилизатора. В настоящей работе в качестве стабилизатора использован поливиниловый спирт. Размеры полимерных наночастиц, полученных методом динамического светорассеяния, варьируются от 226,7 нм до 397,2 нм, с узким распределением частиц по размерам (значения полидисперсности (PDI) составили 0,01–0,2). Степень связывания тамоксифена с полимером, рассчитанная УФ-спектрофотометрическим методом ( $\lambda=275,5$  нм), составила около 82 %, что делает его перспективным при использовании для доставки лекарств. Методом сканирующей электронной микроскопии изучены форма и морфология наночастиц. Исследована кинетика высвобождения препарата из наночастиц полилактидгликолида в условиях, моделирующих биологическую среду. Кроме того, вискозиметрическим методом исследован общий характер биodeградации наночастиц полилактидгликолида, иммобилизованных тамоксифеном в разных значениях pH среды при температурах 310 К.

*Ключевые слова:* наночастицы, полимерные наночастицы, полилактидгликолид, тамоксифен, метод простой эмульсии, иммобилизация, доставка лекарств, полимеры.

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# ХИМИЯНЫ ОҚЫТУ ӘДІСТЕМЕСІ МЕТОДИКА ОБУЧЕНИЯ ХИМИИ METHODS OF TEACHING CHEMISTRY

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## **Presenting lecture materials in English using CLIL technologies**

The article shows the integration of all four Content and Language Integrated Learning elements (content, communication, cognition, and culture) into the «Chemistry of Elements of the Periodic Table» course. Second year students of «5B011200 — Chemistry» major, Institute of Natural Sciences and Geography of Kazakh National Pedagogical University named after Abai listened to lectures of the subject in English using CLIL technology. The course of modelling a lecture using CLIL and results of the evaluation survey are presented. The survey questions were aimed at researching of students' motivation to study the course using CLIL technologies. Also, students' satisfaction with the learning process and the relevance of the course were assessed. The results of the test, which were carried out after the lecture are presented to consolidate the learned material. The results show students' enthusiasm for the learning process and enrichment of their vocabulary with chemistry terms. The article will be of interest of chemistry teachers in higher and secondary educational institutions.

*Keywords:* teaching methods, inorganic chemistry, CLIL technology, lecture, questionnaires, test control, language skills, integration.

### *Introduction*

The practice experience of recent decades shows that the welfare of a country is determined by the availability of competent human resources. Such resources are formed by improving the level of knowledge obtained in higher education institutions. Thus, teacher's task is to find new effective technologies, forms and methods of education, which allow to give students relevant knowledge.

In terms of multilingual education in Kazakhstan teaching basic subjects in English is an actual problem. Since English is a foreign language, there is a problem of presenting materials at an affordable level for students.

Dr. Vinke A. has identified both positive and some negative aspects of the transition to English in the training of engineering students in Dutch universities. As an example, the workload and strain of teachers and students have increased, thus quality of training of engineers as professionals has worsened. Moreover, the quality of training has become highly dependent on the level of teacher's English language skills, so students' performance has slightly decreased. Studies at Korean and Japanese universities during the first decade of the 21st century have generally confirmed these findings [1, 2]. However, considering mentioned disadvantages of teaching students in a foreign language, in terms of the current needs of the country, the demand for specialist who are fluent in English and knows professional terminology is increasing. Considering the world's pedagogical experience, CLIL shows good results in solving this problem. Twenty years ago, the European Union countries recognized CLIL as one of the effective technologies for the development of multilingualism and have successfully applied it in both school and higher education [3]. Bilingual program like CLIL were launched in the Murcia region of Spain in 2009, and since then it has established thorough the country as one

of the best teaching technologies [4,5]. Coyle, Hood, and March [6] defined CLIL as a dual educational approach in which an additional language is used to learn and teach both content and language.

CLIL combines four elements, which authors [6,7] called '4C' — content, communication, cognition, and culture. Within the course «Chemistry of elements of the periodic system» these elements are described and presented as follows (Table 1).

Table 1

**CLIL elements and their description within the course**

CONTENT	COGNITION	CULTURE	COMMUNICATION
Includes the basic concepts – electron configuration; – change of properties of elements according to their group; – general descriptions of groups and subgroups; – structural features of atoms of d- and f-elements	Involves thinking skills: – identification and classification of elements. – data collection for lab report	Includes the student's communication and civic position: – group work; – lab safety; – work presentation.	Includes improving the language skills of both teachers and students.

All these components are in constant communication with each other.

Considering all the advantages and disadvantages of CLIL, the decision to apply this technology in elemental chemistry teaching was based on the fact that CLIL allows students to communicate more effectively with each other using a foreign language, develop communication skills, thinking and creativity. Thus, the main tool for preparing students is a lecture, but such types of work as a laboratory workshop, independent work of students and consultations with the instructor are not excluded. In turn, with this knowledge, skills and abilities, students can use them in the study of subsequent topics, practice and self-study.

The goal of our pedagogical experiment is to activate students' cognitive creative activity and develop their cognitive interest through CLIL training, involving students in independent practical activities. And also, to interest students in the learning process by adapting the educational material to different levels of English language proficiency, conducting questionnaires and testing.

#### *Experiment*

Pedagogical experiment was conducted in the English group of the 2<sup>nd</sup> year students of Chemistry Department, Institute of Natural Sciences and Geography of the Kazakh National Pedagogical University named after Abai. Second year students of the specialty «5B011200 — Chemistry», listened to lectures of the discipline «Chemistry of Elements of the Periodic Table» in the first semester of 2019–2020 academic year in English using CLIL technologies.

According to the educational and methodical complex of the discipline the main task of the subject includes the integration of content (C) and language (L):

1. To know and formulate all basic stoichiometric laws of chemistry. Be able to apply these laws to solving computational problems; (C)
2. To be able to record the electronic configuration of any element on the basis of its position in the periodic system; theoretically describe changes in the properties of elements in the period, as well as in rows s, p, d, f-elements (common properties and differences); (C)
3. To be able to give in English a general description of the group, subgroup, basic chemical properties of the element and its compounds based on the electronic structure of the element's atom; (L)
4. To know the chemistry of elements of the main subgroups; (C)
5. To know the structural features of atoms of d- and f-elements, physicochemical properties of simple substances and features of chemical properties of their compounds. (C)
6. To be able to write laboratory report in English using a specific vocabulary; (L)
7. To present a report on laboratory work to a group of students in English. (L)

*Presentation of lecture materials.* As an example of CLIL implementation, let's consider lecture No. 10 «Elements of subgroup II-B. Scandium, yttrium, thallium. Obtaining, properties, compounds». The lecture was delivered using Hard CLIL, where teaching and learning is focused mainly on the content of the subject and therefore oriented to the content [5]. Since the requirements for the content of the lecture have changed over time, in addition to the fact that the lecture should have a systematic, consistent, and accessible presentation

of the teaching material, it is necessary to visualize it; special attention was paid to the preparation of visual and schematic teaching material using MS Power Point.

Considering the fact that students' English skills vary for certain reasons, the following measures have been taken to avoid difficulties in understanding:

- a glossary of chemical terms has been compiled and integrated into the lecture (Table 2).
- the material has been adapted to different levels.

A glossary of chemical terms was integrated into the lecture in English and Russian, for better understanding of the term.

Table 2

### Chemistry Terms Glossary

Leach	When a chemical substance leaches or is leached from a material, especially soil, it is removed by the action of water passing through the material.
сущ. выщелачиватель гл. выщелачивать	Перевод в раствор (обычно водный) одного или нескольких компонентов твёрдого вещества.

In the introductory part of the lecture the topic and questions were indicated (Fig. 1).

The questions of the lecture, presented in Figure 1, were discussed in the lesson, using various methods, which in our opinion contributed to better learning and memorization of the material. The main attention during the lecture was to the characteristic properties of the elements, which help to distinguish them from each other. A table of physical and chemical properties of the elements was created to visually compare their characteristics (Fig. 2).

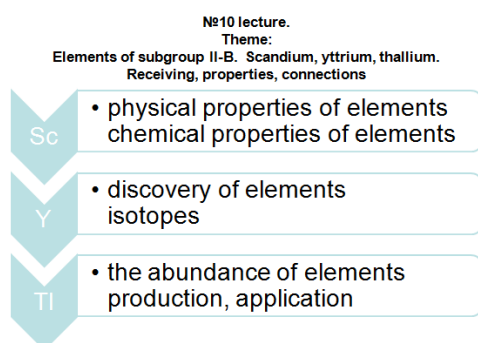


Figure 1. Introduction to the lecture

	Sc	Y	Tl
<b>Classification:</b>	Scandium is a transition metal and rare earth (due to similar chemical properties and existence in the same ores)	Yttrium is a transition metal & rare earth	Thallium is a post-transition
<b>Color:</b>	silvery-white	silvery-white	silvery-gray
<b>Atomic weight:</b>	44.9559	88.9059	204.383
<b>State:</b>	solid	solid	solid
<b>Melting point:</b>	1540 °C, 1813.2 K	1525 °C, 1798 K	304 °C, 577 K
<b>Boiling point:</b>	2830 °C, 3103 K	3340 °C, 3613 K	1473 °C, 1746 K
<b>Electrons:</b>	21	39	81
<b>Protons:</b>	21	39	81
<b>Neutrons in most abundant isotope:</b>	24	50	124
<b>Electron shells:</b>	2,8,9,2	2,8,18,9,2	2,8,18,32,18,3
<b>Electron configuration:</b>	[Ar] 3d1 4s2	[Kr] 4d1 5s2	[Xe] 4f14 5d10 6s2 6p1
<b>Density 20°C:</b>	3.0 g/cm <sup>3</sup>	4.47 g/cm <sup>3</sup>	11.85 g/cm <sup>3</sup>

Figure 2. Comparison table of physical and chemical properties of elements

Visual presentation of the lecture helps to increase the mastery of the teaching material in a foreign language, so the slides show photos of discoverers, minerals, schemes of extracting materials from ores, application, etc. (Fig. 3)

Gadolin isolated the yttrium within the mineral, which was later named gadolinite in his honor. Yttrium was named for Ytterby.



Johan Gadolin

The radioactive isotope yttrium-90 is used in radiation therapy to treat liver cancer and some other cancers.

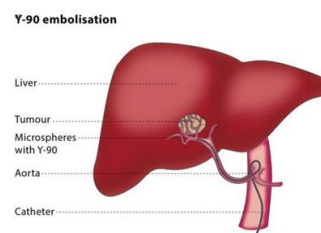


Figure 3. Examples of visual follow-up of the lecture

When developing the teaching material, the lectures used information from scientific articles, monographs, visual materials and other. Besides the description of the main physical and chemical characteristics, the lecture contained general information about the stages of production of the elements, their cost to date the (Fig. 4).

According to **Mineral commodity summaries**, global supply and consumption of scandium are estimated at 10-15 tons per year. In 2019, the price of scandium oxide ( $\text{Sc}_2\text{O}_3$ ) with a purity of 99.99% amounted to \$ 5,000 per kg, and for metal - \$ 206 per gram

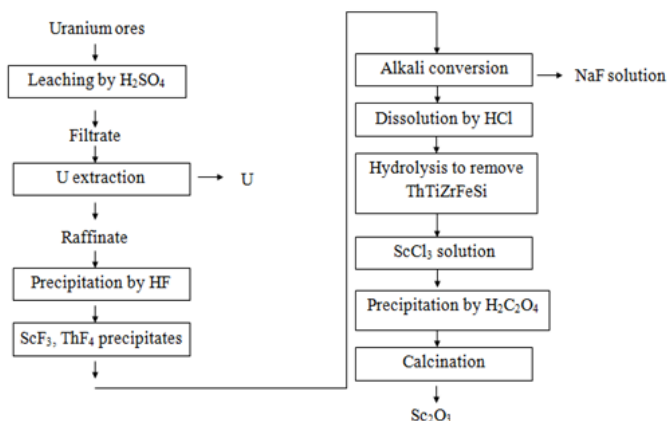


Figure 4. Scheme of scandium extraction from uranium ores

In order to consolidate the information of the slides, the students were presented with a summary slide with key data of the learned materials (Fig. 5).

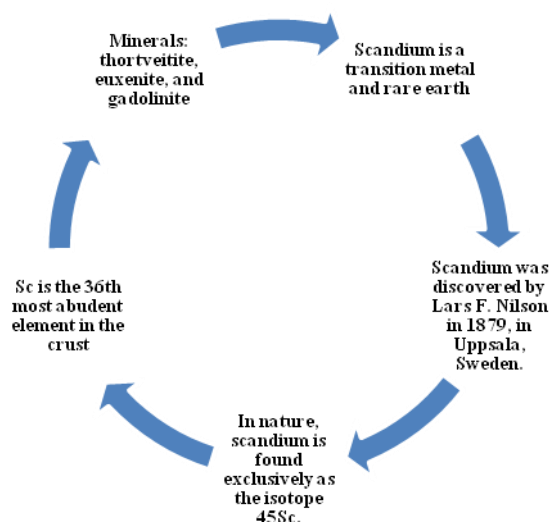


Figure 5. Review slide with key data

According to the results of the lecture, all the set tasks were achieved, and the goals of developing the skills of communicative, informational and subject competencies as well. The students have acquired knowledge of «Elements of subgroup II-B: Scandium, yttrium, thallium. Obtaining, properties, compounds», learned a lot of new terms in English, and worked in groups using play methods of learning.

*Conducting a survey.* A three-stage questionnaire was conducted to assess learning outcomes. The first stage was organized at the beginning of the lesson, and the topics of the questions asked were aimed at researching the motivation of students to study the course, assessing their satisfaction with the learning process and the overall assessment of the importance of the course for the professional skills development. The survey was attended by 22 students. Results of the survey are given below.

1. Do you think your English is good enough to study this course?
2. How important is a course in elemental chemistry in English to your professional activity?
3. Have you previously dealt with CLIL training technology?
4. Do you know what does CLIL and its basic principles mean?

The second stage took place in the middle of the course. Questions explored satisfaction with the learning process.

5. Are you satisfied with your teacher's English level?
6. Did you face difficulties in understanding new material?

The third phase of the survey was conducted to evaluate the course.

7. How satisfied are you with the implementation of CLIL techniques in this course?
8. Do you think your listening skills in English have improved?

*Test control.* After the lecture, students were offered a test control to assess the level of learning material. Since the discipline is taught in a foreign language, it is much more difficult to assess the knowledge and skills of students, it is necessary to assess the knowledge of subject terminology in English and the educational thematic material. For this reason, tests were compiled in which students were asked to summarize their answers within 15 minutes. Examples of the test assignments are given below.

#### Control questions

1. Describe the chemical element (3 points).

Yttrium is \_\_\_\_\_

Scandium is \_\_\_\_\_

Thallium is \_\_\_\_\_

2. Match the electronic configurations of elements (3 points).

Scandium [Kr] 4d1 5s2

Thallium [Xe] 4f14 5d10 6s2 6p1

Yttrium [Ar] 3d1 4s2

3. Match when and by whom the elements were discovered (3 points).

Thallium Lars F. Nilson in 1879, Sweden

Scandium Carl Axel Arrhenius in 1787, Sweden

Yttrium Sir William Crookes in 1861, London.

4. Write compound name, the formula, the description and application of the studied material in the table (9 points).

№	Name of compound	Formula	Description	Application
1	Scandium fluoride	ScF <sub>3</sub>	White powder	For the production of optical glass, catalyst, electroceramics, lasers

5. Write about the toxic properties of thallium, and about precautions when working with it (2 points)

#### Results and discussions

By analyzing the answers shown in Table 3, it can be concluded that not all students were ready to study the teaching material in a foreign language, but most students understood the importance of studying the course of chemistry of elements in English. Students are not familiar with CLIL technology and its principles. The teacher's English level satisfied 70 % of the students. And most students had no difficulty understanding the material in English. Overall, according to the results of the survey the trends are positive.

It took 15 minutes to pass the test control. Figure 5 shows the results of the test on «Elements of subgroup II-B. Scandium, yttrium, thallium. Obtaining, properties, compounds». On average, 14 out of 20 points were scored.

## Survey results

Answers and questions	Graphical representation
<p>1. Do you think your English is good enough to study this course?</p> <p>Yes — 27.2 % No — 9.2 % Not sure — 63.6 %</p>	
<p>2. How important do you think a course in elemental chemistry in English is to your professional activity?</p> <p>The knowledge gained during the course is very important for future activities — 72.7 % I think the impact of English on chemistry is slightly overrated — 18.1 % Hard to answer — 9.2 %</p>	
<p>3. Have you previously dealt with CLIL training technology?</p> <p>Yes, I have — 0 % No — 100 %</p>	
<p>4. Do you know what does CLIL and its basic principles mean?</p> <p>Yes — 0 % No — 100 %</p>	
<p>5. Are you satisfied with your teacher's English level?</p> <p>Yes, I'm satisfied — 77.2 % No, I'm not — 22.8 %</p>	
<p>6. Did you face difficulties in understanding new material?</p> <p>Yes — 31.8 % No, the materials were easy to understand — 45.5 % Not sure — 22.7 %</p>	
<p>7. How satisfied are you with the application of CLIL techniques during this course?</p> <p>Excellent — 0 % Good — 63.6 % Satisfactory — 31.8 % Unsatisfactory — 0 % Very bad — 4.6 %</p>	
<p>8. Do you think your listening skills in English have improved?</p> <p>Yes — 72.7 % I don't see much change — 22.7 % No — 4.6 %</p>	

## Conclusions

According to the results of the pedagogical experiment, 63.6 % of students said that training using CLIL technology is effective. Also, 45.5 % of students understood the material in English well, and 72.7 % of students showed an improvement of their listening skills.

Therefore, it can be noted that students can show positive results in learning through integration with the language of instruction. Implementation of the subject-language teaching method helps students to form a whole view of the properties of the elements and the relationship between them. Subject-language integration

performs a number of functions in teaching and their planning helps the teacher to successfully implement all these functions, consider all types of independent work of students.

The use of CLIL technology is not a new practice. In our opinion, the use of CLIL technology allowed us to get specific data that tells us about the students' enthusiasm for the learning process, enriching their vocabulary and chemical terms.

In our opinion, the data obtained show that students are interested in the learning process and enrich their vocabulary with chemical terminology in a foreign language, which in turn sets us the task of further optimization of teaching materials using CLIL technology.

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## CLIL технологиясын қолдану арқылы ағылшын тіліндегі дәріс материалын ұсыну

Мақалада «Chemistry of Elements of the Periodic Table» пәнінің шеңберінде CLIL технологиясының төрт элементінің байланысы, пән аясында мазмұн мен тілдің интегралдануы көрсетілген. CLIL қолдану арқылы дәрісті құру барысы, сондай-ақ бағалау сауалнамасының нәтижелері ұсынылған. Қойылған сұрақтардың тақырыбы студенттердің курсты оқу мотивациясын зерттеуге, оқыту үрдісімен қанағаттанушылықты бағалауға және кәсіби дағдыларды қалыптастыру үдерісі үшін курстың маңыздылығын жалпы бағалауға бағытталған. Өткен материалды бекіту үшін тыңдалған дәрістен кейін тест ұсынылған. Тест нәтижелері студенттердің оқу үрдісімен, олардың сөздік қорын химиялық терминдермен байыта білгенін көрсетті. Мақала химияны ағылшын тілінде оқытатын орта және жоғары оқу орындарының оқытушыларына пайдалы. Әлемдік тәжірибеге сүйене отырып, CLIL технологиясын дәрісте қолдану арқылы бұл мәселелерді шешуге мүмкіндік береді. Абай атындағы Қазақ ұлттық педагогикалық университетінің жаратылыстану және география институтының «5B011200 — Chemistry» мамандығының екінші курс студенттері «Chemistry of Elements of the Periodic Table» пәнін ағылшын тілінде CLIL қолдануымен дәрістер алды.

*Кілт сөздер:* оқыту әдістемесі, бейорганикалық химия, CLIL, дәріс, сауалнама, тестілік бақылау, тілдік дағдылық, кіріктіру.

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## Представление лекционного материала на английском языке с использованием технологии CLIL

В статье показана связь четырех элементов CLIL и интегрирование содержания и языка в рамках дисциплины «Chemistry of Elements of the Periodic Table». Студенты второго курса специальности 5B011200 — «Химия» Института естествознания и географии при Казахском национальном педагогическом университете им. Абая прослушали лекции дисциплины «Chemistry of Elements of the Periodic Table» на английском языке с применением технологии CLIL. Представлен ход построения лекции с использованием CLIL, а также результаты оценочного анкетирования. Тематика задаваемых вопросов



была нацелена на исследование мотивации студентов, изучение курса, оценку удовлетворенностью процессом обучения и общую оценку значимости курса для процесса формирования профессиональных навыков. Представлены результаты теста, выполненного после прослушанной лекции, для закрепления пройденного материала. Результаты теста показали увлеченность студентов процессом обучения, обогащение их словарного запаса химическими терминами. Статья будет интересна преподавателям химии высших и средних учебных заведений, обучающим на английском языке.

*Ключевые слова:* методика преподавания, неорганическая химия, CLIL технология, лекция, анкетирование, тестовый контроль, языковые навыки, интегрирование.

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## **Features of teaching Chemistry in English: continuity of traditional and new technologies**

The article describes the study results of the continuity of traditional and new technologies in teaching chemistry in English in secondary schools. In the study, alongside a variety of traditional methods, the CLIL method, Content and Language Integrated Learning was explored to enhance pupils' interest in chemistry and to improve their knowledge. Special attention was drawn to the learners' motivation, knowledge level and English language proficiency during the study of chemistry. The ways to apply new approaches towards teaching chemistry in English were considered and the practice of integrating chemistry and English on the basis of a new curriculum was studied. Terminology, glossary, English language-based text work and calculation methodology were selected for the classroom use of CLIL technology. At chemistry lesson pupils were surveyed and a pedagogical observation was performed to determine the effectiveness of using CLIL technology. According to the survey results the effectiveness of teaching chemistry in English was proven. Working on terminology and glossary the learners' interest in the subject was increased by using chemistry terminology in the classroom. The use of CLIL approach is based on integrating language in teaching the subject content allowed the pupils not only to gain information about the subject but also to master the language.

*Keywords:* CLIL method, teaching chemistry in English, Content and Language Integrated Learning, glossary, terminology, English language based text, CLIL technology, a survey, traditional method.

### *Introduction*

Nowadays the development of the future generation as an intellectual person and multilingual education is an actual issue in the education system. The educational activity results of the implementation of the interdisciplinary connections are manifested in the expansion of pupils' knowledge of universal character, the substantive content aspect enrichment of foreign language communication, their learning motivation increase, individual development, self-education, and self-improvement.

The education system is improving and opening new horizons in accordance with modern requirements. Consequently, this is a renewal of secondary education content. This requires the development and implementation of an education program allowing the gradual transition to a competency-based teaching model and the application of non-traditional methods and forms of teaching organization, as well as the integrated teaching of various disciplines. First and foremost, the consideration of interdisciplinary connections development in the integrated teaching classroom is of paramount importance. Teaching language and subject content in an interdisciplinary connection creates many opportunities for the development of cognitive tasks, suggestions and the realization of learners' creative potential [1].

In the context of teaching natural science disciplines, English is regarded as the most important language in Kazakhstan since it forms the basis of the integrated teaching. The introduction of English into the integrated teaching process is primarily focused on learners' academic development during lessons and opportunities to strengthen teaching taking into consideration their psychological conditions.

Several recent studies have considered the importance of investigation of integrated English teaching. In their studies, G.I. Belyaeva, E.A. Samrodova, O.V. Voron, and E.S. Zakirova have described the integrated teaching methods of foreign languages for special purposes and analyzed their effectiveness. According to the study result, in the opinion of the humanitarian specialty students, discussions, ICT (information and communication technology) and SCRUM (framework that helps groups to work together and encourages team to learn through on a problem) were found to be the most effective methods of teaching foreign languages for special purposes, while debates, ICT and round table discussions were estimated as the best ones in conformity with the opinions of the teachers interviewed. According to the students' opinion, the «dilemma» method was determined to be inefficient, while the CLIL (Content and Language Integrated Learning) method was found to be the most ineffective one by teachers [2]. This means that the CLIL methodology has not been fully investigated

and needs to be improved. The results of the scientific literature analysis show that in modern educational practice the most widely applied methods integrating English with traditional methods are project method [3,4], case study [5, 6], brainstorming [7, 8], role method [9], round table [10], audio-linguistic method [11], content and language of integrated learning (CLIL method) [12, 13].

Researchers have shown that the CLIL method provides a number of benefits to students, and its success depends on the context in which the method is applied. In secondary schools, the research results were proved to be effective, the CLIL method was found to have no negative effect on pupils' English language proficiency, L1 level, and subject knowledge; this, in turn, encourages pupils to become more active in the learning process. The global need for language teaching, especially English, has given rise to the necessity of new approaches towards language teaching. The CLIL method is a flexible and efficient way of responding to the needs [14]. Teaching a subject content integrating with English has aroused great interest in Kazakhstan, as the CLIL method is expected to improve students' fluency in the English language and to impact on better preparation for their future careers.

In her study, D. Recatala conducted works aimed at combining active methods of teaching introduced to the physical chemistry course in a higher education institution in Spain, as well as integrating the subject content in this discipline with the English language. In this study, a number of factors that influence the world practice of teaching including the active teaching and the CLIL method in the physical chemistry class were analyzed. Some examples of these include views related to the discipline, interest and motivation in the course, attitudes towards the English language acquisition and overall students' satisfaction with the learning process [15]. In their works, B.A. Zhetpisbayeva and A.E. Kubeeva emphasized the effectiveness of using internationally recognized CLIL technology and focused on the relevance of learning and mastering the technology by future professional teachers. The essence of the Kazakh trilingual education model is the possibility of further development of the trilingual education ideas of the CLIL technology in the educational process. There are also survey results of higher education institution students and teachers who introduced trilingual education into the learning process [16].

Despite the comprehensive description of the importance and benefits of integrated teaching in English, the methods of teaching chemistry have been rarely studied. In this regard, to study the methodological basis of teaching chemistry in English is of great importance.

The main purpose of the proposed study is to build students' knowledge and skills based on the continuity of traditional teaching and new methods by taking into consideration the importance of teaching chemistry in English in secondary schools. The research tasks are the effective application of new methods and techniques in teaching chemistry based on the new curriculum; to illustrate and describe new methods, effective techniques of teaching chemistry in English; the formation of pupils' knowledge and interest; the development of learners' scientific vocabulary and the vocabulary related to the chemistry science.

### *Experimental*

The pedagogical experiment of teaching chemistry in English was conducted among the 8<sup>th</sup>-grade pupils of the specialized boarding school named after N. Ondasynov in Turkestan.

In the first lesson, the main attention was paid to chemistry rather than English. Therefore, the simple terminology of the most common terms used during the chemistry class was applied.

Despite the fact that the textual work is one of the most significant ways in Content and Language Integrated Learning both in terms of learning objectives and language objectives, all types of classroom activities were applied in the lesson planning. When selecting the study material, original texts with a variety of styles were selected to meet the pupils' age requirements and language proficiency level. In teaching chemistry in English, the relevance of teaching terminology, glossary, work on the text composed on the English language basis and calculations were explored through the continuity of the CLIL method and traditional teaching methods.

A lot of work was accomplished on the terminology in teaching chemistry to stimulate the pupils' interest. The assignments were given to test previously obtained knowledge and for the acquisition of new knowledge. The new CLIL technology was used in continuity with traditional methods, brainstorming and «Five Ws» method to consider the significance of terminology in teaching chemistry in English. The terminology effectiveness was defined by the questionnaire taken from the pupils after the completion of the following tasks: The «brainstorming» method was applied to consolidate the topic that was covered at the beginning of the lesson:

1. Define the concepts of protons, neutrons, electrons in English.

2. Write the words that correspond to the chemical bond.

Water; Bond; Electron; Chemistry; Ionic; Flask; Filter; Book; Shell; Matter.

3. Find names of metals and write them below

1. O; 2. Zn; 3. Si; 4. Hg; 5. C; 6. Fe; 7. Ca; 8. Ne; 9. Na; 10. Cl.

4. Write the symbols of the elements in 3 languages and calculate proton, electron, and neutron numbers Al, Cl, F, Fe, Zn, O, H, P, Ca, Na, K, Ag.

This method contributed to the pupils' knowledge acquisition speed and the accumulation of English language knowledge. Due to this, they could easily find the chemical elements names and became more active in the classroom.

«Five Ws» method is a method in which questions are asked in English by pupils in the classroom to increase their comprehension of the topic and to develop their discussion skills.

1. Students answered in English the questions which were asked in Kazakh.

What is the salt of hydrochloric acid?

What is the element used for disinfection?

What is the substance consisting of two elements, one of which is oxygen?

How is the element type change called?

What is the lightest element?

2. Carbon is a metal or a \_\_\_\_\_ (non-metal)

Iron, copper, sodium are \_\_\_\_\_ (metals)

Oxygen, silicon, carbon are \_\_\_\_\_ (non-metals)

Most of elements in Periodic Table are \_\_\_\_\_ (metals)

Sulfur is a \_\_\_\_\_ - (non-metal)

To determine the effectiveness of working on a glossary during the course of teaching chemistry in English, a glossary «Electronegativity. A covalent bond» was given to the pupils in two languages:

Electronegativity is the ability of atoms to pull electrons towards themselves.

A chemical bond is the formation of a bond of chemical elements interacting with each other.

Cation is a positively charged particle.

Anion is a negatively charged particle.

An ion is a charged atom or group of atoms.

A covalent bond is a type of a chemical bond that involves the sharing of electron pairs between atoms.

Non polar bond is a bond formed between chemical elements with the same electronegativity.

A polar bond is a type of bond formed between atoms of various nonmetals.

During the lesson conducted using the glossary, the pupils learned to be more careful and to express their ideas in a short and easy way. The glossary was prepared in two languages which allowed pupils to remember the terms and definitions of chemistry in English. The results were positive. Initially, it was difficult for the pupils since they had not been accustomed to working on the glossary prepared in two languages. Later, they realized that the lesson was interesting and they also could benefit from using the time efficiently. The effectiveness of the glossary in teaching chemistry in English was determined by the survey results taken from the pupils.

The effectiveness of the text composed on the English-language basis in teaching chemistry in English was also investigated by the Jigsaw method alongside the CLIL method [17].

An acid is a substance that produces  $H^+(aq)$  ions when dissolved in water.

The commonest acids in the laboratory are sulfuric acid ( $H_2SO_4$ ), hydrochloric acid (HCl) and nitric acid ( $HNO_3$ ). These are known as the mineral acids. Another common acid is acetic acid (acetic acid,  $CH_3COOH$ ), a smelly liquid that boils at  $118\text{ }^\circ\text{C}$ . Acetic acid is the chemical that gives vinegar its sour taste.

A base is a substance that reacts with an acid in solution producing only water and salt.

Generalizing:

acid + base  $\rightarrow$  salt + water

This reaction is known as neutralization.

An alkali is a base that dissolves in water. A solution of an alkali contains the hydroxide ion,  $OH^-(aq)$ .

Alkalis are usually hydroxides of metals. The common alkalis are the hydroxides of calcium, potassium and sodium. They are all ionic solids which completely dissociate into ions in water.

Ammonia solution is also regarded as an alkali because it contains the hydroxide ion.

Bases which are insoluble in water include the oxides of metals such as magnesium oxide ( $Mg^{2+}$ ,  $O^{2-}$ ) and copper (II) oxide ( $Cu^{2+}$ ,  $O^{2-}$ ) and organic compounds (compounds based on carbon) which contain nitrogen atoms such as propylamine ( $C_3H_7NH_2$ ) [18].

The pupils were asked questions about the text and their acquisition of the text given in English which was determined (Table 1).

Table 1

## English language based text questions

Questions	Yes	No
Is the topic about bases?		
Were alkaline metals written?		
Are there any insoluble bases?		
Are Arabic numerals used in writing the bases?		
Was the work conducted through classifying bases?		
Is it explained why alkali metals are caustic?		

The CLIL method was applied in continuity with the heuristic method of teaching calculations by using English in chemistry classes [19]. During the lesson some calculations were done only after the new topic had been explained and the new words related to the lesson topic had been written in Kazakh and English.

Firstly, calculations on the first topic of «Solutions» were performed in Kazakh.

1. If 20 g of the substance is in 190 g of solution, find the mass fraction of the dissolved substance in this solution.

2. How much salt and water are needed to make 300 g of a 35 % solution?

3. Calculate the mass fraction of the dissolved substance in the solution formed when 45 g of salt is dissolved in 220 ml of water.

4. How many substances should be dissolved in 250 ml of water to prepare a 12 % solution by mass?

5. What is the mass fraction of 74 g of table salt dissolved in 274 g of solution?

The work with English terminology was carried out before starting the calculations in English. The terminology found in the calculation was used to help the pupils to understand problems in English and to solve them (Table 2).

Table 2

## Terms used in the calculation

Массалық үлес	Mass percentage
Молярлық концентрация	Molar concentration
Көбейту	To multiply
Бөлу	Divide
Дистильденген су	Distilled water
Қатынас	Proportion
Байланысты болу	To depend on
Берілгені	Given
Табу керек	To find
Шығару жолы	Way to solve
Еріген зат	Solute
Еріткіш	Solvent
Ерігіштік	Solubility
Қанықпаған	Unsaturated
Қаныққан	Saturated
Аз ериді	Slightly soluble

The problems given in English were solved after getting acquainted with the terms necessary for doing calculations.

1. 20 g of sodium reacts with nitric acid. Find the mass of sodium nitrate.

2. 3.9 g of potassium reacts with oxygen. Find the mass of potassium oxide.

3. 25 g of salt is dissolved in 75 g of water. What is the mass percentage of salt?

4. Find the mass of sodium carbonate to prepare 50 g of 7 % solution?
5. 25 g of salt was added to 200 g solution. What is the mass percentage of salt?
6. How much sodium nitrate should be taken to prepare 15 g of 30 % solution?

The increase in the pupils' thinking ability was observed while doing chemistry calculations in English.

### Results and Discussion

With a view to determining the glossary effectiveness in a pedagogical experiment conducted using the CLIL method in the chemistry class, the learners were taken a questionnaire consisting of the following questions:

1. Did you like the lesson?
2. Has the glossary helped you to understand the text given in two languages?
3. Do you want to work with a glossary in the future?
4. Have you ever worked with a glossary?
5. Did you face any challenges in working with the glossary?

Most of the surveyed pupils supported the glossary efficiency in teaching chemistry in English, while a few of them did not (Fig. 1). The survey result revealed that the pupils had a desire to work on a glossary and working on the glossary had a positive impact on learning outcomes.

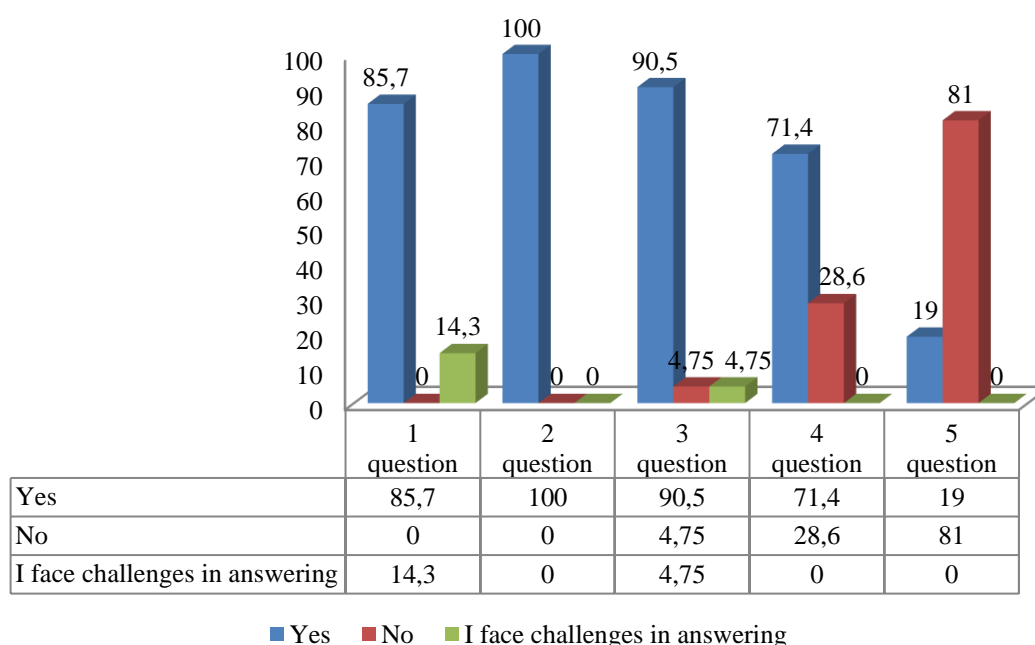


Figure 1. The survey results to determine the glossary work effectiveness

The pupils were surveyed to determine the effectiveness of working on the text in English, which was used to develop language skills in integrated chemistry teaching. The questionnaire consisted of the following questions:

1. Did working hard with «an English text» exercise help you to develop your English language skills?
2. Have you ever worked with «an English text» exercise before?
3. Did you enjoy working with «the English text» exercise?
4. Was it fun to work with «the English text» exercise?
5. Did the English text help you to understand the lesson better?

Almost half of the pupils who were surveyed gave a negative answer to the question «Have you ever worked with an English text exercise before?» This indicates that English has not been used before in teaching chemistry. The rest of the questionnaire answers indicates that most learners liked working on the English text and understood the lesson (Fig. 2).

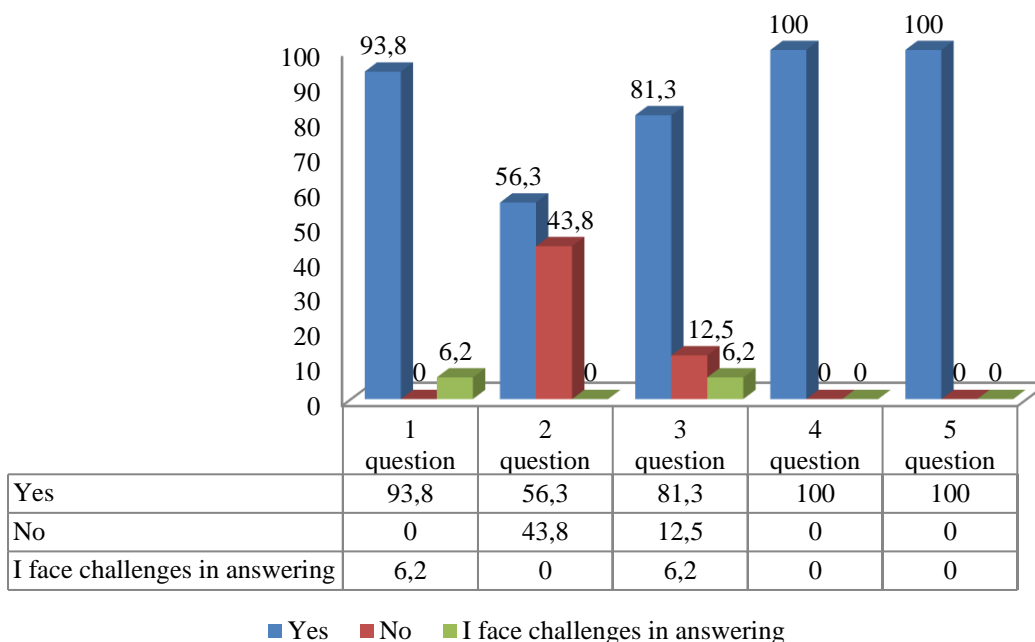


Figure 2. The survey results to determine the effectiveness of working on a text in English

The pupils were asked to complete the summative assessment (SA) according to sections 1 and 2 to identify how their progression in knowledge, skills, and understanding related subject content is changed. The summative assessment on the first section was taken before the experiment, i.e. when used traditional teaching strategies. In the second section, the summative assessment was obtained after application CLIL method teaching in the Chemistry classroom. The maximum score of the summative assessment task for each section was 15 points. 21 pupils took part in the tasks. The SA were used to evaluate effectiveness of the CLIL method.

By analyzing the pre- and post-experiment results it was observed upward in pupils' learning outcomes after using the CLIL teaching method in the class. Before the experiment, the summative assessment average score of the pupils for the first section was 9.76 points. When the experimental group was taught through the CLIL method, the average score of the pupils for the second section reached 12.85 points. (Fig. 3). The academic performance of pupils in this group is explained by the fact that chemistry was taught in English in the continuity of the traditional method and the CLIL method.

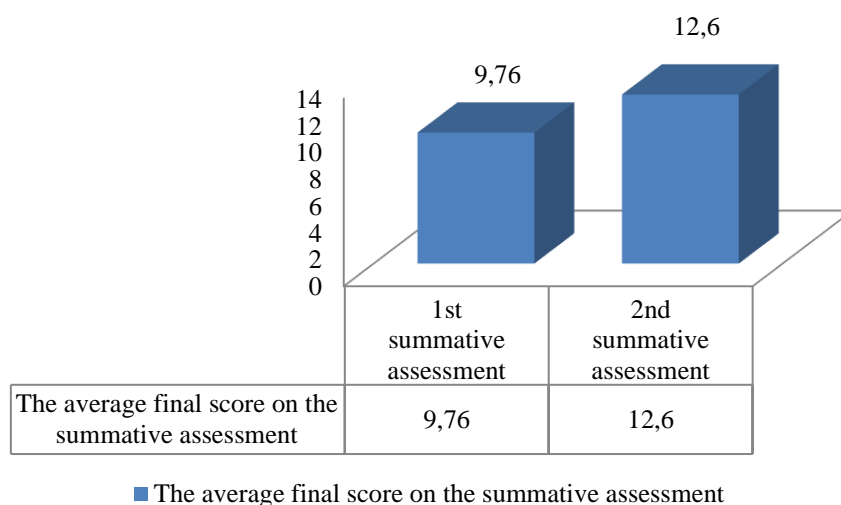


Figure 3. Results of the summative assessment on sections 1 and 2 on the mastery of the lesson materials

The peculiarity of teaching chemistry in English is to increase pupils' interest in chemistry and English by using active teaching methods based on modern teaching idea. To implement this idea, the chemistry was taught in English by applying the CLIL method for the first time in the specialized boarding school named after N. Ondasynov in Turkistan. The study results allowed to change the practice of teaching the subject. The use of CLIL methods was expanded to increase pupils' interest in chemistry and to improve their comprehension of chemical terminology in English. The CLIL teaching method was applied in combination with active methods («Jigsaw», «Five Ws») and traditional methods which contributed not only assimilation and understanding of subject content but also the development of critical thinking, improving vocabulary and language skills of the pupils. Implementation of the CLIL method teaching in Chemistry classroom based on the continuity of traditional methods and new technologies allowed the pupils to acquire chemistry in English thoroughly.

### Conclusions

The application of the CLIL teaching method in the Chemistry classroom increases learners' interest in both subject and language context. At each lesson the pupils had the opportunity to access basic concepts and skills relating to the subject content, to express their thoughts clearly and to enhance their knowledge. As a result of the proposed research, it was proved that the implementation of CLIL teaching methodology develop pupils' progression in knowledge, skills, and understanding Chemistry subject content. It based on the principle to support and improve the pupils' thinking process by teaching Chemistry subject content through English. The survey results revealed formation not only content-learning outcomes but also language-learning outcomes and the effectiveness of working on terminology, glossary, an English-language based text and calculations in integrated teaching. As for features of teaching Chemistry in English, the CLIL approaches proved to be effective in developing subject competencies, develop multilingual interest and attitudes, increase motivation in learning, interest in the subject and increased academic performance.

The integrated chemistry course takes teachers a lot of time to prepare for the lesson since teaching chemistry in another language requires much attention to be drawn to the subject, as well as the language. However, the integrated approach towards teaching chemistry is more successful than the traditional one.

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### **Химияны ағылшын тілінде оқытудың ерекшелігі: дәстүрлі және жаңа технология сабақтастығы**

Мақалада орта мектепте химия пәнін ағылшын тілінде оқытудың дәстүрлі және жаңа технологиялардың сабақтастығы туралы зерттеу нәтижелері сипатталған. Оқушылардың химия пәніне деген қызығушылықтарын арттыру және білімін жетілдіру үшін түрлі дәстүрлі әдістермен бірге қазіргі жаңа технология пәнімен тілді кіріктіре оқыту — CLIL әдісі зерттелген. Зерттеу өткізу кезінде сыныптағы оқушылардың химия пәнін оқу кезіндегі оқушылардың ынтасына, білім деңгейлеріне және тілді меңгеру қабілеттеріне ерекше назар аударылған. Химия пәнін ағылшын тілінде оқытуда жаңа әдіс-тәсілдерді тиімді пайдалану жолдары қарастырылып, жаңа оқу бағдарламасы негізінде химия пәнін ағылшын тілінде байланыстыра оқыту тәжірибесі зерделенген. CLIL технологиясын сабақ барысында қолдану үшін терминология, глоссарий, ағылшын тіліндегі мәтінмен жұмыс және есептеулер жүргізу әдістемесі таңдалған. Химия сабағында CLIL технологиясын қолданудың тиімділігін анықтау үшін мектеп оқушыларынан сауалнама алынып, педагогикалық бақылау жүргізілген. Жүргізілген сауалнама нәтижелері бойынша химия пәнін ағылшын тілінде оқытудың ұтымдылығына көз жеткізілген. Терминология және глоссариймен жұмыс жасау барысында терминдерді сабақта қолдана отырып, оқушылардың химия пәні бойынша сөздік қоры көбейіп, пәнге деген қызығушылықтары артқан. Мәтінмен жұмыс барысында оқушылардың ағылшын тілінде сөйлеу, ойлау дағдысы қалыптасқан. Пән мен тілді кіріктіре оқытуда CLIL әдісін қолдану оқушыларға пән бойынша ақпарат алумен қатар, тілді меңгеруге де мүмкіндік берді.

*Кілт сөздер:* CLIL әдісі, химияны ағылшын тілінде оқыту, пән мен тілді кіріктіре оқыту, глоссарий, терминология, ағылшын тіліндегі мәтінмен жұмыс, CLIL технологиясы, сауалнама, дәстүрлі әдіс.

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### **Особенности преподавания химии на английском языке: преимущество традиционных и новых технологий**

В статье описаны результаты исследования о преимущественности традиционных и новых технологий в преподавании химии на английском языке в средней школе. С целью повышения интереса учащихся к предмету и совершенствования знаний по химии, наряду с различными традиционными методами, был изучен метод CLIL (интегрированное обучение предмета на языке современной технологии). В ходе проведения исследования особое внимание было уделено мотивации учащихся к изучению химии, уровню знаний и способности овладения языком. Рассмотрены пути эффективного использования новых методов и приемов в преподавании химии на английском языке по новой учебной программе. Для использования технологии CLIL в ходе урока были выбраны терминология, глоссарий, работа с текстами на английском языке и методика проведения вычисления. Для определения эффективности применения технологии CLIL на уроках химии был проведен опрос учащихся и педагогический контроль. По результатам опроса была доказана эффективность преподавания химии на английском языке. В ходе работы над терминологией и глоссарием наблюдается увеличение словарного запаса учащихся по химии и повышение интереса к предмету. При работе с текстом у учащихся сформировались навыки устной речи, мышления на английском языке. Интеграция предметного и языкового обучения позволила учащимся не только получить информацию по предмету, но и освоить язык.

*Ключевые слова:* метод CLIL, обучение химии на английском языке, интегрированное обучение предмета и языка, глоссарий, терминология, работа с текстом на английском языке, технология CLIL, опрос, традиционный метод.

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## **Group learning activities as a condition of implementing competence-based approach to students' inorganic chemistry teaching at university**

The article presents the results of experimental testing the effectiveness of group learning activities of students at Inorganic Chemistry laboratory classes. The future teachers had their classes according to a technique based on research paper analysis findings with due account for practice of implementing the concept of group educational activity of senior pupils in Ukraine. The following issues were briefly addressed: special aspects of activities performed by group learning individuals; educational result of inorganic chemistry students presented in the form of general and special (occupational and subject) competences; preparation and order of laboratory classes for small groups of students as subjects. The order, course and results of the pedagogical experiment are presented. The results suggest that using the students' group learning activities is an effective tool for implementation of the competence-based approach to inorganic chemistry educational process, which contributes to lining-up the order and course of inorganic chemistry laboratory practicals. We wish to make a point that using group learning for actualization of the competence-based approach to learning chemistry of students requires certain methodological training of the faculty.

*Key words:* competency-based approach, the Inorganic Chemistry academic discipline, group learning activity, group learning technique, group learning individual, students, academic staff, laboratory practicals.

### *Introduction*

Teaching based on the competency-based approach is a global trend in higher and secondary education, which has been supported by the United Nations (UN), the Organization for Economic Cooperation and Development (OECD) and other world communities for a long time [1].

The teaching process, which takes into account the above-mentioned trend, is a system of «scientific, methodological and pedagogical measures aimed at the development of a personality by forming and applying his/her competencies» [2]. Based on the foregoing, the policy in the sphere of the national higher education is aimed at the development of general and special (professional, subject) competencies of students [3].

This actualizes the problem of theoretical substantiation and practical implementation of competence-based teaching at higher education institutions. We brought attention to a group learning activity of students in the course of addressing this problem. In order to develop a group learning technique, it was fundamentally important to answer the following questions:

- how to organize a group learning activity of students at inorganic chemistry laboratory practicals;
- what should be done methodologically for successful group learning;
- what is the role of academic staff in this process;
- what educational outcome should we expect.

The analysis of the national scientific sources made it possible to find out that the degree of development of group learning of senior pupils as for the theory and methodology of teaching chemistry is much higher than that of college students. O.G. Yaroshenko substantiated, among other things, the didactic concept of the group learning activity of senior pupils on the basis of chemistry learning using the results of a continuous study of the group learning activities at school [4], and developed a variety of learning and methodological support instructions for teaching senior pupils in small groups [5–10].

A long-term pedagogical experiment [5, 11, 12] and mass introduction of group learning activity into school practice confirmed its effectiveness.

Our study and the best domestic practices of senior pupil group learning brought us to the conclusion of reasonableness of extrapolation of the main provisions of the high school group learning concept to the teaching process at a college level. It is about approaches to forming small groups, the distribution of roles in a small group, and the ratio of faculty leading role and independence of a group learning individual. However,

the chemistry teaching process at college level, types and duration of educational classes, the chemistry learning goals, and the age characteristics of students differed significantly. That's why the possibility of a mechanical transfer of a competence-based educational paradigm prevailing at the high school to the college level is excluded. This fact brings a new problem, which consists in the necessity of theoretical substantiation and methodological support to using group learning didactic potential for shaping general and subject competencies of future teachers based on the experience of group learning at high school. We commenced solving this problem with the analysis of previous relevant domestic and international surveys.

Domestic researchers focus mostly on using student group learning activities for development of collaborative communication skills, consider it as a framework for trainings, brainstorming, business games, educational projects, etc. [13–16].

Foreign researchers make an accent on learning, educational, social and organizational functions of group classes, and contemplate the conditions for effectiveness thereof (comprehension of a collaborative objective by a group member, correct lineup of the group in which each member has a positive experience of a certain activity, and adoption of general collaboration rules by the team) [17]. J.R. Hackman (2005), R.M. Gillies and M. Boyle (2010) conclude that group work contributes to effective acquisition of academic knowledge and development of interpersonal communication skills [18, 19]. E.F. Barkley, C.H. Major, and K.P. Cross (2014) instruct on small student grouping, the distribution of roles, the development of team spirit, addressing unexpected problems, and assessing students' involvement in addressing team assignments in the recommendations for teachers on organization and resourcing of effective collaborative classes. The authors also call attention to the role of faculty in the organization of learning activity, the need to combine individual and collaborative responsibility in grading group learning activities [20].

According to L. Rabekova and J. Hvorecky (2015), the collaborative learning activity is one of the components of various student learning techniques intended for improvement of the quality of their professional training [21].

As we see, researchers consider group learning activities mainly as the external side of the educational process, the framework of which makes interactive learning possible. The fundamental difference of our approach consists in the idea that learning in a small group is considered as the activity of a uniform group subject, which is a way of acquisition of the expected result. Therefore, it is about a group learning technique. From the author's point of view, the student group learning technique is a scientifically based, clearly planned, substantively, methodically and procedurally supported process leading to achieving the expected result, which is the formation of general and professional competencies.

*Study object* is an inorganic chemistry teaching process at higher education institutions of Ukraine.

*Study subject* is a student group learning technique used for implementation of the competence-based approach to inorganic chemistry classes.

*The purpose of the article* is to explore a didactic potential of students' group learning activity in the implementation of a competence-based approach to inorganic chemistry learning process.

*The article objectives* are to justify the group learning technique in the inorganic chemistry learning process at higher pedagogical education institutions and to present quantitative and qualitative results of experimental verification of systematic use of group learning activity of students, future chemistry teachers, at inorganic chemistry laboratory practicals.

*Structure of the article.* The article consists of four parts. The first part presents the conceptual foundations of the group learning activity of students, the relevance of the topic, its object, subject and purpose. The second part describes the methods and material of the study and explains tailoring the pedagogical experiment conducted at the Mykhailo Kotsiubynskyi Vinnytsia State Pedagogical University with involvement of students of the first (High-School Instruction (Natural Science)) and the second (High-School Instruction (Human Biology and Health, Chemistry)) courses. The third part describes the results of the pedagogical experiment. The fourth part is inclusive of conclusions basing on the results of the study.

### *Experimental*

To achieve the goal and solve the tasks set, we used the methods of scholastic attainments: analysis, description, interpretation, measurement, survey, questionnaire, test method, the study of educational documentation and documents regulating the teaching activities of the academic staff, the study of pedagogical experience, experiment, comparison, generalization of the data obtained and mathematical processing thereof.

Let's further characterize the organization of experimental learning. We guess the student group learning technique has significant didactic potential for development of both subject and general competencies of a

future specialist. We consider subject competency of inorganic chemistry students as a dynamic combination of knowledge, skills, methods of activity and values in the field of inorganic chemistry, which determines the ability of students to further effective learning and professional activity. We distinguish cognitive, activity- and value-based components in its structure. Below we provide an example of subject competency components presented as the results of studying the *Hydrogen* topic [22].

Cognitive component presumes the following actions: a student names hydrogen isotopes and compounds; gives examples of hydrogen production reactions; describes the properties and distribution of hydrogen in the nature and classification of hydrogen compounds of chemical elements.

Activity-based component presumes the following actions: the student compiles electronic and graphic formulas of the hydrogen atom, the equations of chemical reactions characteristic of hydrogen and appropriate schemes of electronic balances; substantiates the place of hydrogen in the periodic system, its valency and oxidation number; characterizes hydrogen by its place in the periodic system and atomic structure; experimentally produces, collects and checks hydrogen for purity; follows the rules of safe hydrogen handling; solves computational and experimental tasks.

Value-based component consists of the following actions: the student evaluates the role of hydrogen as an environmentally friendly fuel; proves the practical significance of hydrogen and its compounds; comprehends the need to preserve his/her own health and the environment when using chemical compounds and the importance of acquired knowledge for future professional activities.

The curriculum of Vinnitsia State Pedagogical University, the experiment home, provided 120 hours (4 credits) for studying the *Inorganic Chemistry* discipline, of which 24 hours were lectures, 40 hours — laboratory practicals, and 56 hours were assigned for the independent work. The final control point was a pass-fail exam.

Students independently shaped small learning groups consisting of 3–4 individuals of different progress in each group and elected a leader (consultant) in order to apply the group learning technique at the preparatory stage of the experiment. *'A consultant is a group student nominated as an unofficial leader, which is responsible for organization of collective activities for the most rapid and successful achievement of a goal'* [5, p. 31]. All members of the small group acted in turn as a consultant throughout the inorganic chemistry study period in order to implement the principles of binary and professional orientation in teaching. The experimental technique presumed using both uniform (all groups perform the same task) and collaborative (each group performs part of a task common for the academic subgroup) group work.

At the preparatory stage, the academic staff drew up tasks for the group work, developed interdisciplinary communication cards for each topic, allowing to demonstrate the importance of learning material for further education and professional activities and secure interdisciplinary integration in order to develop students' ability to systemic, critical thinking; analysis and synthesis; application of knowledge in practical situations.

One laboratory class in inorganic chemistry with collaborative student activity is designed for 2 academic hours. There are the following stages of the laboratory class: motivation of collaborative activities; actualization of knowledge; application of knowledge and formation of skills; knowledge control; reflections of the group activity.

Let's consider the types of activities of the learning process members at each stage. At the motivation stage, the students attending the session consider and realize the purpose of the forthcoming collaborative activity, the ways of achieving the goals, and the significance of acquired educational results for the future professional activity. This is the shortest stage (3–5 minutes). The stage of knowledge actualization is designated for small learning groups. The consultant performs oral examination of students' theoretical knowledge on the class topic and puts the points scored in the account card. At this stage the learning material is complemented and updated through group learning activity in parallel with oral examination of knowledge and discussion of theoretical material. Meanwhile the teacher checks the students' performance of tasks of independent extracurricular assignment. The duration of the knowledge actualization stage is up to 20 minutes.

Students continue working in groups at the stage of application of knowledge and skill development: they perform tasks and carry out laboratory experiments. Tasks prepared by the teacher must meet the following requirements: consolidate the theoretical material of the topic; develop practical skills; promote development of the ability to put knowledge into practice; and be differentiated by complexity. The importance of this stage consists in promotion of a solid and conscious consolidation of theoretical knowledge, the formation of skills and proficiency, and development of value-based orientations. For this purpose, the group members work collaboratively and actively helping each other, using, where necessary, supporting notes, algorithms, textbooks and the like. Upon completion of the stage of knowledge application and formation of skills, the results of the

collaborative class are summarized, collectively discussed, and, if necessary, corrected by the academic staff. The duration of the work of students in small learning groups at this stage is 35–40 minutes.

The consultant assesses the group's work. The following types of students' collaborative activities are subject to assessment: oral response at the stage of knowledge actualization; the quality of tasks performed at the stage of knowledge application and skill development.

The next stage is designated for individual control by a teacher and final evaluation of results achieved by students at the group laboratory class. At this stage, students individually complete written assignments or tests that allow the teacher to check subject competency under the conditions of collaborative learning. The duration of the knowledge control stage is about 15 minutes.

Upon completing the control assignments, students and the academic staff reflect on the progress and results of group learning activity. At this stage of the class, a value-based component of subject competency in inorganic chemistry is purposefully formed, as well as general competency (the ability to be critical and self-critical, the ability to evaluate and maintain the quality of work, etc.) is developed. The reflection lasts about 5 minutes. The final stage of the lab session is summarizing the results and informing the students of the next topic and the tasks of preparation for the next class (about 5 minutes).

From the standpoint of both parties of the educational process (students and academic staff), the group learning technique is actualized through interconnected actions aimed at achievement of the expected result (Fig. 1).

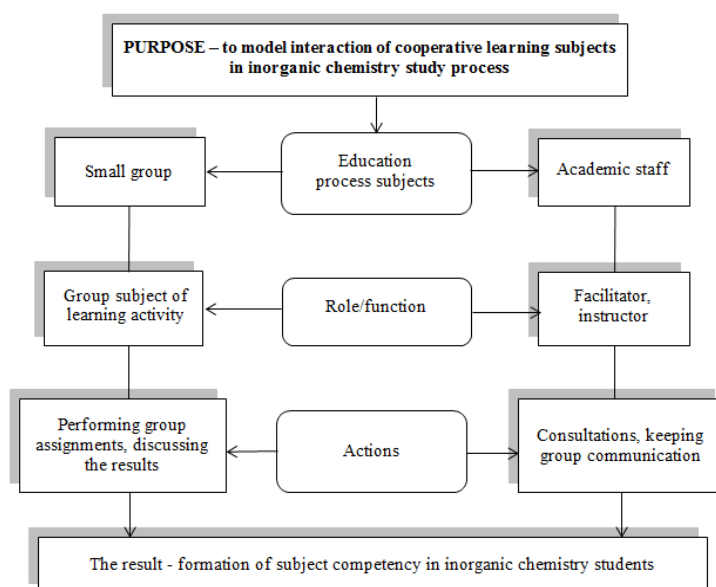


Figure 1. Scheme of interaction of group learning subjects

We designed an experiment to compare the performance of students in the flipped classroom with the traditional teaching. The pedagogical experiment involved 50 students, prospective teachers of Chemistry, including 24 students enrolled in the educational program «Secondary education (Biology and Human Health. Chemistry)» as an experimental group, and 26 students enrolled in the educational program «Secondary Education (Natural Sciences)» as a control group.

The effectiveness of students' group educational activities in the process of studying inorganic chemistry was determined by using the following criteria:

- 1) developing subject competence in inorganic chemistry;
- 2) students' satisfaction with the progress and results of training in small groups.

At the stage of preparation for the pedagogical experiment, we analyzed the curriculum and found out what educational elements of the content of the discipline students have to learn. Under the educational element of the content, we understand the knowledge, skills, and values that are developed in the process of teaching inorganic chemistry. To get a complete picture of the effectiveness of the group learning technology proved in the research, we measured the subject competence for each component: cognitive (knowledge, concepts, facts, rules), activity (skills, methods of activity), and value (attitude, awareness). To identify the influence of group

learning technology on shaping students' subject competence in inorganic chemistry, we conducted a statistical comparison of the results in the experimental and control groups.

We developed a test measuring and defining the level of the cognitive component of subject competence in inorganic chemistry. It contained 30 closed-form tasks of various types (multiple choice, determining the sequence, and matching). The test allowed us to check up 50 educational content elements that make up the students' subject (special) competence in inorganic chemistry. According to the educational programs «Secondary education (Biology and Human Health. Chemistry)», and «Secondary education (Nature Sciences)», the cognitive component of the subject competences is formed by knowledge of the properties of the elements, simple and complex inorganic substances; it includes the ability to use modern symbols and terminology in chemical language, and understand the traditional names and trivial nomenclature of inorganic compounds. In addition, it deals with the general structure and content of chemical sciences based on the teachings about the structure of matter, periodic changes in the properties of chemical elements and their compounds, about the direction of chemical reactions (chemical thermodynamics), rates of chemical processes (chemical kinetics) and their mechanisms.

We measured and defined the level of shaping the activity component of students' subject competence of inorganic chemistry by observing the chemical experiments done by students in laboratory classes, analyzing the way they solve chemical problems, do exercises, and perform cognitive tasks. Conclusions about forming the activity component were also based on the results of observing the students design an experiment plan, select the necessary equipment and reagents, assemble devices, do the experiment and formulate its results, write down the equations of chemical reactions, solve computational and experimental problems, and observe safety rules.

Shaping of the value component was proved by the students' attitude to inorganic chemistry as a source of knowledge, which not only increases their scientific potential, but also serves as a basis for successful teaching activities at school. Here are the examples of professionally oriented tasks for out-of-class work used to develop the value component of subject competence: 1. Analyze and compare the program of the standard and advanced study of Chemistry concerning differences in inorganic chemistry knowledge level. 2. Using the school textbook of the 11th grade (profile level), read the content of one of the practical works in the section «Chemical Elements of Group V-A». Determine what knowledge and skills in the study of inorganic chemistry you need to prepare for this practical work with high school students.

The level of shaping the value component was determined based on the results of analyzing the information submitted by the student in their self-assessment map.

The effectiveness of students' group learning activity in the process of studying inorganic Chemistry by the criterion 'Student satisfaction with the course and results of learning in small groups' was determined according to Z.I. Vasilyeva's method presented in 'Assessment of Satisfaction with Different Aspects of Life' [23].

### Results and Discussion

Below are Table 1 and Figure 2 that summarize the quantitative analysis of the results obtained.

Table 1

#### Inorganic chemistry subject competency maturity of students in experimental and control groups

Maturity of subject competency components	Subject competency components											
	Cognitive				Activity-based				Value-based			
	Experimental group		Control group		Experimental group		Control group		Experimental group		Control group	
	q-ty	%	q-ty	%	q-ty	%	q-ty	%	q-ty	%	q-ty	%
Low	4	16.6	6	23	5	20.8	5	19.2	2	8.3	9	34.6
Average	6	25	10	38.4	5	20.8	12	46.1	5	20.8	7	26.9
Sufficient	9	37.5	6	23.0	10	41.6	6	23	11	45.8	8	30.7
High	5	20.8	4	15.4	4	16.6	3	11.5	6	25	2	7.69

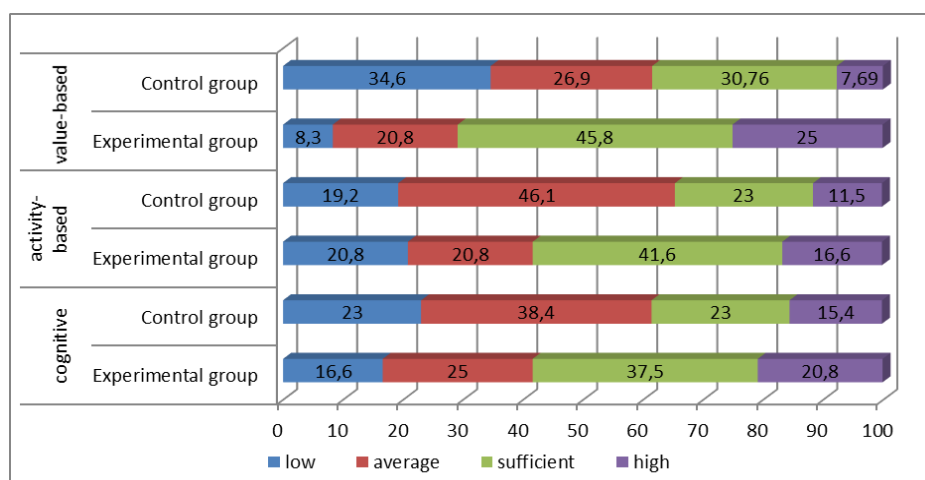


Figure 2. Inorganic chemistry subject competency component maturity of students in experimental and control groups

As you can see, the number of students with a sufficient and high level of subject competence in inorganic chemistry for all components in the experimental group is larger than in the control group.

A generalized indicator of shaping the cognitive component of the students' subject competence in inorganic chemistry was the coefficient of knowledge assimilation, which was 0.71 in the control group and 0.8 in the experimental group.

The generalized indicator of shaping the activity component of the students' subject competence in inorganic chemistry was chosen as the coefficient of mastering practical skills. In the control group, it was 0.64 and in the experimental group, it was 0.78.

A general indicator of shaping the value component was the coefficient of students' awareness of the importance of knowledge in inorganic chemistry for further use in their future professional activities. This indicator was 0.82 in the experimental group and 0.7 in the control group.

We also made a comparative analysis of the results of the final assessment of students in the experimental and control groups for a course of inorganic chemistry, conducted according to the curriculum in the form of a test. The outcomes are shown in table 2 and graphically presented in the histogram (Fig. 3). As we can see, the results of the experimental group are higher in absolute and percentage terms.

Table 2

#### Results of final attestation of inorganic chemistry students of experimental and control groups

Student group	Number of students (Q-ty/% ) assessed under ECTS scale													
	F		FX		E		D		C		B		A	
	q-ty	%	q-ty	%	q-ty	%	q-ty	%	q-ty	%	q-ty	%	q-ty	%
Experimental group	–	–	–	–	5	20,8	5	20,8	3	12,5	6	25,0	5	20,8
Control group	–	–	–	–	8	30,7	7	26,9	5	19,2	3	11,5	3	11,5

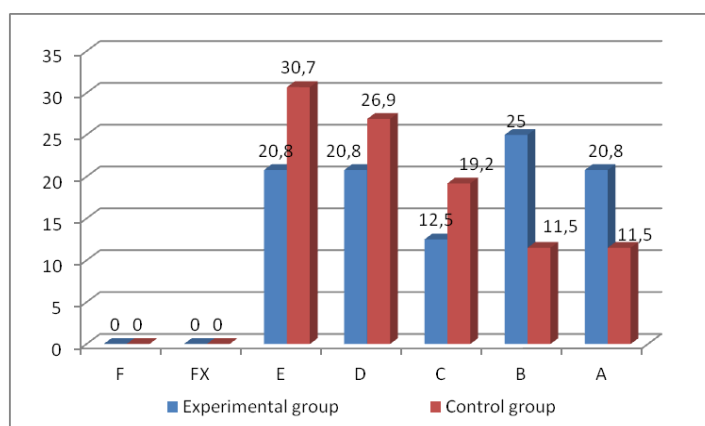


Figure 3. Results of final attestation of inorganic chemistry students of experimental and control groups



For the purpose of a statistical conclusion on the reliability of the obtained results, Student's *t*-test was used for independent samples. The value of the *t*-test for the experimental sample is 0.843. Comparing it with a tabular value at a significance level of 0.05, we concluded that there is a difference between the experimental and control groups in shaping subject competence in inorganic chemistry.

The materials of the questionnaire survey of students, conversations with them, and observations of the teachers taking part in the experiment informed about the satisfaction of students in the experimental group with learning under experimental conditions. The coefficient of satisfaction with experimental training was quite high 0.9.

The obtained results of the pedagogical experiment confirm the positive influence of group educational activities of students on shaping the subject competence in the process of teaching inorganic chemistry.

### Conclusions

The results of the study provided the basis for the following conclusions. The didactic potential of group educational activities is diverse, which allows to develop effectively knowledge, skills, methods of activity and values, as well as students' communication skills. The work of students in small educational groups increases the motivation for studying inorganic chemistry, actualizes existing knowledge and promotes the development of new one, creates conditions for the acquisition and application of skills, and increases the accuracy of a chemical experiment.

The results obtained in the study of shaping the students' subject competence in inorganic chemistry for each of the components (cognitive, activity, value), student satisfaction with the course and learning outcomes of small groups indicate the multifunctional didactic potential of group educational activities. Its implementation in the process of teaching inorganic chemistry to future teachers increases the effectiveness of developing subject competence in inorganic chemistry provides optimization of the scientific, methodological and effective components of the educational process.

The scientific novelty of the study lies in the fact that for the first time, the technology of group training of students studying inorganic chemistry in institutions of higher pedagogical education is theoretically substantiated, methodically developed and experimentally tested.

The practical significance of the obtained results arises from the fact that scientific and pedagogical workers of higher education institutions can use the educational technology substantiated in the study as a methodological guide in their own teaching activities.

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### Топтық оқу іс-әрекеті университет студенттеріне бейорганикалық химияны оқытуда құзыреттілік тәсілді іске асырудың шарты ретінде

Мақалада бейорганикалық химияны оқыту барысында университет студенттерінің топтық оқу іс-әрекетінің тиімділігінің тәжірибелік тексеру нәтижелері келтірілген. Эксперименттік оқыту ғылыми жұмыстарды талдау деректеріне және Украинада қалыптасқан оқушылардың топтық оқу іс-әрекетінің тұжырымдамасын іске асыру тәжірибесіне негізделген технология бойынша жүзеге асырылған. Студенттерді топтық оқыту технологиясында білім беру нәтижелерін жалпы және арнайы (кәсіптік, пәндік) құзыреттіліктер түрінде алу қарастырылған. Субъекті студенттердің шағын топтары болып табылатын бейорганикалық химия бойынша зертханалық сабақтарды дайындау және өткізу қысқаша сипатталған. Педагогикалық университетте «Бейорганикалық химия» пәні бойынша зертханалық сабақтарда топтық оқыту субъектілерінің қызметінің ерекшеліктері ашылған. Өткізілген педагогикалық эксперименттің ұйымдастырылуы, барысы және нәтижелері ұсынылған. Алынған нәтижелер негізінде жасалған негізгі қорытынды — университет студенттерін оқытуда топтық іс-әрекетті пайдалану бейорганикалық химия бойынша білім беру үдерісінде құзыреттілік тәсілді жүзеге асырудың тиімді шарты болып табылады. Шағын топтарды оқыту бейорганикалық химия бойынша сабақтарды ұйымдастыруды және өткізуді онтайландырады, студенттердің кәсіби құзыреттілігін қалыптастыруға оң әсерін тигізеді. Сонымен қатар, басқа оқу пәндері бойынша зертханалық сабақтарда жоғары білім алушылардың топтық оқу қызметін жүйелі түрде пайдаланудың орындылығы туралы қорытынды жасалған. Студенттерге химиялық білім беруде құзыреттілік тәсілді іске асыру мақсатында топтық оқытуды пайдалану ғылыми-педагогикалық қызметкерлерден белгілі бір әдістемелік дайындықты талап ететіндігі атап өтілген.

*Кілт сөздер:* құзыреттілік тәсіл, «Бейорганикалық химия» оқу пәні, топтық оқу іс-әрекеті, топтық оқыту технологиясы, топтық оқыту субъектісі, студенттер, ғылыми-педагогикалық қызметкерлер, зертханалық сабақтар.

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### Групповая учебная деятельность как условие реализации компетентностного подхода в обучении неорганической химии студентов университета

В статье приведены результаты экспериментальной проверки эффективности групповой учебной деятельности студентов университета в процессе изучения неорганической химии. Экспериментальное обучение осуществлялось по технологии, обоснованной с учетом данных анализа научных работ и сложившейся в Украине практики реализации концепции групповой учебной деятельности школьников. Технологией группового обучения студентов предусмотрено получение образовательных результатов

в виде общих и специальных (профессиональных, предметных) компетентностей. Кратко описаны подготовка и проведение лабораторных занятий по неорганической химии, субъектами которых являются малые группы студентов. Раскрыты особенности деятельности групповых субъектов обучения на лабораторных занятиях по учебной дисциплине «Неорганическая химия» в педагогическом университете. Представлены организация, ход и результаты проведенного педагогического эксперимента. Основной вывод, сделанный на основе полученных результатов, использование групповой учебной деятельности студентов университета является эффективным условием реализации компетентностного подхода в образовательном процессе по неорганической химии. Обучение малыми группами оптимизирует организацию и проведение занятий по неорганической химии, положительно сказывается на формировании профессиональных компетентностей студентов. Сделан также вывод о целесообразности систематического использования групповой учебной деятельности соискателей высшего образования на лабораторных занятиях по другим учебным дисциплинам. Отмечено, что использование группового обучения с целью реализации компетентностного подхода в химическом образовании студентов требует от научно-педагогических работников определенной методической подготовки.

*Ключевые слова:* компетентностный подход, учебная дисциплина «Неорганическая химия», групповая учебная деятельность, технология группового обучения, групповой субъект обучения, студенты, научно-педагогические работники, лабораторные занятия.

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