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ҚАРАҒАНДЫ  
УНИВЕРСИТЕТІНІҢ  
ХАБАРШЫСЫ

ВЕСТНИК  
КАРАГАНДИНСКОГО  
УНИВЕРСИТЕТА

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### Synthesis and characteristics of metal-polymer complexes of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>

Possibility of using the copolymers of poly-(ethylene)-propylene glycol maleate (p-EGM, p-PGM) with acrylic acid (AA) as a matrix for obtaining effective metal-polymer complexes of different application was shown. The compositions, structures and dimensions of particles of nickel and cobalt stabilized in polymeric matrix were determined using the methods of transmission electron microscopy and scanning microscopy, infrared spectroscopy, laser-emission spectroscopy, dispersive microscopy and thermogravimetric analysis. The average size of nanoparticles, which have spherical shape and equal distribution along cross-section of polymer, was 100–170 nm. Percentage content of nickel and cobalt in the complex was equal to 0.52 and 0.48, respectively, in the p-EGM/AA copolymer, 0.49 and 0.51 in the p-PGM/AA copolymer. The analysis of electromagnetic force-pictures of p-EGM/AA (14.8:85.2 mass.%) and p-PGM/AA (15.1:84.9 mass.%) copolymers' films showed a relatively equal distribution of the filler (Ni<sup>0</sup>, Co<sup>0</sup>) along the cross-section of polymer. The average number of metal particles on 10 microns was 600–700 units for particles of Ni and 550–650 units for particles of Co. Thermal decomposition of metal-polymer complexes occurred in the temperature range of 200–500 °C. The average weight loss on TG — curves was 80 %. Therefore, p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> metal-polymeric complexes obtained can be used as a template for the creation of catalytically effective composite materials.

*Keywords:* copolymer, polyethylene glycol maleate, polypropylene glycol maleate, polymeric matrix, nanoparticles, catalyst, metal-polymer complex, matrix.

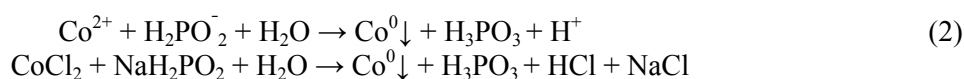
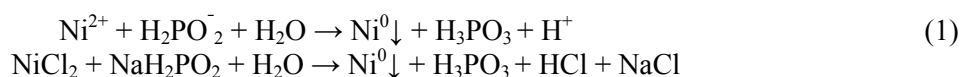
#### Introduction

Catalytic hydrogenation is one of the most important processes used in chemical industry. The main fields of applying such process are the fields of production of synthetic fuel by destructive hydrogenation of coal, purification and refining of liquid transportation fuel, hydrogenation industry and so on [1]. As it is known, catalytic reactions are divided into two basic classes, namely, homogeneous and heterogeneous. Heterogeneous catalysts are chemical compounds insoluble in the reaction medium. According to literature data nanostructured polymer systems are used as nanoreactors for nanoparticles formation [2] and these metal-polymeric complexes demonstrate a high level of catalytic activity, stability and selectiveness of effect. Reducing catalyst particles up to nanometric dimensions lets us broaden polymer surface contacting with reaction medium and increase the effectiveness of catalysis in several times, and gel matrix preserves particles against coagulation and oxidation. New type of nanocatalysts based on metal-polymeric matrix and catalytically effective transition metals based on polymer carriers can be used in many spheres. At the present time the search for new catalytic systems, particularly nanocatalysts characterized by high degree of activity and selectivity is the relevant task.

Polymers based on unsaturated polyester resins are economically profitable and these polymers can be used as obtainable carrier of metals nanoparticles. Comparing hydrophobic polymers with other thermally active polymers we can see that attractiveness of these hydrophobic polymers is due to their ability to solidify at room temperature or other relatively low temperature and almost without separation of co-products [3]. The aim of this work is the synthesis of new metal-polymeric complexes with transition metals based on the «smart» copolymers of p-EGM/AA, p-PGM/AA obtained by us earlier [4].

### Experimental

On the basis of copolymers p-EGM/AA, p-PGM/AA contained (14.8:85.2 mass.%) and (15.1:84.9 mass.%) metal-polymeric nanocomposites were obtained using the reduction method of salt solution of transition metals such as nickel and cobalt, namely, p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>, p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>. Ions reduction of metals (from Ni<sup>+2</sup>, Co<sup>+2</sup> up to Ni<sup>0</sup>, Co<sup>0</sup>) was carried out by sodium hypophosphate in the presence of ammonia solution of silver chloride used as a catalyst according to the following equations (1–2):



Reduction of Ni<sup>+2</sup>, Co<sup>+2</sup> in the volume of p-EGM/AA, p-PGM/AA polymeric matrix is carried out in the several stages (Fig. 1):

- insertion of ions (Ni<sup>+2</sup>, Co<sup>+2</sup>) in polymeric matrix;
- diffusion of reagents in polymeric matrix;
- reaction between chlorides of nickel, cobalt and sodium hypophosphate leading to the formation of metals nanoparticles.

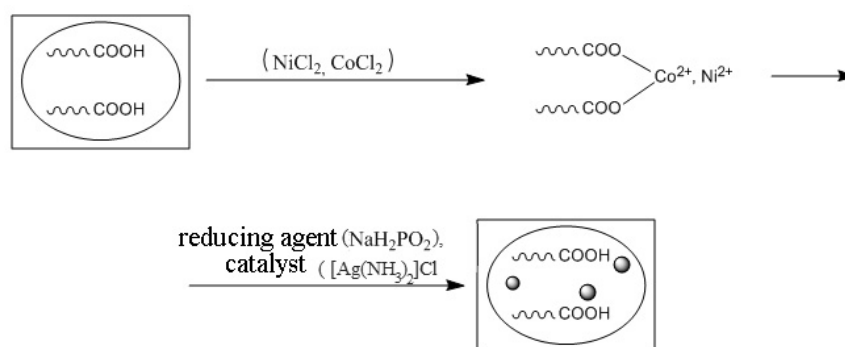
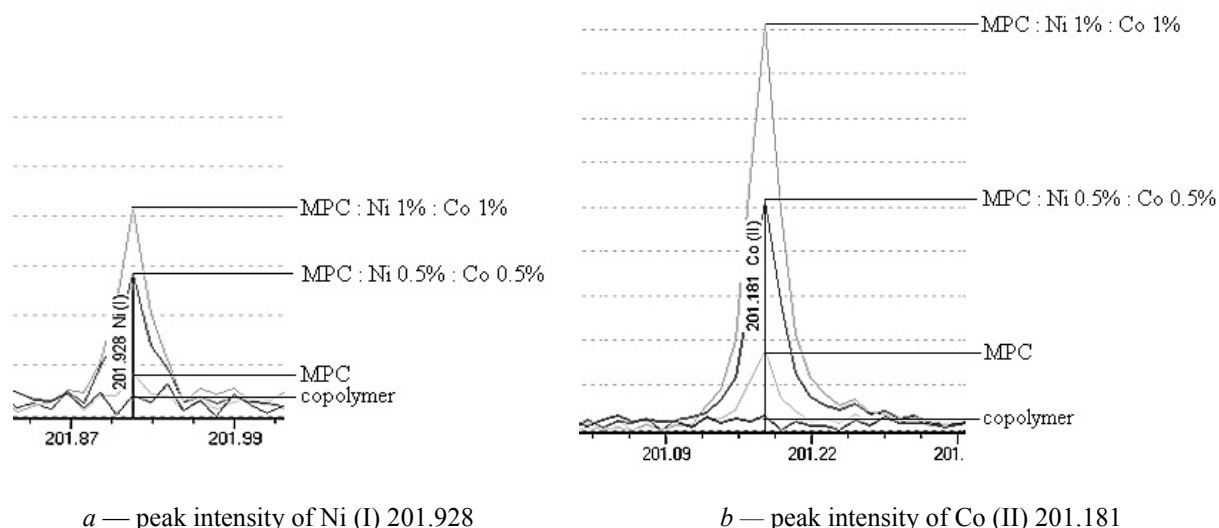


Figure 1. Principle diagram of obtaining the metal-polymeric complex (formation of metals' nanoparticles in polymer)

Reaction between chlorides of nickel, cobalt and sodium hypophosphate leading to the formation of metals nanoparticles was performed during two hours at room temperature. Quantitative content of nickel and cobalt in a complex was determined by the use of laser-emission spectrometer (Laes matrix spectrometer produced by «Spectroscopic systems» firm, Russia, 2014). Elementary and phase analysis of nanocomposites were determined by the method of energy dispersive spectroscopy with the use of highly effective X-Max80T silicium-drift detector (with superfine window) and X-Max80TLE (without window). Active area of detectors is 80 mm<sup>2</sup>. Infrared spectra of copolymer were registered on FSM 1201 infrared Fourier spectrometer. Thermal properties of copolymer were studied on DTA/DSC differential scanning calorimeter produced by the «Setaram» firm under dynamic conditions in 0–1500 °C temperature range with the heating rate 10 degree/minute in a nitrogen atmosphere in an Al<sub>2</sub>O<sub>3</sub> crucible. Characteristics of surface relief pattern were analyzed using scanning electron microscopy (REM) on the instrument MIRA 3, TESCAN «Oxford Instruments», England.

### Results and discussion

In this work, hydrophilic copolymers based on ethylene-(propylene) glycol maleate with acrylic acid of the following compositions: p-EGM/AA (14.8:85.2 mass.%), p-PGM/AA (15.1:84.9 mass.%) were used as the matrix for metals immobilization. These compositions demonstrate «smart» qualities in the course of free radical copolymerization with variation of the initial monomers compound, particularly, reaction ability to slight changes of environmental conditions, the sharp and reversible change of their volumes, consequently they can be used as polyfunctional materials in quite diverse fields [4]. The initial task was improvement of quantitative content of nickel and cobalt in new metal-polymer complexes based on «smart» copolymers of p-EGM/AA, p-PGM/AA (Fig. 2).



a — peak intensity of Ni (I) 201.928

b — peak intensity of Co (II) 201.181

Figure 2. Dependence of peaks intensity from the content of metal salts at the variation of metal mass

The spectra given point out (Fig. 2) that percent composition of metals is equal to ~0.4 mass.%, and the correlation of Ni-Co is 52:48 % for p-EGM/AA copolymer, and 49:51 % for p-PGM/AA copolymer. Results of MPC (metal-polymeric complex) morphology investigation carried out are given below in the Table.

Table

#### Morphology of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>, p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> metal-polymer complexes

Sample	Content of metal, % (mass.)	Ratio Ni-Co, %	Dimension of NP (nanoparticles), nm	Morphology of NP (nanoparticles)	Distribution of NP (nanoparticles) in a matrix	Average number of metal particles on 10 microns
p-EGM/AA-Ni <sup>0</sup> -Co <sup>0</sup>	0.40	52:48	500–700	Spherical, rhombic	Proportional	600–700 units for Ni and 550–650 units for particles of Co
p-PGM/AA-Ni <sup>0</sup> -Co <sup>0</sup>	0.35	49:51	600–800	Spherical, rhombic	Proportional	600–700 units for Ni and 550–650 units for particles of Co

Consequently, it was interesting to evaluate and compare qualitative and quantity characteristics of copolymers synthesized. The method of energy dispersive spectroscopy was chosen as the most appropriate determination method of the content of metal-polymer complexes p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>, p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (Fig. 3a and b).

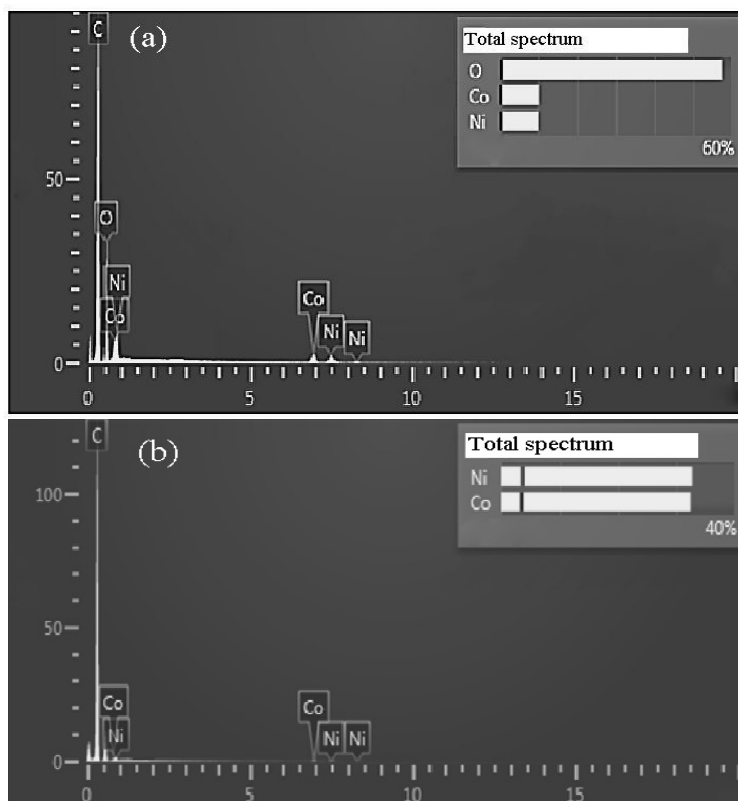


Figure 3. Energy-dispersive analysis: elementary composition of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (a) and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (b)

Also, it has been carried out comparison of infrared-spectra, which are presented in the Figure 4a and 4b to explain the results of the study. We can observe troughs due to stretching vibrations of methyl groups at 2923 cm<sup>-1</sup>; troughs of carbonyl groups are found in the region of 1633–1639 cm<sup>-1</sup>; hydroxyl groups are detected at 3448 cm<sup>-1</sup>, and troughs detecting nickel and cobalt are found in the region of 513–650 cm<sup>-1</sup> of the IR spectra of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>, p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> composites, respectively (Fig. 4a and 4b). Infrared spectroscopy data were proved by the results of thermal analysis.

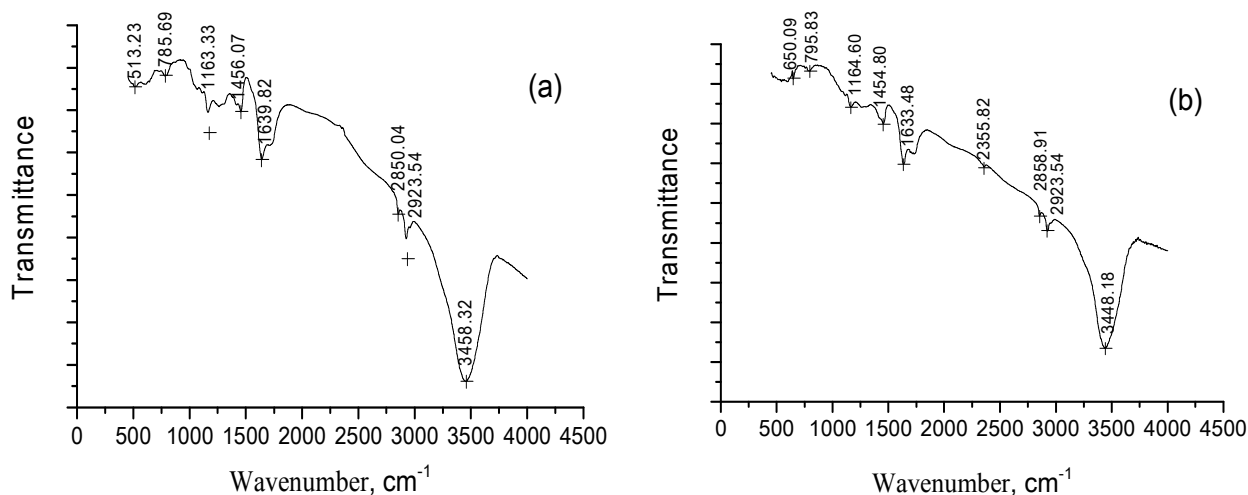


Figure 4. Infrared spectra of bimetal complexes of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (a) and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (b)

During the work, samples of metal-polymer complexes were studied by the method of thermogravimetric analysis. Data of thermogravimetric analysis (TGA) of metal-polymer complexes samples are presented in the Figure 5a and b: p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> with composition 14.8:85.2 mass.% and 15.1:84.9 mass.%.

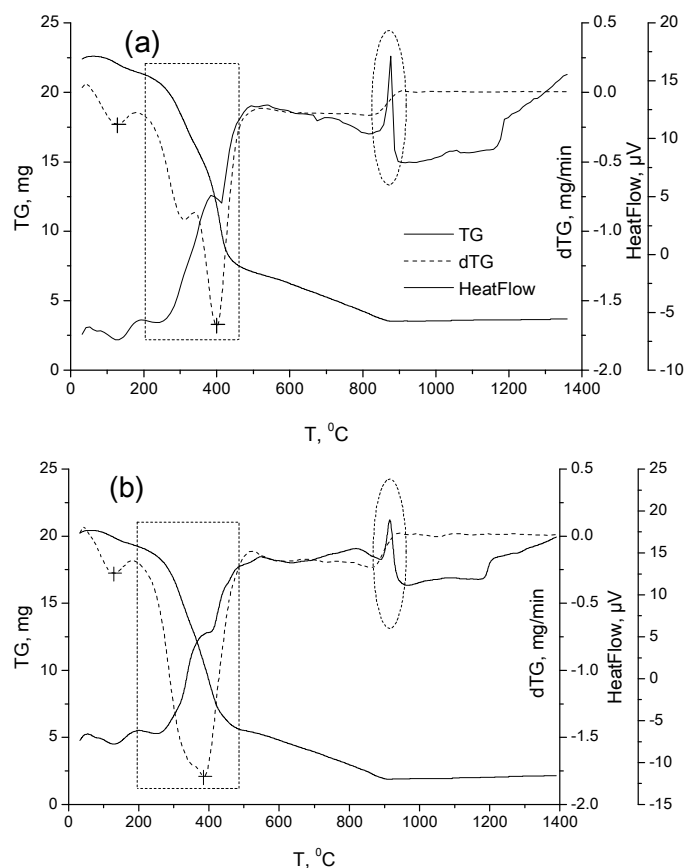
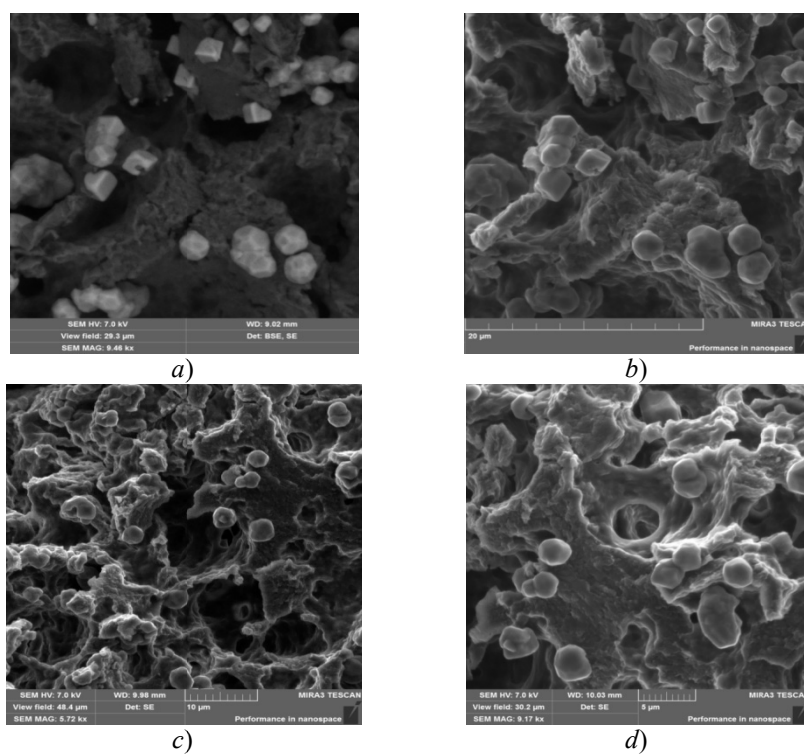


Figure 5. TG, DTG/HF curves of metal-polymer complexes p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (a) and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> (b)

Comparing thermogravimetric curves (Fig. 5a, b) obtained by the TG and HF methods, we can make a conclusion about the rate of thermal decomposition processes in main stages. Preceding slight weight loss on TG-curves at 95–100 °C temperature can be explained by evaporation of free water from the sample. As it is seen from Figure 5 (a and b) thermal decomposition of metal-polymer complexes was carried out within the temperature range of 200–500 °C. Moreover, weight loss on TG-curves is on an average 80 %, and we can see exothermic peak at 880 °C and 915 °C on the HF curves for the metal-polymer complexes of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>, respectively. Therefore, heat aging leads to the development of competitive structural processes in the material and these processes change the structure of the material and its resistance to aging. Morphology of the sample obtained as a result of micro-structural experiments has peculiarity, which is shown in Figure 6a–d.

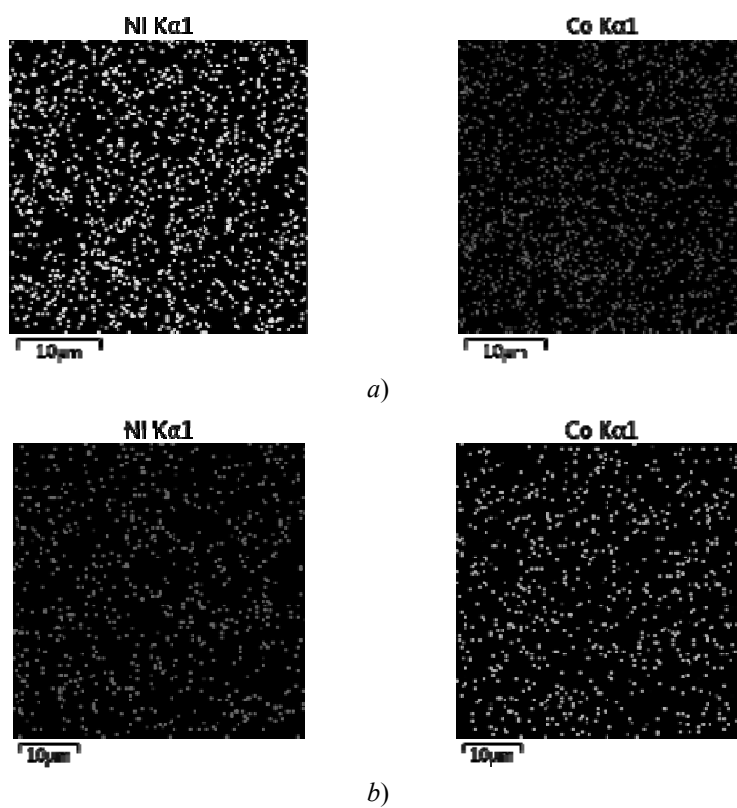
We can see that the metal filler was dispersed on certain grains from the pictures presented in Figure 6, where shape of Ni<sup>0</sup> is similar to spherical, and the shape of Co<sup>0</sup> is similar to rhombic. Also Figure 6 shows that the particle dimensions of metallic nickel and cobalt dispersed in the volume of gels are range within 500–800 nm. Therefore, stability of these metal-polymer complexes (p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>; p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>) to aggregating and oxidation was proved. Taking into account the fact that surface morphology is one of the most important characteristics of nanocatalysts we can approve that the study of the surface morphology using the method of scanning electron microscopy and its analysis is required to characterize the properties of metal-polymer complexes, and to plan the fields of their further study, as well as their further practical application. Results of EMF (electromotive force) analysis of metal particles distributed on matrix of p-EGM/AA and p-PGM/AA copolymers are presented in Figure 7a, b.

Analysis of EMF-pictures of p-EGM/AA (14.8:85.2 mass.%) and p-PGM/AA (15.1:84.9 mass.%) copolymers films revealed a relatively equal distribution of filler (Ni<sup>0</sup>, Co<sup>0</sup>) along the cross-section of the polymer. Average number of metal particles on 10 microns is 600–700 units for Ni and 550–650 units for particles of Co (Fig. 7a, b).



*a, b* — cobalt particles; *c, d* — nickel particles

Figure 6. Electron micrographs of metal particles in nanocatalysts of p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>; p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>



*a* — p-EGM:AA; *b* — p-PGM:AA

Figure 7. Distribution of metal particles on the copolymer matrices

### Conclusions

Ions of such metals as nickel and cobalt in polymeric matrix on the basis of polyethylene glycol maleate and polypropylene glycol maleate with acrylic acid were reduced by the method of wet synthesis. Compositions, structures and dimensions of particles of nickel and cobalt stabilized in polymeric matrix were determined using the methods of transmission electron microscopy and scanning microscopy, infrared spectroscopy, laser-emission spectroscopy, dispersive microscopy and thermogravimetric analysis. It was determined that nanoparticles of metals well-distributed on a whole volume and dimensions and correspond to 500–700 nanometer for p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> bimetal catalyst and 600–900 nanometer for p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup>. The shape of nickel nanoparticles is spherical and the shape of cobalt nanoparticles is rhombic. Therefore, characteristics of obtained p-EGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> and p-PGM/AA-Ni<sup>0</sup>-Co<sup>0</sup> metal-polymeric complexes can be used as a template for the creation of catalytically effective composite materials.

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### п-ЭГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup> және п-ПГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup> негізіндегі металл-полимерлі комплекстердің синтезі мен сипаттары

Металл-полимерлі комплекстердің синтезінде поли-(этилен)-пропиленгликольмалеинаттар (п-ЭГМ, п-ПГМ) мен акрил қышқылы (АК) негізіндегі сополимерлерді қолданудың ықтималдығы көрсетілді. Жүргізілген сараптамалар арқылы полимерлі матрицаларға тұрақтандырылған никель және кобальт бөлшектерінің құрамы, көлемдік сипаттары, құрылымы трансмиссионды-электронды және сканерлеуші микроскопия, инфрақызыл және лазерлі-эмиссиондық спектроскопия, дисперсионды микроскопия және термогравиметриялық талдау әдістерімен анықталды. Нанобөлшектердің орташа көлемі 100–170 нм, сонымен қатар полимерлі матрица бойында біркелкі таралған, сфера формасына ие екендігі көрсетілген. Никель мен кобальттың проценттік мәні сәйкесінше 0,52/0,48 п-ЭГМ/АК және 0,49/0,51 п-ПГМ/АК құрады. 10 мкм-де металл бөлшектерінің таралуы Со үшін 550–650 бірлік, ал Ni үшін 600–700 бірлікке тең. Металл полимерлі комплекстердің термиялық ыдырауы 200–500 °С температурада жүрді. TG-қисығының масса жоғалту мәні орта есеппен 80 %-ды құрады. Синтезделген п-ЭГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup> және п-ПГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup> металл-полимерлі комплекстер каталитикалық белсенді жүйе ретінде пайдалану мүмкіндігіне ие.

*Кілт сөздер:* сополимер, полиэтиленгликольмалеинат, полипропиленгликольмалеинат, полимерлі матрица, нанобөлшек, катализатор, металл-полимерлі комплекс, матрица.

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### Синтез и характеристики металл-полимерных комплексов п-ЭГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup> и п-ПГМ/АК-Ni<sup>0</sup>-Co<sup>0</sup>

Показана возможность использования сополимеров поли-(этилен)-пропиленгликольмалеинатов (п-ЭГМ, п-ПГМ) с акриловой кислотой (АК) в качестве матрицы для получения эффективных металл-полимерных комплексов различного назначения. Методами просвечивающей и сканирующей

микроскопии, ИК-спектроскопии, лазерно-эмиссионной спектроскопии, дисперсионной микроскопии и термогравиметрического анализа установлены состав, структура, размеры стабилизированных в полимерной матрице частиц никеля и кобальта. Средний размер наночастиц, имеющих сферическую форму и равномерное распределение вдоль поперечного сечения полимера, составил 100–170 нм. Процентное содержание никеля и кобальта в комплексе составляет соответственно 0,52, 0,48, в сополимере п-ЭГМ/АК и 0,49, 0,51 в сополимере п-ПГМ/АК. Анализ электродвижущей силы — изображения пленок сополимеров п-ЭГМ:АК (14,8:85,2 масс.%) и п-ПГМ:АК (15,1:84,9 масс.%) показал относительное равномерное распределение наполнителя ( $\text{Ni}^0$ ,  $\text{Co}^0$ ) вдоль поперечного сечения полимера. Среднее количество частиц металлов на 10 мкм составляет 600–700 ед. для Ni и 550–650 ед. для Co. Термическая деструкция металл-полимерных комплексов происходила в интервале температур 200–500 °С. Потеря массы на ТГ-кривых составляет в среднем 80 %. Таким образом, полученные металл-полимерные комплексы п-ЭГМ/АК- $\text{Ni}^0$ - $\text{Co}^0$  и п-ПГМ/АК- $\text{Ni}^0$ - $\text{Co}^0$  могут быть использованы в качестве основы для создания каталитически активных композитных материалов.

*Ключевые слова:* сополимер, полиэтиленгликольмалеинат, полипропиленгликольмалеинат, металл-полимерный комплекс, полимерная матрица, катализатор, наночастица, матрица.

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## **Investigation of the processes of titanium dioxide dispersion in the presence of various surfactants**

An essential factor affecting the effectiveness of protective and decorative properties of paint and varnish compositions due to the use of surfactants with inhibitory activity in their formulations, as well as the ability to form permanent (cohesive, adhesive), decorative, insulating films based on their selective adsorption, seems to be a promising improvement of the coating performance characteristics. The mechanism of their physico-chemical effects on the interface and the dispersed medium as a whole depends on the nature of the surfactants and the contacting phases, as well as their quantitative ratio. The paper presents the results of experimental studies of the regularities of the processes of titanium dioxide disaggregation in an aqueous dispersion medium in the presence of three types of surfactants. Introduction of three versions of surfactants intensify processes of disaggregation of particles of titanium in an aqueous dispersion medium. The maximum dispersing effect with respect to titanium dioxide is set for sodium polyacrylate solution. The average diameter of the solid-phase particles in comparison with the characteristics of the base composition decreased from 13 to 4 microns, when this modified additive was introduced at the level of 0.25 g/L.

*Keywords:* paint-and-lacquer materials, dispersion, pigment, titanium dioxide, aggregation, surfactants, disaggregation, suspension, average diameter, fraction, aggregate, modification.

### *Introduction*

The process of combining a solid component, a pigment with a liquid dispersion medium in the production of paint-and-lacquer coating, is very important, since the technological properties of paints depend on it, as well as many of the operational properties of coatings. An important technological characteristic of paint-and-lacquer materials (PLM) determining the structural and mechanical (covering capacity, wetting [1], hardness, strength) properties of their coatings is the degree of disaggregation of pigments and fillers [2].

Surfactants, molecules of which contain polar groups in the hydrocarbon radical that are lyophilic with respect to the polymer dispersion medium (i.e., bifunctional compounds of various types), are used as pigment surface modifiers for polar dispersion media [3]. This applies to all types of paintwork materials containing polymer solutions in organic solvents (or water for water-soluble polymers) as binder, water-dispersible binders. In recent years, polymeric surfactants have been developed and used due to their high affinity for the polymer medium, can be even more effective than their low-molecular analogues. The method of this pigment surface modification for subsequent incorporation into the polymer medium is very simple, accessible and effective due to the diversity of the polar groups present in the modifier molecules and also to the different structure of their hydrocarbon radicals [4]. However, the action of surfactants in paint-and-lacquer systems is subject to certain physico-chemical laws that must be observed for their effective application.

Development of aggregation and disaggregation processes depends both on the surface properties of the solid-phase particles themselves and on the quantitative-qualitative composition of the film-forming, solvents and surface-active additives in paint-and-lacquer coating suspensions. In this regard, it is necessary to know the effect of all these components on dispersion processes in order to optimize the composition of the paint-and-lacquer coating. The purpose of this work is to study the effect of various surfactants on the processes of dispersing solid-phase particles.

### *Experimental*

We established the patterns of development of the titanium dioxide disaggregation processes (grade R-02) in the composition based on polar solvent (water) and surface-active additives are (TEGO:Glide 100 (polyether siloxane copolymer), Dispers 715W (sodium polyacrylate solution) and Dispers 750W (aqueous copolymer solution).

Surface-active effect of surfactants was established with usage of a computer-optical analyzer [5], which allows determining the fractional composition of suspensions in an automatic mode, as well as the

geometric dimensions and configuration characteristics of individual dispersions. A calculated index  $d$  that characterizes the average particle diameter of pigments in suspensions was used to quantify the degree of disaggregation.

An electronic converter-attachment with a magnification of  $\times 35$  equipped with a standard USB port and a software package was used for an adequate transfer of the image observed in the eyepiece of the microscope. The principle of the electronic video eyepiece is analogous to the principle of the photocell function and consists in converting light energy into electrical energy. The system unit of the attachment with small-format CCD cameras transforms the images fixed in the eyepiece of the microscope into signals acceptable for perception by the Windows XP system in personal computers. Electronic configuration attachments are compatible with traditional microscopes. The CARLZEISS 451422 microscope was used in the system developed by us.

At the first stage, individual image elements were recognized within the software package «Spectrum of differential distribution» using the method of continuous scanning, then they were transferred to the system unit of the computer and stored (documenting). At the second stage, the processing of the video image was performed with obtaining quantitative information about the specific number of particles (per unit area), their geometric parameters (linear dimensions, configuration, and area) and, finally, the general data on fractional composition were obtained in the automatic mode.

The algorithm for data processing includes the following basic operations:

1. Binarization of the previously saved image is the conversion of the image into black and white. In terms of Photoshop, this concept is called «by level 50 %», as this selects a threshold, all values below which turn into a background color (white), and above — to the main color (black).

2. Recognition for continuous scanning and sorting of individual dispersions by the number ( $N$ , units), size and fractional composition ( $P$ , %) by reading their area in pixels ( $S$ , px). Transformation of the calculated particle size index expressed in pixels into metric units (microns).

3. Calculation of the integral and differential characteristics of the particle distribution (by their number, linear parameters and area) and their reflection in the form of diagrams, distribution functions or in tabular form depending on the optimization parameters (in the studies).

4. Derivation of functional dependences (in the form of equations or graphs) of the different integral and differential characteristics of the particle distribution (by number, linear dimensions or area) depending on the above factors. The latter makes it possible to estimate the contribution of each of them to the development of particle aggregation processes in comparative regimes, namely, the theoretical dependence (the additive function obtained with the assumption of the absence of interactions between the particles), and with respect to some basic variant (for example, in the absence of surfactants) [5–7].

The use of metric particle sizes expressed in micrometers is accepted in the daily practice of the production of pigmented paint-and-lacquer materials. In connection with the variety of shapes of pigment particles, for their size, the so-called equivalent diameter of an ideal spherical particle is accepted. The values of  $d$  (microns) were calculated from the results of the determination (for a given multiplicity of magnification  $\times 350$ ) of the total number of particles or their individual associates ( $N$ , pieces) and the total area ( $S_p$ , pixel) they occupy on a fixed (in the eyepiece) image in accordance with the equation (1):

$$D_{med} = 1.129 \cdot k \cdot \frac{S_p}{N}, \quad (1)$$

where  $S_p$  — is an area of all particles, pixel;  $N$  — is a total number of particles; 1.129 — is a constant;  $k$  — is a conversion factor to metric units (2):

$$k = \sqrt{\frac{S_0}{S_{p_0}}}. \quad (2)$$

For a standard sample with  $S_0 = 4 \cdot 10^4 \mu\text{m}^2$  at a given (in the experiments) multiplicity of the increase by  $\times 350$ , the area ( $S_{p_0}$ ) in DPI units is 32.400; value  $k = 1.235 \mu\text{m}/\text{pixel}^{1/2}$ . The disaggregating effect was additionally established by the content of fractions ( $P$ , %) of the class — (minus) 44.34 microns.

The procedure for the preparation of suspensions with different surfactant contents (0–8 g/dm<sup>3</sup> (for pigment weight) consisted in preliminary dissolution of a certain mass in a solvent. The resulting solutions (hereinafter A) were sent to prepare suspensions, which was carried out at a temperature of 20 °C in a sealed reactor (volume — 0.2 dm<sup>3</sup>, cover factor — 0.60) equipped with an agitator (impeller agitator, frequency — 300 min<sup>-1</sup>). The quantitative contents of the titanium dioxide pigment (1 % by weight of the suspension) in the system were varied due to the change in mass loading into solutions A. To stabilize the deformation pro-

cesses, the samples of suspensions analyzed with a pneumodosimeter (drop volume — 0.02 ml) were placed on a specimen slide, then fixed with a cover slip and kept under static load (10 g/cm<sup>2</sup>) and were subjected to microanalysis for 5 minutes.

*Results and discussion*

*System «solvent-pigment-surfactant»*

Distribution of dispersions of titanium dioxide pigment by size classes in suspensions containing no surfactant is characterized by the diagram shown in Figure 1. Fractions with a size of +198.30–451.56 microns predominate in suspensions; the content of fractions of this class — 198.30 microns is 52.00 %, fine fractions — not more than 25.00 %. Specific amount of pigment particles of titanium dioxide in the absence of surfactants was 2,300 microns, and their average size is 13.00 microns.

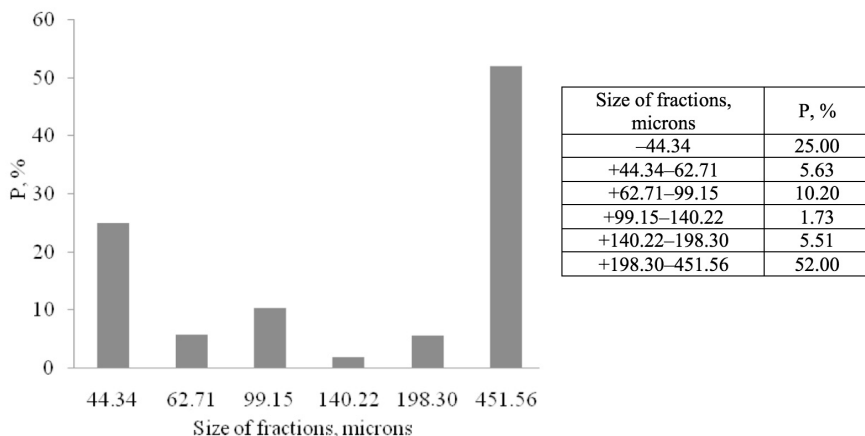


Figure 1. Differential distribution curves by the fineness of the titanium dioxide pigment fractions in a polar solvent

The processes of disaggregation of solid-phase particles of titanium dioxide were intensified significantly with insignificant dosing of surface-active compounds. The positive effect of the surfactants presented is consistent with the patterns of changes in the content of fine fractions (*P*) and average diameter (*d*) of the particles (Fig. 2a, b) in suspensions. The experimental values of the main parameters of the dispersion of solid-phase dispersions in the presence of various types of surfactants are shown in Figure 2.

The maximum disaggregating effect with respect to the titanium dioxide pigment judging by the nature of the change in the average particle size (minima in Figure 2a) is provided at the Dispers 715W surfactant discharge at 0.25–0.50 g/dm<sup>3</sup>. The mean statistical particle diameter in the same row decreased by no less than 60.00 % (from 13.00 microns to 4.00–7.00 microns) in the presence of Glide 100, Dispers 715W and Dispers 750W in comparison with the characteristics of the basic composition (without surfactant additives).

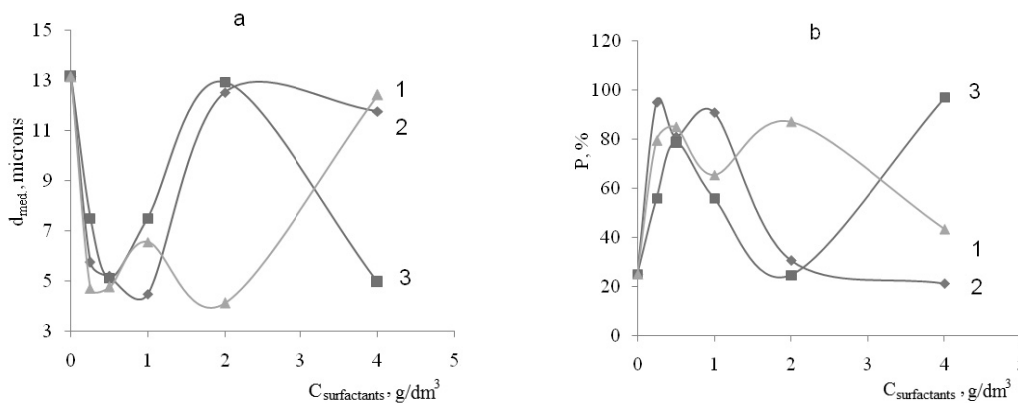


Figure 2. Effect of surfactant coverage rate (1-Dispers 715W, 2-Dispers 750W, 3-Glide 100) on the average diameter (a) and on the content of fine particles of the pigment particles (b)

The positive contribution of surfactants to the development of disintegration processes is confirmed (Fig. 2b) and the increased content of fine fractions ( $\leq 44.34$  microns) in the case of Dispers 750W dispersant, from 25.00 to 73.00 %; at the above coverage rate of Glide 100 and Dispers 715W, the relative content of particles of this class increased by 55.00 and 68.00 %. Thus, the dispersion effect in the presence of surfactant is ensured by the destruction of large aggregates of titanium dioxide.

The development of the opposite process is observed with an increase of coverage rate (from 1.00 to 2.50 g/dm<sup>3</sup>) of Glide 100 and Dispers 750W surfactants, an aggregation of solid-phase particles, which corresponds to an increase in the average diameter of the pigment particles from 4.00 to 12.50 and from 7.00 to 13.00 microns, respectively. The aggregation processes were practically not observed in the presence of Dispers 715W and when the coverage rates varied from 0.25 to 0.80 g/dm<sup>3</sup>, the characteristics of the dispersed pigment composition of titanium dioxide remained practically at the same level ( $d \approx 4.00$ – $6.00$  microns;  $P \approx 79.00$ – $85.00$  %). Based on this, it follows that the concentration range of the Dispers 715W is less restricted than that of Dispers 750W and Glide 100. It should also be noted that with an increased concentration of Dispers 750W and Dispers 715W (4.00 g/dm<sup>3</sup>), the average statistical diameter of the pigment particles is increased almost identically to the initial value of the diameter in the absence of surfactants (12.00 microns) and a decrease in the fine fraction by 77.00 and 50.00 %, respectively, which indicates the inappropriate use of these surfactants at high concentrations. A slightly different mechanism is observed in the case of the Glide 100 surfactant at the same concentration. The average statistical diameter of solid-state particles decreases up to 62.00 % and, as a consequence, the content of the fine fraction increases in the high-coverage rates region of this modifier (4.00 g/dm<sup>3</sup>). This phenomenon suggests the possibility of using this surfactant at elevated system concentrations (above 4.00 g/dm<sup>3</sup>).

### Conclusions

As a result of investigations it can be concluded that introduction of three versions of surfactants intensify the processes of disaggregation of particles of titanium in an aqueous dispersion medium. The maximum dispersing effect with respect to titanium dioxide is set for Dispers 715W. The average diameter of the solid-phase particles in comparison with the characteristics of the base composition decreased from 13.00 to 4.00 microns when this modified additive was introduced at the level of 0.25 g/dm<sup>3</sup>.

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## Түрлі беткі белсенді заттардың қатысуымен титан қос тотығының ыдырау процестерін зерттеу

Лак-бояу жабындарының қорғау және сәндік қасиеттерінің тиімділігіне ықпал ететін елеулі фактор оларды құрамына енетін дақтар мен толтырғыштардың бытырағыштық дәрежесі болып табылады. Лак-бояу композицияларын құрамына баяулатқыш белсенділікке, сондай-ақ олардың негізінде саралы

сіңіруді қалыптастыру қабілетіне ие беткі белсенді заттарды (ББЗ) енгізу есебінен оларды түрлендіру, берік (жұғу, жабысу), сәндік, оқшаулау қабықшалары, жабындардың пайдалану сипаттамаларын жақсартудың перспективалық бағыты болып танылады. Олардың фазалар бөлігінің бетіне және шашыранды ортаға физика-химиялық әсерінің механизмі тұтастай алғанда ББЗ және жанасатын фазалардың табиғатына, сондай-ақ олардың сандық арасалмағына байланысты. Жұмыста титан қос тотығының сулы шашыранды ортада ББЗ үш түрінің қатысуымен агрегатсыздану процестерінің дамуы заңдылықтарының тәжірибелік зерттеу нәтижелері келтірілген. Беткі белсенді заттардың үш түрін енгізу су-дисперсиялық ортада титан диоксидінің бөлшектерін дезагрегациялау үдерісін қарқындатады. Титан диоксидіне қатысты максималды диспергирлеуші әсер натрий полиакрилаты ерітіндісі үшін тағайындалған. Осы түрлендірілген қоспаны 0,25 г/л деңгейінде енгізген кезде базальқ құрамның сипаттамаларымен салыстырғанда қатты фазалық бөлшектердің орташа статистикалық диаметрі 13 мкм-ден 4 мкм-ге дейін төмендейді.

*Кілт сөздер:* лак-бояу жабындары, бытырағыштық, дақ, титан қос тотығы, агрегаттану, беткі-белсенді заттар, агрегатсыздану, суспензия, орта статистикалық диаметр, фракция, агрегат, түрлендіру.

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## Исследование процессов диспергирования диоксида титана в присутствии различных поверхностно-активных веществ

Существенным фактором, влияющим на эффективность защитных и декоративных свойств лакокрасочных покрытий, является степень дисперсности входящих в их составы пигментов и наполнителей. Модифицирование лакокрасочных композиций за счет введения в их составы поверхностно-активных веществ (ПАВ), обладающих ингибирующей активностью, а также способностью формировать, на основе их избирательной адсорбции, прочные (когезионные, адгезионные), декоративные, изолирующие пленки, представляется перспективным направлением улучшения эксплуатационных характеристик покрытий. Механизм их физико-химического воздействия на поверхность раздела фаз и дисперсную среду в целом зависит от природы ПАВ и контактирующих фаз, а также их количественных соотношений. В статье приведены результаты экспериментальных исследований закономерностей развития процессов дезагрегации диоксида титана в водной дисперсионной среде в присутствии трех разновидностей ПАВ. Введение трех разновидностей поверхностно-активных веществ интенсифицирует процессы дезагрегации частиц диоксида титана в водной дисперсионной среде. Максимальный диспергирующий эффект по отношению к диоксиду титана установлен для раствора полиакрилата натрия. При введении данной модифицированной добавки на уровне 0,25 г/л среднестатистический диаметр твердофазных частиц по сравнению с характеристиками базового состава уменьшился с 13 до 4 мкм.

*Ключевые слова:* лакокрасочные покрытия, диспергирование, пигмент, диоксид титана, агрегация, поверхностно-активные вещества, дезагрегация, суспензия, среднестатистический диаметр, фракция, агрегат, модификация.

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(E-mail: l-a.13@mail.ru)***Study of paint and varnishes systems structuring in the presence of surfactants**

Introduction of surfactants in paintwork materials composition is one of the effective ways to improve their quality. It is obvious that introduction of surface-active additives in coating compositions changes not only the dispersity of the pigments and fillers included into the composition, but also the nature of the adsorption and intermolecular interactions in the system. With the help of low-frequency dielectrometry, a physical grid of intermolecular bonds was detected in the process of its formation. The regularities of the structurization of amines and polyphenylsiloxane in solutions of toluene were established by viscosimetric method. According to the results of viscosimetric analysis, the regularities of surface tension change for polyphenylsiloxane solutions were revealed: as the concentration increases from 0 to 2 g/dm<sup>3</sup>, the surface tension decreases from 28 to 26 mJ/m<sup>2</sup>. Rheological data showed that deviations from the ideal system exist in the region of the studied concentrations, i.e., there is an association of molecules of the amino derivatives with macromolecules of polyphenylsiloxane (heteroassociation). It is proved that formation of macromolecular structures is inherent in all three varieties of amines and is substantially enhanced in concentrated solutions.

*Keywords:* organosilicon paint and varnishes, intermolecular interactions, viscosimetry, dielectrometry, toluene, additive, amines, polyphenylsiloxane, relative viscosity, surface tension.

*Introduction*

Organosilicon (silicone) paint and varnishes historically occupy a significant share of the paint and varnishes market [1]. These materials are hybrid organo-inorganic composites. Combining the characteristics of both organic and inorganic substances, such structures have great potential in the development of new materials that have a variety of physical, technical and operational characteristics [2]. One of the effective ways to improve the quality of paint and varnishes is to introduce surfactants into their composition [3]. It is obvious that the introduction of surfactants in paint and varnishes changes not only the dispersability of the pigments and fillers included in them, but also the nature of the adsorption and intermolecular interactions in the system. According to the molecular (adsorptive) theory of polymer adhesion, the interactive data, which are manifested in the establishment of the molecular contact of macrochains with the active centers of the substrate and the following formation of adhesion bonds, depends largely on the polarity and flexibility of the polymer chains [4]. The purpose of this work is to study the effect of various surfactants on intermolecular interactions in silicone paint and varnishes.

*Experimental*

During the research, the following substances were used, namely, silicone film-forming (polyphenylsiloxane varnish), toluene solvent (State Standard 14710–78) and three varieties of amine-based surfactants of different molecule-weight composition (Table 1).

Table 1

**Surfactants Characteristics**

Surfactants name	Weighted average molecular mass, a.m.u	Amine number, mg HCl/g	Brief Description
HMA	250	30	Mixture of primary and secondary amines
CMA	350	32	Condensation product of vegetable oils with diamines
BMA	600	31	High-molecular amine mixture

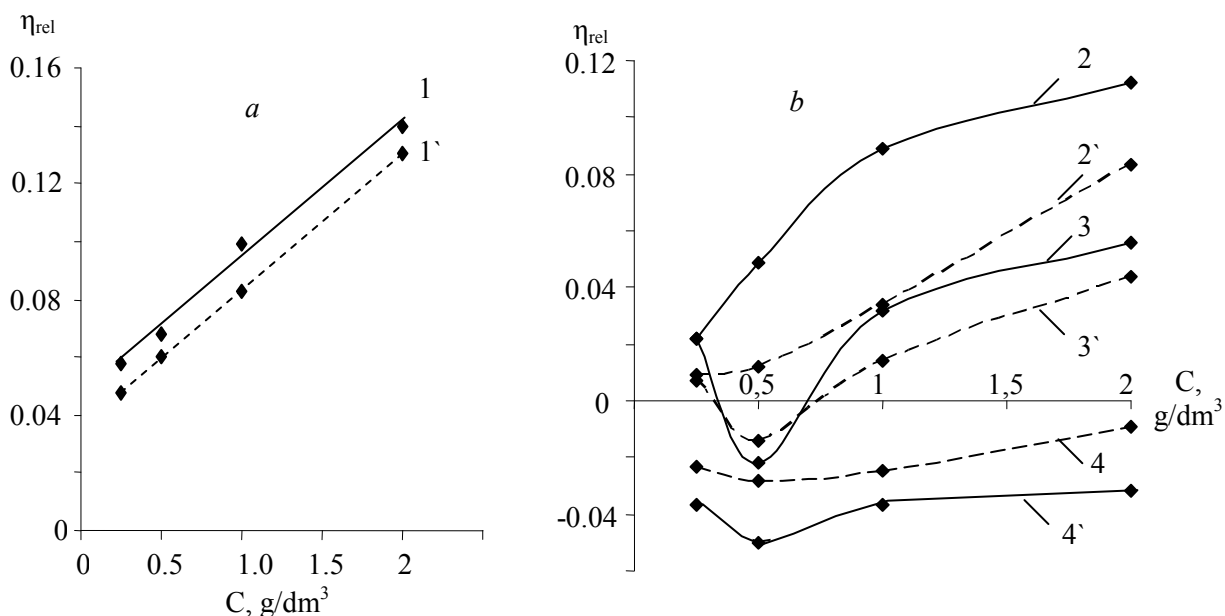
A viscosimetric method was used to assess the nature and regularities of amines and polyphenylsiloxane structuring in toluene solutions. The dynamic viscosity of the prepared solutions was measured with a capillary viscosimeter ( $d = 0.56$  mm) in a temperature-controlled mode [5].

A low-frequency dielectrometry has been successfully applied to detect the physical grid of intermolecular bonds in the process of its formation [6]. Orientational polarization, as well as deformation, was record-

ed for the periods of charge and discharge of the capacitance sensor by a stable current in the frequency range of 1–10 kHz. The experimental values of the dielectric capacitance ( $\epsilon'$ ) and the dielectric loss tangent ( $\tan \delta$ ) were used to find the dipole-segment loss coefficient  $\epsilon''$  ( $\epsilon'' = \epsilon' \times \tan \delta$ ) [4], which usually increases with polarity increase and molecular mobility of the polymers. Considering the fact that the development of structuring processes is accompanied by an increase in the cohesive interaction of molecules, it seemed reasonable to determine the change in this parameter from the results of measuring the solutions surface tension by the method of the greatest pressure of air bubbles (the Reh binder device) [5]. The volume-surface properties of individual solutions (toluene-additive, toluene-polyphenylsiloxane) and solutions of mixed composition (toluene-polyphenylsiloxane-additive) were established by varying the content of amines and polyphenylsiloxane (0–2 g/dm<sup>3</sup>) and T (295–313 K).

### Results and discussion

The results of rheological studies of individual solutions are shown in Figure 1a, b. The analysis of the change in the relative viscosity of polyphenylsiloxane (PPS) solutions showed (Fig. 1a) that at a constant temperature, as the concentration increases, a linear increase in viscosity is observed. These results are consistent with the literature data [7] and indicate weak intermolecular interactions in PPS solutions. The latter is obviously connected with the special structure of the PPS macromolecules, in which the inorganic chain of silicon and oxygen atoms is surrounded by aryl radicals. The argument for this observation is that for amino derivatives containing amino groups with different degrees of substitution, and at the ends of chains, as well as primary concentrations dependences of the relative viscosity have an entirely different nature and reflect their tendency to associate processes (Fig. 1b). The formation of associated structures judging by the significant deviation from the linear dependence  $\eta_{rel.}=f(C)$  was noted in solutions of all amino derivatives varieties at concentrations above 0.5 g/dm<sup>3</sup>; and the association effects increase with the further increase of their concentration in the solution. The viscosity increase at the concentration range of 0.5–2g/dm<sup>3</sup> corresponds to the molecule-mass ratio of the amino derivatives and increases in the series: BMA>CMA>HMA.



Full line — 298 K; dashed line — 313 K; 1, 1' — PPS; 2, 2' — BMA; 3, 3' — CMA; 4, 4' — HMA

Figure 1. Dependence of individual solutions relative viscosity on the concentration of polyphenylsiloxane (a) and amino derivatives (b) at different temperatures

The changes observed in the relative viscosity agree with the surface tension isotherms ( $\sigma$ ) of the solutions at the interface with air and simultaneously find an explanation from the intermolecular associates formation positions and the localization degree of active functional groups. The features of the amino deriva-

tives surface activity in solutions under study clearly reflect the extremes, which differ in intensity and width, presented in Figure 2a, b.

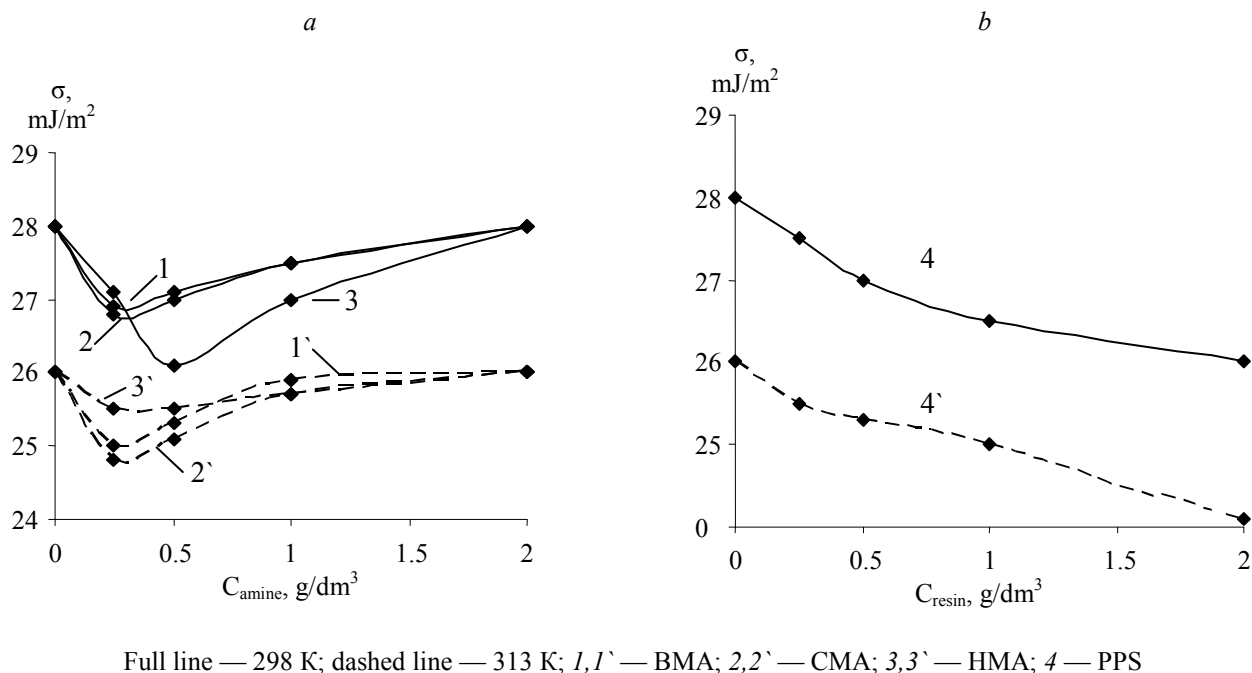


Figure 2. Isotherms of individual solutions surface tension at the interface with air

Judging by the surface tension isotherms ( $T=298$  K), in the concentration range, when association effects are practically not manifested, the presence of unbound amino derivatives diphilic molecules in the solution has stimulated their concentration in the surface layer, which is confirmed by a decrease in the surface tension values. In this case, two concentration sections can be distinguished, which allow to distinguish between low-molecule and higher-molecule types of amino-derivatives by activity. In solutions with  $C \leq 0.25$  g/dm<sup>3</sup>, the highest surface activity is characterized by BMA and CMA. The surface-active properties of a lower molecule mass amine species are enhanced in more concentrated solutions. The maximum depression of surface tension ( $\Delta\sigma = 1.9$  mJ/m<sup>2</sup>) was recorded in HMA solutions at a concentration of  $0.5$  g/dm<sup>3</sup>. As the concentration further increases ( $C > 0.5$  g/dm<sup>3</sup>) the development of the structure formation processes was accompanied by the spontaneous decrease in the unbound (free) molecules of the amino derivatives and the corresponding continuous deterioration of the surface properties (ascending isotherms). At  $C=2.0$  g/dm<sup>3</sup> the surface tension was stabilized in solutions at a level of  $28.0$  mJ/m<sup>2</sup>, which corresponds to the  $\sigma$  value of the solvent (toluene). This indicates that there are no more amino derivatives in the surface layer and about complete localization of the functional groups in the internal structure formed in the volume of the intermolecular associates' solution.

It should be noted that the effect of temperature on the indices of  $\eta_{\text{rel}}$  and  $\sigma$  for the amino derivatives of different molecule-mass composition are not precise. If in the BMA and CMA solutions, at the temperature increase up to  $T=313$  K, the relative viscosity values decrease, then in the solutions of the low-molecule variety of amines, their increase was noted, and the main increase was fixed at  $C=0.5$  g/dm<sup>3</sup> (Fig. 1b). The latter may be due to the intensification of solvation processes binding by HMA solvent.

The legality of this justification confirms a sharp deterioration in the HMA surface activity (Fig. 2a); in comparison with  $\sigma$  solutions at  $T=298$  K, the decrease in the values of surface tension ( $\Delta\sigma$ ) regarding the solvent (without surfactants) decreased by 2–4 times and equaled  $0.5$  mJ/m<sup>2</sup>. The depression of surface tension remained at the same level ( $\Delta\sigma=1.2 \pm 0.2$  mJ/m<sup>2</sup>) on the contrary to BMA and CMA solutions in the same concentration range.

The surface activity deterioration in the first case and the invariance in the second case exclude the release of amines and, consequently, the destruction of intermolecular structures at  $T=313$  K, which would be logical suspect, given the natural increase in the associates thermal motion at temperature increase. At the same time, it is known that the relative viscosity values that exclude the influence of solvent thermal expan-



sion are determined not only by the number of associates, but also by the steric restrictions they create for the liquid flow.

Summarizing the abovementioned, we can state that for HMA, which is characterized by smaller hydrocarbon radical dimensions, the thermodynamic quality of the solvent improves, which leads to swelling of the associate balls and, thus, to an increase in the relative viscosity. The temperature increase causes an increase in intermolecular interactions within the associates for higher molecular amines, which is accompanied by a decrease of their sizes. The intermolecular structures folded into a tight ball give less resistance to the flow and, as a result, the values of  $\eta_{rel}$  decrease in solutions with  $C = 1 \text{ g/dm}^3$  in 2.4–2.6 times, and at a larger content ( $C = 2 \text{ g/dm}^3$ ) in 1.3–1.4 times.

The results of the viscosimetric analysis are confirmed by the regularities of the surface tension change and for PPS solutions (Fig. 2b), which demonstrate the traditional form of silicone surfactants isotherms not prone to association processes: as the concentration increases from 0 to  $2 \text{ g/dm}^3$ ,  $\sigma$  decreases from 28 to  $26 \text{ mJ/m}^2$ . The same maximum depression of surface tension ( $2 \text{ mJ/m}^2$ ) was observed with increasing temperature ( $T=313 \text{ K}$ ).

Similar experiments were carried out for solutions with a fixed polyphenylsiloxane concentration ( $0.5 \text{ g/dm}^3$ ), but with different contents ( $C, \text{ g/dm}^3$ ) of all three amines varieties.

The results of rheological studies and surface tension in mixed composition solutions are presented in Table 2 and Figure 3 (a, b, c). As a quantitative measure of the processes developed in the volume and on the interphase boundaries, along with the experimental indices  $\eta_{rel}$  and  $\sigma$ , and their calculated values for an ideal system (in the absence of intermolecular interactions between the mixture components) were also used. In addition, for a comparative evaluation of these processes, the surface tension differential changes were calculated:

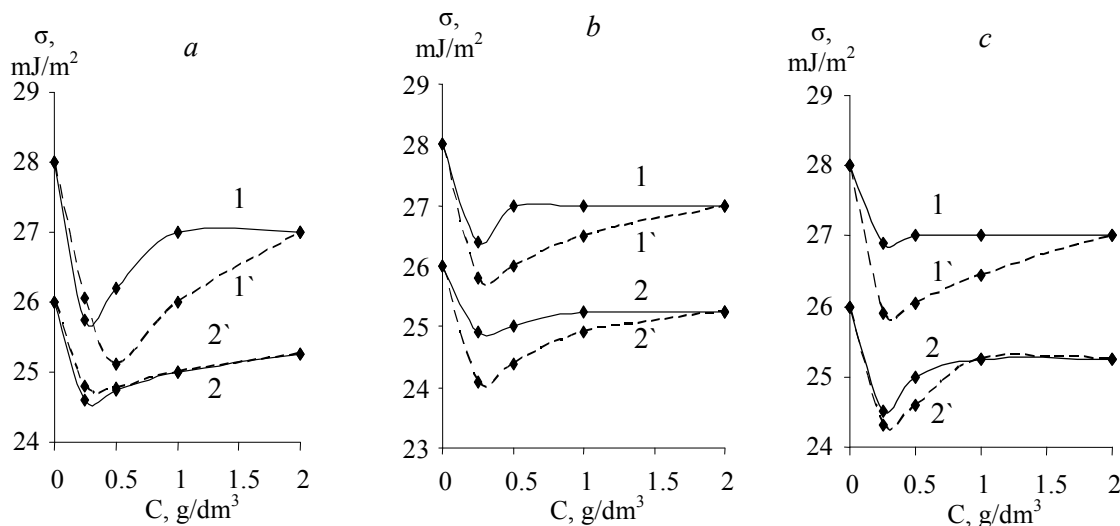
$$\Delta\sigma = \sigma_{exp.} - \sigma_{calc.} \text{ and relative for relative viscosity: } \gamma = \frac{\eta_{rel.exp.}}{\eta_{rel.calc.}}$$

Table 2

Relative viscosity calculated and experimental values

$C, \text{ g/dm}^3$	$T = 298\text{K}$			$T = 313\text{K}$		
	$\eta_{rel.exp.}$	$\eta_{rel.calc.}$	$\gamma$	$\eta_{rel.exp.}$	$\eta_{rel.calc.}$	$\gamma$
HMA						
0.25	0.033	0.031	1.050	0.039	0.037	1.05
0.5	0.063	0.018	3.500	0.048	0.032	1.50
1	0.077	0.031	2.480	0.056	0.035	1.60
2	0.089	0.036	2.470	0.083	0.051	1.63
CMA						
0.25	0.092	0.090	1.020	0.089	0.067	1.33
0.5	0.078	0.066	1.180	0.073	0.046	1.59
1	0.089	0.100	0.890	0.112	0.074	1.51
2	0.107	0.124	0.860	0.131	0.104	1.86
BMA						
0.25	0.078	0.090	0.870	0.092	0.090	1.02
0.5	0.102	0.118	0.860	0.078	0.066	1.18
1	0.121	0.157	0.770	0.089	0.100	0.89
2	0.140	0.187	0.770	0.107	0.124	0.86

The data obtained (Table 2) show that in the studied concentration range, there are deviations from the ideal system, i.e. there is an association of molecules of amino derivatives with PPS macromolecules (heteroassociation). It should be noted that the development of heteroassociation processes is much more noticeable, judging by the value of  $\gamma$ , in solutions with a low molecular mass variety of amines; the greatest change in the relative viscosity (by a factor of 3.5) was noted at  $C = 0.5 \text{ g/dm}^3$  and  $T=298 \text{ K}$ . The formation of intermolecular structures is confirmed by an increase in the cohesive interaction strengthes in HMA solutions and a shift of the surface activity maximum to the region of lower concentrations (Fig. 3a).



Full line — experimental dependence; dashed line — calculated dependence;  
 T, K: 1 — 298; 2 — 313; a — HMA; b — BMA; c — CMA

Figure 3. The effect of the amine-containing surfactants concentration on the surface tension of polyphenylsiloxane solutions ( $C=0.5 \text{ g/dm}^3$ )

In a narrow range of concentrations ( $C \leq 0.25 \text{ g/dm}^3$ ), a negative deviation of the  $\sigma$  values is observed in comparison with the ideal system ( $-0.5 \text{ mJ/m}^2$ ), i.e. in the absence of intermolecular interactions in the solution ( $\gamma=1.05$ ) a synergism is observed in the surface properties of the binary mixture. Outside this interval, a positive deviation of the surface tension experimental values from the additive contribution of the two components (PPS and HMA) was recorded. The maximum intensification of heteroassociation processes at  $C=0.5 \text{ g/dm}^3$  ( $\gamma = 3.5$ ) corresponds to the maximum increase in  $\sigma$  ( $\Delta\sigma=+1.03 \text{ mJ/m}^2$ ), due to the decrease in unbound amines. Stabilization of the structure formation processes ( $\gamma = 2.47-2.48$ ) at  $C=1-2 \text{ g/dm}^3$  is consistent with the invariance of the surface tension in this concentration region, which in its values  $27.0 \text{ mJ/m}^2$  practically coincided with the surface tension of PPS solutions without amines.

The temperature increase (up to  $T=313 \text{ K}$ ) was accompanied by a quantitative destruction of heteroassociates, as indicated by the additive contribution of PPS macromolecules and the released amines (as a result of breaking bonds) in the change in surface tension, and a decrease in the values of  $\gamma$  by a factor of 1.5–2.

The formation of associated structures, judging by the significant increase in  $\sigma$ , is not excluded in solutions of higher molecular varieties of amines (Fig. 3b, c). The association processes are developed at lower concentrations in solution in comparison with HMA, which leads to inversion of surface activity. If in toluene individual solutions, as indicated above, with  $C=0.25 \text{ g/dm}^3$ , the CMA and BMA had the greatest surface activity, then the opposite effect was observed in the joint presence with PPS. The stability of the formed heteroassociates and the variety changes vectorially in the  $\eta_{\text{rel}}$  ( $\gamma < 1$  and  $\gamma > 1$ ) in solutions with higher molecule amines indicate differences in the mechanisms of amine association with PPS macromolecules.

The results of dielectrometric measurements (Fig. 4a) suggest that the amino derivatives, depending on individual characteristics (composition, structure, spatial orientation) undergo two types of over- and intramolecular transformations. The first corresponds to the association of HMA molecules with PPS macromolecules, i.e. the formation of peculiar surfactant-polymer complexes. Movable, easily penetrating into the structure of the HMA polymer, when reaching a critical concentration of association ( $C_{\text{KKA}} > 0.25 \text{ g/dm}^3$ ), being fixed (due to hydrogen and weaker van der Waals forces) along the length of the PPS macromolecule, promotes the expansion of its molecules and the formation of additional bonds between them. As a result, the chain mobility decreases (Fig. 4a), and the structure strength increases, which reflects the increase in dynamic viscosity (Fig. 4b). Process stabilization at a concentration range of  $1-2 \text{ g/dm}^3$  confirms the invariance of the indices  $\epsilon''$  and  $\eta$ .

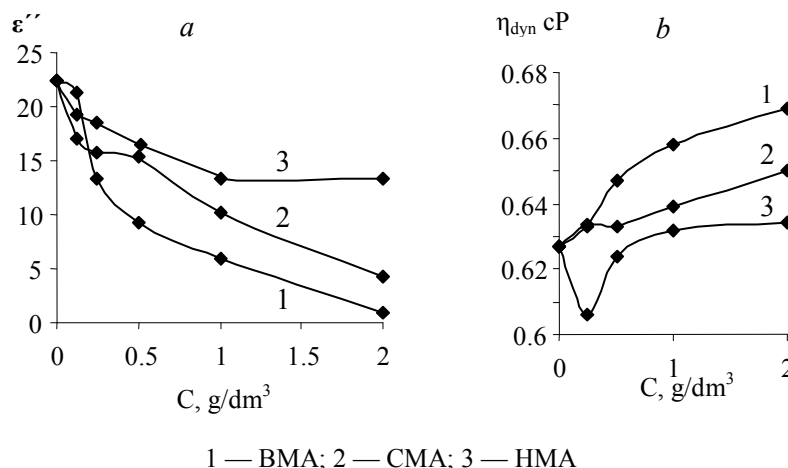


Figure 4. The concentration effect of amine-containing surfactants on the dipole-segmental coefficient (*a*) and the dynamic viscosity (*b*) of polyphenylsiloxane solutions ( $C=0.5 \text{ g/dm}^3$ ) at  $T=298 \text{ K}$

A significantly longer length of the hydrocarbon radical CMA and BMA will limit their migration in the solution volume, and create steric restrictions for this type of heteroassociation. For CMA and BMA, the interaction between each other (monoassociation) is energetically more advantageous with the simultaneous introduction into their composition of PPS macromolecules (mixed micelles). As the PPS macromolecules are included in the association composition, a continuous decrease in the chain mobility and a synchronous increase in the dynamic viscosity (curves 1 and 2 in Fig. 4*a, b*) were recorded.

#### Conclusions

Thus, the formation of macromolecular structures is inherent in all three varieties of amines and is substantially enhanced in concentrated solutions. The processes of heteroassociation reduce the amines surface activity and shift it into the region of lower concentrations.

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### Беткі белсенді заттардың қатысуымен бояу жүйелерін құрылымдауды зерттеу

Лак-бояу материалдарының сапасын жақсартудың тиімді тәсілдерінің бірі болып олардың құрамына беткі-белсенді заттарды енгізу табылады. Әлбетте, лак-бояу композицияларына беткі-белсенді қоспаларды енгізу оның құрамына кіретін пигменттер мен толықтырғыштардың дисперсиялығын ғана емес, сондай-ақ жүйедегі адсорбциялық және молекулааралық өзара әрекеттесулердің сипатын өзгертеді. Төменжілікті диэлектрометрияның көмегімен ол қалыптасу үдерісінде молекулааралық

байланыстардың физикалық торын детекциялау жүргізілді. Вискозиметриялық әдіспен толуол ерітінділерінде аминдер мен полифенилсилоксанды құрылымдастырудың заңдылықтары тағайындалды. Вискозиметриялық талдаудың нәтижелері бойынша полифенилсилоксандар ерітінділері үшін беткі керілістерді өзгертудің заңдылықтары анықталды: концентрация 0 бастап 2 г/дм<sup>3</sup> дейін ұлғаю шамасына қарай беткі керіліс 28 бастап 26 мДж/м<sup>2</sup> дейін төмендейді. Реологиялық деректер көрсеткендей, зерттелетін концентрациялардың аймағында мінсіз жүйеден ауытқымалар бар, яғни полифенилсилоксанның макромолекулалары бар амин туындылары молекулаларының ассоциациясы (гетероассоциация) орын алды. Макромолекулалық құрылымдардың түзілуі аминдердің барлық үш түріне тән екені және концентрацияланған ерітінділерді айтарлықтай күшейетіні дәлелденді.

*Кілт сөздер:* молекулааралық өзара әрекеттесу, вискозиметрия, диэлектрметрия, толуол, қоспалар, аминдер, полифенилсилоксан, беттік керілу, нақты тұтқырлық.

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## Исследование структурирования лакокрасочных систем в присутствии поверхностно-активных веществ

Одним из эффективных способов улучшения качества лакокрасочных материалов является введение в их состав поверхностно-активных веществ. Очевидно, что введение поверхностно-активных добавок в лакокрасочные композиции изменяет не только дисперсность входящих в них пигментов и наполнителей, но и характер адсорбционных и межмолекулярных взаимодействий в системе. С помощью низкочастотной диэлектрметрии было произведено детектирование физической сетки межмолекулярных связей в процессе её формирования. Вискозиметрическим методом установлены закономерности структурирования аминов и полифенилсилоксана в растворах толуола. По результатам вискозиметрического анализа выявлены закономерности изменения поверхностного натяжения для растворов полифенилсилоксанов: по мере увеличения концентрации от 0 до 2 г/дм<sup>3</sup> поверхностное натяжение снижается от 28 до 26 мДж/м<sup>2</sup>. Реологические данные показали, что в области исследуемых концентраций существуют отклонения от идеальной системы, т.е. имеет место ассоциация молекул аминокислот с макромолекулами полифенилсилоксана (гетероассоциация). Доказано, что образование макромолекулярных структур присуще для всех трёх разновидностей аминов и существенно усиливается в концентрированных растворах.

*Ключевые слова:* кремнийорганические лакокрасочные материалы, межмолекулярные взаимодействия, вискозиметрия, диэлектрметрия, толуол, аддитивы, амины, полифенилсилоксан, поверхностное натяжение, удельная вязкость.

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### **Theoretical calculations of natural penicillins: structural and electronic properties**

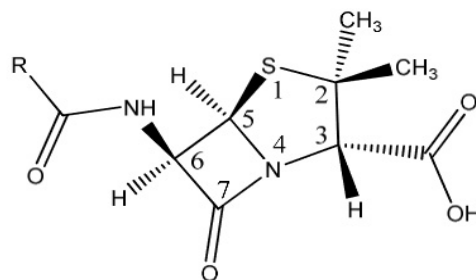
The influence of the calculation method and small structural change in the molecule on the results of geometry and other properties of compounds was studied on the example of known antibiotics. The structural, electronic, and thermodynamic properties of penicillin and phenoxymethylpenicillin were calculated using molecular mechanics and quantum mechanics methods. A comparative analysis of penicillin structures based on experimental data and calculations was carried out. A molecular model of the experimental geometry was considered as the starting structure, which was then optimized. The geometric parameters were computed using the Ellinger MM2 force field method, semi-empirical PM6 one, and *ab initio* Hartree-Fock (HF) method with the Dunning's correlation consistent basis set cc-pVDZ. Although theoretical calculations were carried out in gaseous phase, cc-pVDZ-optimized geometry of the molecules is close to the crystal structure. Some theoretical parameters for optimized structures of the title compounds, such as total electronic energy, zero-point energy, rotational constants and dipole moments were defined by HF method. The electronic properties as HOMO and LUMO energies for both penicillins were calculated. Thermodynamic properties (heat capacity, entropy) of ones were computed by an *ab initio* method that took into account the correlation effects.

*Keywords:* penicillin, phenoxymethylpenicillin, structure, thermodynamic properties, HOMO and LUMO energies, molecular mechanics, cc-pVDZ basis, quantum mechanics methods.

#### *Introduction*

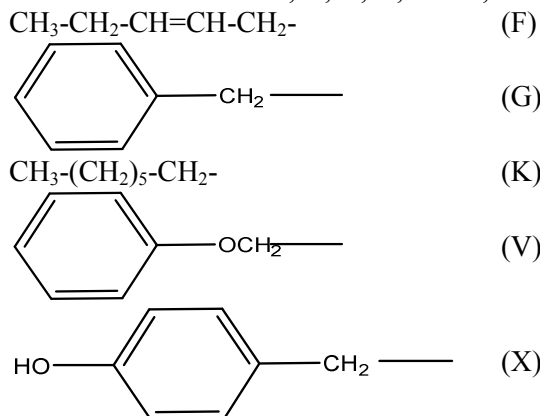
Antibiotics are organic compounds produced in the process of life by bacteria, fungi, molds, yeasts, as well as some higher plants, and possess the property to suppress the growth of microorganisms or kill them. In recent decades, antibiotics have become of great importance for fighting diseases caused by various pathogens. Their study and application in medicine is one of the most remarkable achievements of modern science. The first antibiotic — penicillin was introduced by Scottish scientist Alexander Fleming (1928), and that news had a profound effect on human life. Industrial production and clinical use of penicillin have been achieved thanks to the great work of famous chemists and the collaboration between the pharmaceutical companies of the United States in the 40s of the 20th century [1, 2]. Now a lot of penicillins are known. These are divided into natural (biosynthetic) and synthetic (semi-synthetic) ones. Natural penicillins are fairly selective, semi-synthetic ones manifest a much broader spectrum of antimicrobial action.

Determination of the structure of penicillins was extremely hampered by their ability to undergo various isomeric transformations even under mild conditions. The question of the structure of penicillin was resolved by X-ray diffraction, a method in which the substance under study does not undergo degradation. The structure of penicillin was established by British chemist and biochemist D. Crowfoot-Hodgkin [3]. The general formula for natural and synthetic penicillins is:



Penicillin core structure

The most important penicillins are natural ones F, G, K, V, and X, which differ by the variable group R:



Only two of them, namely, benzylpenicillin (G) and phenoxymethylpenicillin (V) found a wide practical application in medicine [2].

The key structural feature of the penicillins is the four-membered  $\beta$ -lactam ring; this structural moiety is essential for penicillin's antibacterial activity. It undergoes hydrolysis with the disruption of the N4-C7 bond under mild conditions, which leads to a loss of biological activity. The  $\beta$ -lactam ring is itself fused to a five-membered thiazolidine ring [3]. These form a so-called foam-group. X-ray diffraction studies showed that the foam-group of penicillins had a non-planar structure [2]. It was found that antibacterial activity of penicillins depended on the structure of the radical R. The most effective antibiotic is benzylpenicillin (penicillin G), in the molecule of which R is the benzyl radical. A slight change in the structure, the introduction of an oxygen bridge, significantly affects the activity of penicillin. Phenoxymethylpenicillin (penicillin V) is less active against gram-negative bacteria than benzylpenicillin, although it is more resistant to acidic medium [1–4].

Aspects of organic and biological chemistry of penicillins have been well studied [1, 2, 5]. Crystallographic data and the conformational analysis of penicillin molecules are given in Refs [3, 6–9]. In this paper, a comparative quantum-chemical analysis of the above mentioned penicillins, their structural and electronic properties, is performed.

#### *Computational part*

The software like ChemBioOffice, GaussView were applied to modelling the structure of molecules. To calculate their characteristics, the molecular mechanics MM2 [10] method, quantum chemical semi-empirical PM6 and *ab initio* methods [11] were used.

Benzylpenicillin has a compact structure according to the X-ray data [3]. We tried to model the crystal structure of penicillin G molecule due to the computer possibilities of above mentioned programs (Fig. 1). Similarly a model of penicillin V was built.

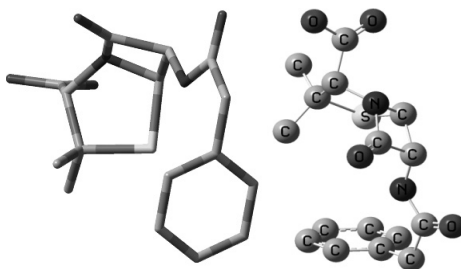


Figure 1. Molecular model of crystal structure of penicillin G (H atoms are not shown; GaussView 5.0 program)

Using the Hartree-Fock (HF) method with the Dunning's correlation consistent basis set cc-pVDZ, a calculation has been performed on the molecular models of the crystal structure of penicillins to determine the structural, electronic, and thermodynamic properties of ones.

### Results and discussion

The optimization of the geometry leads to changes in the positions of atoms and atomic groups. The most important difference is in the orientation of the amide moiety of the side chain. In the crystal structure, oxygen is on the convex face and hydrogen on the concave face of the molecule ( $\angle\text{H6-C6-N-H} = -156^\circ$ ) [6] (in our calculations, for instance,  $178^\circ$  in the cc-pVDZ structure (Fig. 2c)). The locations of these two atoms are altered in the calculated structures. A greater difference is observed in the case of the structure optimized by MM2 method, less for PM6 and cc-pVDZ models (Fig. 2).

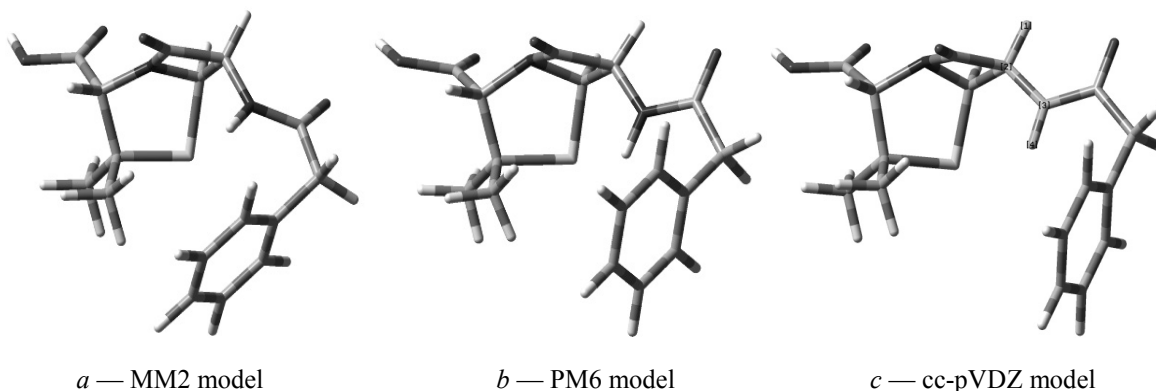


Figure 2. Calculated structures of penicillin G

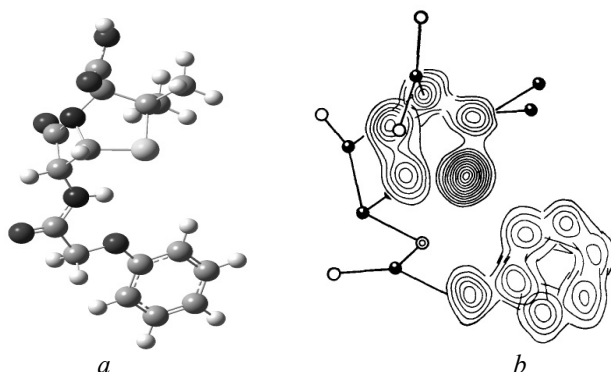


Figure 3. Optimized structure (HF/cc-pVDZ method) (*a*) and crystal structure (*b*) [9] of phenoxymethylpenicillin

Optimized structure of penicillin V in comparison with the crystal one is shown in the Figure 3. Differences in spatial structure of molecules in a crystal and other phases can and should be. A preferred conformation is determined by packing in the crystal, but it corresponds to a global minimum in gas. If we compare

three gaseous-phase models the differences can be explained as follows: MM2 structure is considered in the framework of classical mechanics. The molecule is accepted as an electron-nuclear system in quantum-mechanical models. Basis cc-pVDZ takes into consideration the correlation effects.

As we can see on the Figure 2a position of benzyl group in space is also not the same for MM2, PM6 and cc-pVDZ models of benzylpenicillin. The corresponding values of angles are shown in Table 1. MM2 method gives mostly smaller angle values and practically perpendicular arrangement of aryl group, while taking into account the correlation effects leads to an increase in the valence and torsion angles. However, according to the method HF/cc-pVDZ, the bonds N-C and C(H<sub>2</sub>)-C<sub>Ar</sub> are almost coplanar, whereas MM2 and PM6 show them out of the plane (42° and -41°, respectively).

Another significant difference in the geometry calculated at different levels is the position of the amide group relative to the β-lactam ring: in accordance with the molecular mechanics method they are located nearly orthogonally, semi-empirical and non-empirical methods provide approximately twice as much angle (140° and 130° respectively). Introduction of the oxygen bridge leads to transfer the benzene ring from the position perpendicular to the amide group to the coplanar one. Relevant angle data are listed in Table 1.

Table 1

Some theoretical geometric parameters for penicillins at different levels

Angles (°)	MM2	PM6	HF/cc-pVDZ
C6-N-C	122.026 <sup>a</sup>	120.351	122.015
	121.747 <sup>b</sup>	120.160	122.127
N-C-C(H <sub>2</sub> )	113.688	115.556	117.000
	114.156	116.235	116.214
C-C(H <sub>2</sub> )-C <sub>Ar</sub>	109.215	114.269	118.005
	110.420	106.455	110.887
C5-C6-N-C	76.863	140.174	129.784
	63.730	137.687	132.159
H6-C6-N-H	126.045	-172.476	177.831
	107.877	-168.035	-178.047
C6-N-C-C(H <sub>2</sub> )	-176.903	-179.326	179.513
	-179.093	-179.793	178.961
N-C-C(H <sub>2</sub> )-C <sub>Ar</sub>	42.099	-41.224	-11.154
	-21.041	14.749	3.311
C-C(H <sub>2</sub> )-C <sub>Ar</sub> -C	-97.101	-64.594	-81.770
	179.807	-178.427	179.477

Note. <sup>a</sup> — Parameters for penicillin G; <sup>b</sup> — Parameters for penicillin V.

Some theoretical parameters calculated for optimized structures of the title compounds by *ab initio* HF method, such as total energy, zero-point energy, entropy, heat capacity, rotational constants and dipole moments are given in Table 2.

Table 2

Theoretically calculated physical-chemical parameters for the compounds (HF/cc-pVDZ method)

Parameters	Penicillin G	Penicillin V
Total energy (Hartree)	-1422.3671554	-1497.2201151
Zero-point energy (kcal/mol)	231.623	235.530
Entropy (cal/(mol×K))	158.037	161.240
Heat capacity (C <sub>v</sub> , cal/mol×K)	76.423	79.499
Rotational constant (GHz)		
A	0.4341207	0.4597905
B	0.1476509	0.1029334
C	0.1291843	0.0913024
Dipole moment (Debye)		
μ <sub>total</sub>	5.40	4.49
μ <sub>x</sub>	1.0285	-0.2300
μ <sub>y</sub>	5.2714	-4.4706
μ <sub>z</sub>	-0.5204	-0.3566



The data of Table 2 permit the following conclusions: a) the values of the total electronic energy show an energetical stability of penicillin V, and are consistent with its reduced activity; b) when increasing a number of atoms, a correction to the electronic energy of the molecule, which accounts for the effects of molecular vibrations at 0 K, rises; c) when appearing of additional degrees of freedom in an anisotropic molecule, entropy of penicillin V increases; d) the constant volume molar heat capacity is in the same dependence on the molecular mass; e) both molecules are asymmetric tops due to the different rotational constants; f) penicillin V has a lower polarity.

The ability of electron giving is characterized by the highest occupied molecular orbital (HOMO) energy and the ability of electron accepting is characterized by the lowest lying unoccupied molecular orbital (LUMO) energy. These correspond to the ionization potential (I) and the electron affinity (A), respectively: in the Hartree-Fock approximation, the ionization potential is equal to the orbital energy of the ionized molecule taken with the opposite sign, the electron affinity is defined by the same way. The values  $E_{\text{HOMO}} < 0$  correspond to the positive ionization potentials. The gap between HOMO and LUMO characterizes the molecular chemical stability [12]. Some of the molecular properties have been calculated theoretically by using HOMO and LUMO energy difference, for example, electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ) and chemical softness (S) (Table 3).

Table 3

**The calculated frontier orbital energies, the absolute electronegativity, the absolute hardness and softness of the compounds (HF/cc-pVDZ method)**

Parameters	Penicillin G	Penicillin V
$E_{\text{HOMO}}$ (a.u.)	-0.34034	-0.32318
$E_{\text{LUMO}}$ (a.u.)	0.12085	0.12414
$\Delta E_{\text{HOMO-LUMO}}$ (eV)	12.55	12.17
I (eV)	9.26	8.79
A (eV)	-3.29	-3.38
$\chi$ (eV)	2.99	2.71
$\eta$ (eV)	6.28	6.09
S (eV)	0.080	0.082

The absolute electronegativity has been calculated as a half-sum of the ionization potential and the electron affinity, the absolute chemical hardness has been identified as their half-difference. The chemical softness is the inverse of the hardness. Benzylpenicillin is a fairly strong acid ( $\text{pK}_a = 2.7\text{--}2.76$ ). Therefore, it has the greater ionization potential, electronegativity, the negative electron affinity (as well as penicillin V). The HOMO-LUMO gap value indicates a lower polarizability of the benzylpenicillin molecule, which is consistent with the value of its permanent dipole moment (Table 2). The measure of resistance to change in the electronic configuration, the so-called hardness of the substance, is higher in the case of penicillin G, and, respectively, its softness is lower than that of penicillin V.

### Conclusions

A comparative analysis of penicillin structures based on experimental data and calculations showed, on the one hand, the significant influence of the calculation method on the results of geometry and other properties of compounds, on the other hand, the influence of the structural change in the molecule on the same properties. Although theoretical calculations were carried out in gaseous phase, Hartree-Fock calculations with a correlation basis allowed us to determine structures close to the experimental ones. The addition of a single oxygen bridge caused a marked change in the physico-chemical properties of the substance. Electronic and thermodynamic properties are also calculated by *ab initio* method that took into account the correlation effects.

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### Табиғи пенициллиндердің теориялық есептеулері: құрылымдық және электрондық қасиеттері

Белгілі антибиотиктердің мысалында қосылыстардың геометриясы мен басқа қасиеттеріне есептеу әдістері және молекуладағы кішігірім құрылымдық өзгерістерінің әсері зерттелді. Молекулалық және кванттық-механикалық әдістерін пайдалана отырып, пенициллин мен феноксиметилпенициллиннің құрылымдық, электрондық және термодинамикалық қасиеттері есептелді. Тәжірибелік деректер мен есептеулер негізінде пенициллиндердің құрылымдарына салыстырмалы талдау жүргізілді. Бастапқы құрылым ретінде тәжірибелік геометриясының молекулалық үлгісі қарастырылды. Құрылым одан әрі оңтайландырылды. Геометриялық параметрлері Эллинджер ұсынған MM2 модификацияланған күштер өрісіне негізделген әдісімен, PM6 жартылай эмпирикалық әдісімен және Даннингтің корреляциялы-реттелген базистік сс-pVDZ жиыны бар эмпирикалық емес Хартри-Фок әдісімен есептелінді. Газ фазасындағы молекулалар үшін орындалған теориялық есептеулерге қарамастан, сс-pVDZ-оңтайландырылған геометриясы кристалдық геометрияға жақын. Жоғарыда аталған қосылыстардың оңтайландырылған құрылымдары үшін толық электрондық энергия, нөлдік тербеліс энергиясы, айналмалы тұрақтылар, диполь моменттері сияқты кейбір теориялық параметрлер анықталған. Сондай-ақ екі пенициллин үшін шекаралық молекулалық орбитальдардың электрондық қасиеттері есептелді. Корреляциялық әсерлерін ескеретін *ab initio* әдісімен қосылыстардың термодинамикалық қасиеттері (жылусыйымдылығы, энтропиясы) анықталды.

*Кілт сөздер:* пенициллин, феноксиметилпенициллин, құрылым, термодинамикалық қасиеттер, ЖТМО мен ТБМО энергиялары, молекулалық механика, сс-pVDZ базисі, кванттық механика әдістері.

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### Теоретические расчеты природных пенициллинов: структурные и электронные свойства

На примере известных антибиотиков изучено влияние метода расчета и небольшого структурного изменения в молекуле на результаты по геометрии и другим свойствам соединений. С использованием методов молекулярной и квантовой механики рассчитаны структурные, электронные и термодинамические свойства пенициллина и феноксиметилпенициллина. Выполнен сравнительный анализ структур пенициллинов на основе экспериментальных данных и расчетов. В качестве стартовой структуры была рассмотрена молекулярная модель с экспериментальной геометрией, которая далее была оптимизирована. Геометрические параметры были рассчитаны методом молекулярной механики с модифицированным силовым полем MM2, разработанным Эллинджером, полумпирическим PM6 методом и неэмпирическим методом Хартри-Фока с корреляционно-согласованным базисным набором Даннинга сс-pVDZ. Несмотря на то, что теоретические расчеты были выполнены для молекул в газовой фазе, сс-pVDZ-оптимизированная геометрия близка к кристаллической. Методом ХФ определены некоторые теоретические параметры для оптимизированных структур названных выше соединений, та-

кие как полная электронная энергия, энергия нулевых колебаний, вращательные постоянные, дипольные моменты. Для пенициллинов были рассчитаны также электронные свойства граничных молекулярных орбиталей. *Ab initio* методом, учитывающим корреляционные эффекты, определены термодинамические свойства соединений (теплоемкость, энтропия).

*Ключевые слова:* пенициллин, феноксиметилпенициллин, структура, термодинамические свойства, энергии ВЗМО и НСМО, молекулярная механика, базис *cc-pVDZ*, методы квантовой механики.

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## Topological transformation of phase diagrams water – ethoxylated nonylphenols – sodium chloride systems

In this work phase equilibria in water – ethoxylated nonylphenol (Neonol) – sodium chloride systems was investigated, and temperature ranges of two-phase liquid and monotectic equilibrium region existence were established. These regions exist at temperature of more than 23 °C in system with Neonol AF-9-12 and more than 42 °C in system with Neonol AF-9-25. A feature of water – Neonol AF-9-12 – sodium chloride system is the salting-out of double water – Neonol AF-9-12 subsystem at the temperature of more than 84 °C. A scheme of phase diagrams of topological transformation of water – ethoxylated surfactant – inorganic salt systems for cases, when salt has only salting-out effect and water – surfactant subsystem is characterized by a lower critical solubility temperature (Neonol AF-9-12) or homogeneous throughout liquid state interval was developed. The correspondence of developed schemes to generalized scheme for the salt – binary solvent systems was shown. The data obtained allow evaluating surfactant ethoxylation degree effect to sodium chloride salting-out ability. It was found that ethoxylation degree increase is accompanied by increase in surfactant micelles hydration, which leads to decrease in the salting-out ability of sodium chloride. The obtained data can be used to optimize the temperature and concentration extraction parameters.

*Keywords:* surfactants, ethoxylated nonylphenol, sodium chloride, stratifying systems, salting-out, phase diagrams, solubility, topological transformation.

### Introduction

Surfactant based optimization of temperature-concentration parameters for extraction in the systems can be done with the methods of physical chemical analysis. Typically, the first stage is aimed to decide on a salting-out agent and temperature of the process for a particular surfactant or to choose a surfactant for extraction with a particular salting-out agent. Many published works consider the impact of surfactant structure on stratifying temperature for its water solutions [1–3], as well as the impact of non-organic salt nature on a salting-out capacity of ethoxylated surfactant [4–6], with surfactant structure during its formation and temperature transformation in the stratifying area in water – ethoxylated surfactant – inorganic salt systems being hardly examined.

Earlier, a scheme of topological transformation for phase diagrams of water – ethoxylated surfactant – inorganic salt systems has been proposed in cases when a water – surfactant subsystem remains homogeneous in all temperature intervals, while salt salts out, and in case of a water – surfactant system with the lower critical solubility point (LCSP) and salting-in – salting-out effect of salt [7]. The present paper is aimed to identify the schemes of topological transformation for phase diagrams of water – ethoxylated surfactant – inorganic salt for the salt with salting-out effect only with regard to ethoxylated nonylphenols with different – ethoxylation degree.

Sodium chloride which was extensively used in surfactant-based extraction systems was chosen to be a salting-out agent [8, 9]. Some papers give the information about the impact of sodium chloride on the stratifying temperature of water solutions of ethoxylated octylphenols [4, 10], ethoxylated dodecanols [11], and polyethyleneglycols [12]; although no regularities in transformations of phase areas are looked at.

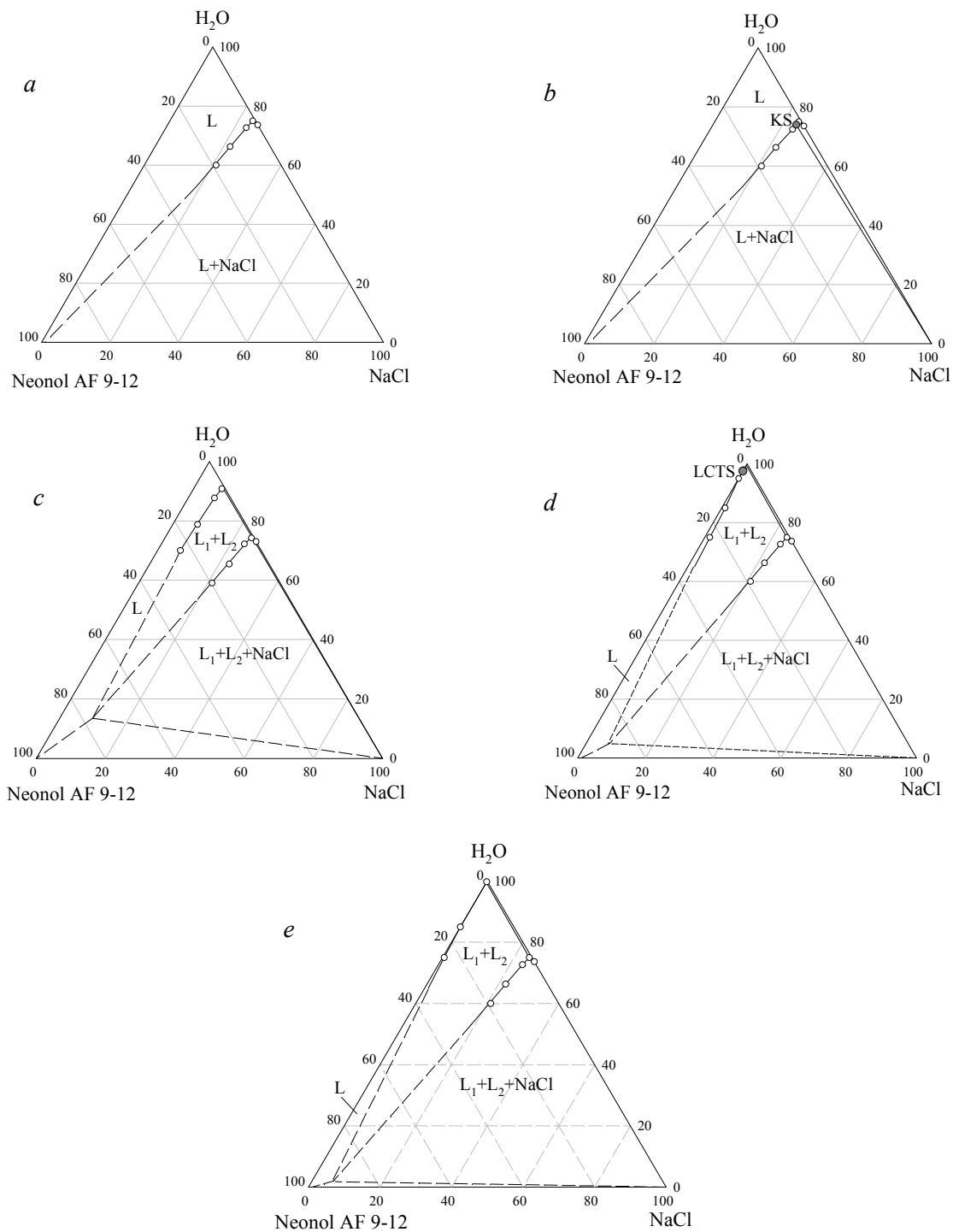
### Experimental

The paper uses ethoxylated nonylphenols ( $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$ ,  $n = 12$  for neonol AF-9-12,  $n = 25$  for neonol AF-9-25, TU 2483-077-05766801-98), analytic grade sodium chloride, distilled water ( $n_D^{25} = 1.3325$ ).

Visual-polythermal method identified the stratifying area boundaries. Sections method was used to obtain solubility isotherms at temperatures below 75 °C. The paper [7] examines the methodology of the experiment in detail.

Results and discussion

Sodium chloride crystallizes into waterless salt in the specified temperature range and has positive solubility temperature index. Water – neonol AF-9-12 system is characterized by the lower critical solubility point (LCSP), namely, 84 °C (3.0 mas. % neonol AF-9-12). Stratifying area in the system is within the temperature interval — from 84 °C to the boiling temperature. Water – neonol AF-9-25 double system is homogeneous within the whole interval of liquid state. Experiments showed that sodium chloride was practically insoluble in surfactant under question.



a — 10 °C; b — 23 °C; c — 60 °C; d — 84 °C; e — 90 °C

Figure 1. Phase equilibrium in the water – Neonol AF-9-12 – NaCl system

Solubility in a water – neonol AF-9-12 – NaCl system, which fits the case when water – surfactant binary subsystem is characterized by LCSP, while the salt is a salting-out agent, has been analyzed in five sections.

Four sections connect the solutions of neonol AF-9-12 with different concentration and the sodium chloride peak; the fifth section connecting the peak of neonol AF-9-12 and a heterogeneous mixture of water and sodium chloride with the mass content of 40.0 % were used to identify the critical point (KS).

The temperature range of 10–23 °C in the system (Fig. 1a) is known to have two areas: unsaturated solutions (L) and crystallization of sodium chloride (L+S). Salt solubility slightly increases with temperature in the solutions of neonol AF-9-12.

At 23 °C, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 1b). Composition of a critical point is as follows: 24.0 % NaCl, 3.0 % neonol AF-9-12, 73.0 % water. Further temperature increase results in the formation of stratifying area ( $L_1+L_2$ ) together with its neighboring monotectonic equilibrium area ( $L_1+L_2+NaCl$ ). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 1c).

At 84 °C, the area of critical point stratification is connected with the lower critical solubility point (LCSP) of water — neonol AF-9-12 binary subsystem with the homogenous area being divided into two fields (Fig. 1d). Further temperature increase expands stratifying area and salts out the heterogeneous system of water — surfactant (Fig. 1e). Further temperature increase does not change significantly the solubility diagram; one can only observe the expansion of stratifying area and the decrease of the unsaturated solution area.

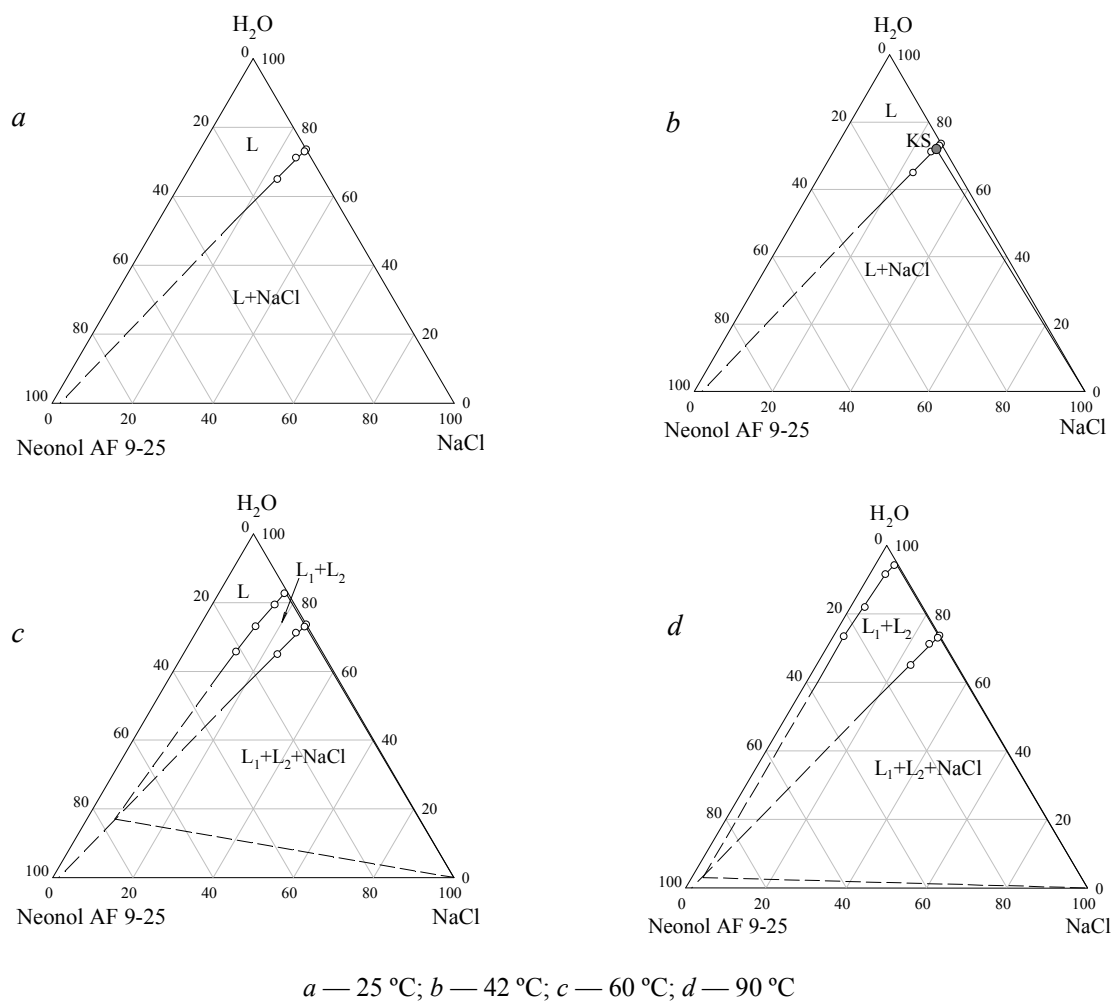


Figure 2. Phase equilibrium in the water – Neonol AF-9-25 – NaCl system

Solubility in water – neonol AF-9-25 – NaCl system, which fits the case when water – surfactant binary subsystem is homogeneous in the whole interval of liquid state and the salt serves as a salting-out agent, has been analyzed in the same sections described for neonol AF-9-12. The temperature range of 25–42 °C in the system is known to have two areas: unsaturated solutions (L) and crystallization of sodium chloride (L+S). Temperature growth leads to a slight increase in sodium chloride solubility in surfactant solutions, with the salting-out effect of neonol AF-9-25 in relation to sodium chloride being minimal (Fig. 2a).

At 42 °C, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 2b). Composition of a critical point is 26.0 % NaCl, 3.0 % neonol AF-9-12, 71.0 % water. Further temperature increase results in the formation of stratifying area (L<sub>1</sub>+L<sub>2</sub>) together with its neighboring monotectonic equilibrium area (L<sub>1</sub>+L<sub>2</sub>+NaCl). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 2c). Further temperature increase does not change the phase diagram significantly; one can only observe the expansion of stratifying and monotectonic equilibrium areas. Data obtained supports previously published scheme for water – synthanol DS-10 – KBr system [7].

It is relevant to see the impact of surfactant ethoxylation on temperature dependent changes in salting-out capacity of sodium chloride. Ethoxylation degree increase raises the temperature to form both stratifying and monotectonic equilibrium areas. Observed regularities are determined by greater salting-out capacity of salt and a drop in micelle hydration degree with temperature growth. Temperature dehydration of micelles with their further aggregation depends on surfactant molecule hydrophilicity which can be expressed in hydrophilic-lipophilic balance (HLB) or water – surfactant system LCSP. The Table gives the calculated values for HLB by Davis [13] and LCSPs for water – surfactant binary systems. Neonol AF-9-25 is even more hydrated at 60 °C and higher than neonol AF-9-12, therefore its salting-out capacity is significantly lower than the one for neonol AF-9-12.

Table

**Main characteristics determining the salting-out ability NaCl to neonols**

Surfactant	HLB	LCSP, °C
Neonol AF-9-12	6.93	84
Neonol AF-9-25	11.22	> 100

### Conclusion

Thus, the obtained data from the experiments proved the possibility for two summarized schemes of topological transformation of phase diagrams for water – ethoxylated surfactant – inorganic salt systems, when salt serves as a salting-out agent only, while water – surfactant binary system is characterized by LCSP (water – neonol AF-9-12 – NaCl system) or is homogeneous in the whole interval of liquid state (water – neonol AF-9-25 – NaCl system). These schemes perfectly fit the summarized scheme of topological transformation of phase diagrams for triple stratifying systems of salt – binary solvent [14].

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### Су – оксиэтилденген нонилфенол – NaCl жүйелері фазалық диаграммаларының топологиялық трансформациялануы

Мақалада су – оксиэтилденген нонилфенол (неонол) – натрий хлориді жүйелеріндегі фазалық тепе-теңдіктер зерттелген, екіфазалық сұйық және монотектикалық тепе-теңдіктердің мүмкін болу аумақтарының температуралық интервалдары анықталған. Көрсетілген аумақтар АФ-9-12 неонолмен жүйесінде 23 °С астам, ал АФ-9-25 неонолмен жүйесінде 42 °С астам температурада бола алады. Су – неонол АФ-9-12 – натрий хлориді жүйесінің ерекшелігі болып 84 °С асқан температурада екі қабатқа бөлінетін су-неонол АФ-9-12 жүйесінің тұзсыздануы табылады. Су – оксиэтилденген ББЗ – бейорганикалық тұз жүйелері жағдайлары үшін, тұз тек тұзсыздану әрекетіне ие болатын, ал су – ББЗ (неонол АФ-9-12) жүйесі төменгі шекті еру температурасымен сипатталатын немесе сұйық жағдайдың барлық интервалдарында гомогенді болатын жағдайлары үшін фазалық диаграммалардың топологиялық трансформациялануының сызбасы өңделген. Ол сызбаның тұз – бинарлы еріткіш жүйелері үшін біріктірілген сызбаларына сәйкестігі көрсетілген. Алынған мағлұматтар ББЗ оксиэтилдену деңгейі натрий хлоридінің тұзсыздандыру қабілетіне қалай әсер ететінін бағалауға мүмкіндік берді. Оксиэтилден деңгейінің өсуі ББЗ мицеллаларының гидратациялануы артуымен қатар жүретіні анықталды, бұл енгізілетін натрий хлоридінің тұзсыздандыру қабілетінің төмендеуіне әкеледі. Алынған мәліметтерді тұзсыздандыратын заттар қатысында оксиэтилденген ББЗ негізінде экстракцияның температуралық-концентрациялық параметрлерін оңтайландыруға қолдануға болады.

*Кілт сөздер:* беттік-белсенді заттар, оксиэтилденген нонилфенолдар, натрий хлориді, қабаттарға бөлінетін жүйелер, тұзсыздандыру, фазалық диаграммалар, ерігіштік, топологиялық трансформациялану.

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### Топологическая трансформация фазовых диаграмм систем вода – оксиэтилированный нонилфенол – NaCl

В статье исследованы фазовые равновесия в системах вода – оксиэтилированный нонилфенол (неонол) – хлорид натрия, установлены температурные интервалы существования области двухфазного жидкого и монотектического равновесий. Указанные области существуют при температуре более 23 °С в системе с неонолом АФ-9-12 и более 42 °С в системе с неонолом АФ-9-25. Особенностью системы вода – неонол АФ-9-12 – хлорид натрия является высаливание двойной расслаивающейся подсистемы вода – неонол АФ-9-12 при температуре более 84 °С. Разработана схема топологической трансформации фазовых диаграмм систем вода – оксиэтилированное ПАВ – неорганическая соль для случаев, когда соль обладает только высаливающим действием, а подсистема вода – ПАВ характеризуется нижней критической температурой растворения (неонол АФ-9-12) или является гомогенной во всем интервале жидкого состояния. Показано соответствие разработанных схем обобщенной схеме для систем соль – бинарный растворитель. Полученные данные позволили оценить влияние степени оксиэтилирования ПАВ на высаливающую способность хлорида натрия. Установлено, что рост степе-



ни оксиэтилирования сопровождается увеличением гидратации мицелл ПАВ, что приводит к снижению высаливающей способности вводимого хлорида натрия. Полученные данные могут использоваться для оптимизации температурно-концентрационных параметров экстракции в системах на основе оксиэтилированных ПАВ в присутствии высаливателя.

*Ключевые слова:* поверхностно-активные вещества, оксиэтилированные нонилфенолы, хлорид натрия, расслаивающиеся системы, высаливание, фазовые диаграммы, растворимость, топологическая трансформация.

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### Selective extraction of magnesium from asbestos-containing raw materials

In this work, great attention was paid to identifying the reasons for the absence of practically implemented technologies for processing chrysotile asbestos wastes and searching for new methods for treating wastes with the aim of obtaining magnesium and other useful products of commercial interest. A series of experiments with solutions of ammonium chloride of different concentrations was carried out to study the kinetics of magnesium leaching. The concentration of magnesium leached increases with the concentration of the  $\text{NH}_4\text{Cl}$  solution ( $C_{\text{Mg}} = 0.092\text{M}$ ;  $C_{\text{Mg}} = 0.1\text{M}$ ;  $C_{\text{Mg}} = 0.102\text{M}$ ), as well as with the time of the process itself. It was shown that the difference between the leaching rates of magnesium by 3M and 5M  $\text{NH}_4\text{Cl}$  solutions was not significant, and it was rather large for 1M and 3M solutions. The study of the thermodynamics of magnesium leaching was carried out with 3 molar solution of ammonium chloride at various temperatures. Graphs of the concentration of leached magnesium versus the leaching time at different temperatures of the ammonium chloride solution were plotted based on the results obtained. Experiments showed that the degree of magnesium leaching from asbestos increased with increasing temperature. The activation energy was calculated, which was equal to 44 kJ. Sediment identification was carried out using a laser-atomic emission spectrometer apparatus. The results of the experiment showed that a certain amount of magnesium, calcium and a small amount of other metals were contained in the obtained precipitates. Admixture of calcium does not affect the properties of the precipitate obtained. Leaching tests carried out with the help of ammonium chloride solution of various concentrations showed that the fibrous structure of asbestos was not destroyed.

*Keywords:* selective extraction of magnesium, asbestos-containing raw materials, kinetics, thermodynamics, concentration, magnesium-ammonium phosphate, activation energy, leaching.

#### Introduction

Asbestos is a valuable mineral that is widely used in industry. Despite the fact that asbestos has certain carcinogenicity, its properties are unique. Processing asbestos and its obtaining from mineral raw materials is accompanied by the formation of waste including non-conforming chrysotile asbestos and amphibole asbestos, as well as its other varieties. During the extraction and enrichment of chrysotile asbestos, large-tonnage industrial waste is formed consisting of overburden and processing components [1, 2].

Magnesium extraction is considered to be one of the traditional types of asbestos processing. All metals are leached out from asbestos in a complex by conventional methods under the action of strong acids. The resulting salts need separation and additional purification. In addition, strong mineral acids are used, which also cause intense corrosion of equipment. The development of selective leaching of magnesium without the use of mineral acids is currently a topical issue. In this regard, we studied the selective extraction of magnesium from asbestos-containing raw materials. To achieve this goal, some tasks such as obtaining thermodynamic and kinetic leaching data, obtaining a magnesium — ammonium phosphate precipitate to convert magnesium into an economically applicable form should be accomplished.

*Experimental*

An ammonium chloride solution of the concentrations 1M, 3M, 5M was used to study the leaching kinetics of magnesium from asbestos. It is known from the literature [3, 4] that ammonium chloride dissolves magnesium oxide well, while oxides of other metals do not pass into the solution. A solution of ammonium chloride has been proposed for the selective leaching of magnesium from chromate sludge [5]. 20.0 g of asbestos previously dried to constant weight at 200 °C were added to the solutions obtained. It was kept at room temperature for 2 weeks. The pH was controlled periodically (Table 1) and 5 mL aliquots were taken to determine the concentration of magnesium.

Table 1

**pH readings after leaching with ammonium chloride**

C	τ								
	0.5	1.5	3	24	72	96	192	288	336
1M	8.569	8.69	8.895	8.9	8.907	8.967	9.04	9.013	9.014
3M	8.246	8.465	8.523	8.652	8.793	8.719	8.676	8.672	8.475
5M	8.18	8.094	8.242	8.245	8.249	8.369	8.45	8.55	8.721

Using concentrated ammonia, the pH of the solutions was adjusted to 11 and solutions were titrated with 0.05M solution of Na<sub>2</sub>EDTA (Trilon B) in the presence of an eriochrome black indicator. The magnesium concentration was calculated (Table 2) based on the consumption data of Trilon B using the well-known formula derived from the law of equivalents:

$$C_1V_1 = C_2V_2,$$

where  $C_1$  — is the concentration of Trilon B;  $V_1$  — is the volume of Trilon B consumed during the titration,  $C_2$  — is the concentration of magnesium;  $V_2$  — is the aliquot volume.

Table 2

**Results of magnesium leaching in NH<sub>4</sub>Cl solution at 20 °C**

C <sub>(NH<sub>4</sub>Cl)</sub>	τ								
	0.5	1.5	3	24	72	96	192	288	336
1M	0.021	0.032	0.043	0.057	0.077	0.079	0.081	0.087	0.087
3M	0.024	0.044	0.058	0.071	0.09	0.092	0.096	0.1	0.1
5M	0.032	0.046	0.061	0.079	0.092	0.095	0.098	0.102	0.102

It can be concluded that the concentration of magnesium leached increases with the concentration of the NH<sub>4</sub>Cl solution based on the results presented in the Table 2, as well as with the time of the process itself. It is shown that the difference between the leaching rates of magnesium by 3M and 5M NH<sub>4</sub>Cl solutions is not significant, and it is rather large for 1M and 3M solutions. The kinetic curves for magnesium leaching from asbestos with ammonium chloride solutions of different concentrations at room temperature are shown in Figure 1.

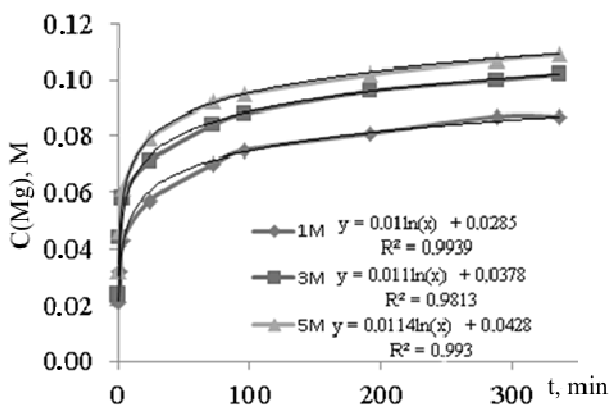


Figure 1. Kinetic curves of magnesium leaching at 20 °C

After the amount of magnesium leached from asbestos was fixed, the solution was filtered off, so the solution was separated from asbestos. The thick mixture was washed with distilled water and dried in a drying cabinet until moisture was completely removed. According to the formulas of the reaction rate constants [6], they were calculated for 3 orders of reaction (Table 3).

Table 3

Indicators of reaction rate constants

$\tau$	c	$c_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$
336	0.826	1	0.00057	0.00043	0.00069
336	2.796	3	0.00021	0.00509	2.5E-05
336	4.782	5	0.00013	0.01551	5.6E-06

Comparison of the rate constants calculated shows that the formula for the first order of reaction gives values that are significantly less different from each other than for the second and third orders. It can be concluded that the reaction order for ammonium chloride is first, but the rate is controlled by diffusion. Then, ammonium phosphate was added dropwise to the solutions to convert the leached elements into the sediment. The ammonium phosphate solution was prepared from 85 % phosphoric acid and 25 % ammonia solution. Phosphoric acid was added to ammonia in small portions, each time waiting for the reaction mixture to cool down. The addition of phosphoric acid was continued to adjust pH = 11. The precipitate obtained was dried and samples were prepared for laser spectrometry. Laser spectrometry clearly shows that the sediment contains a sufficiently large amount of magnesium and some calcium (Fig. 2–4). It does not detect the presence of other metals.

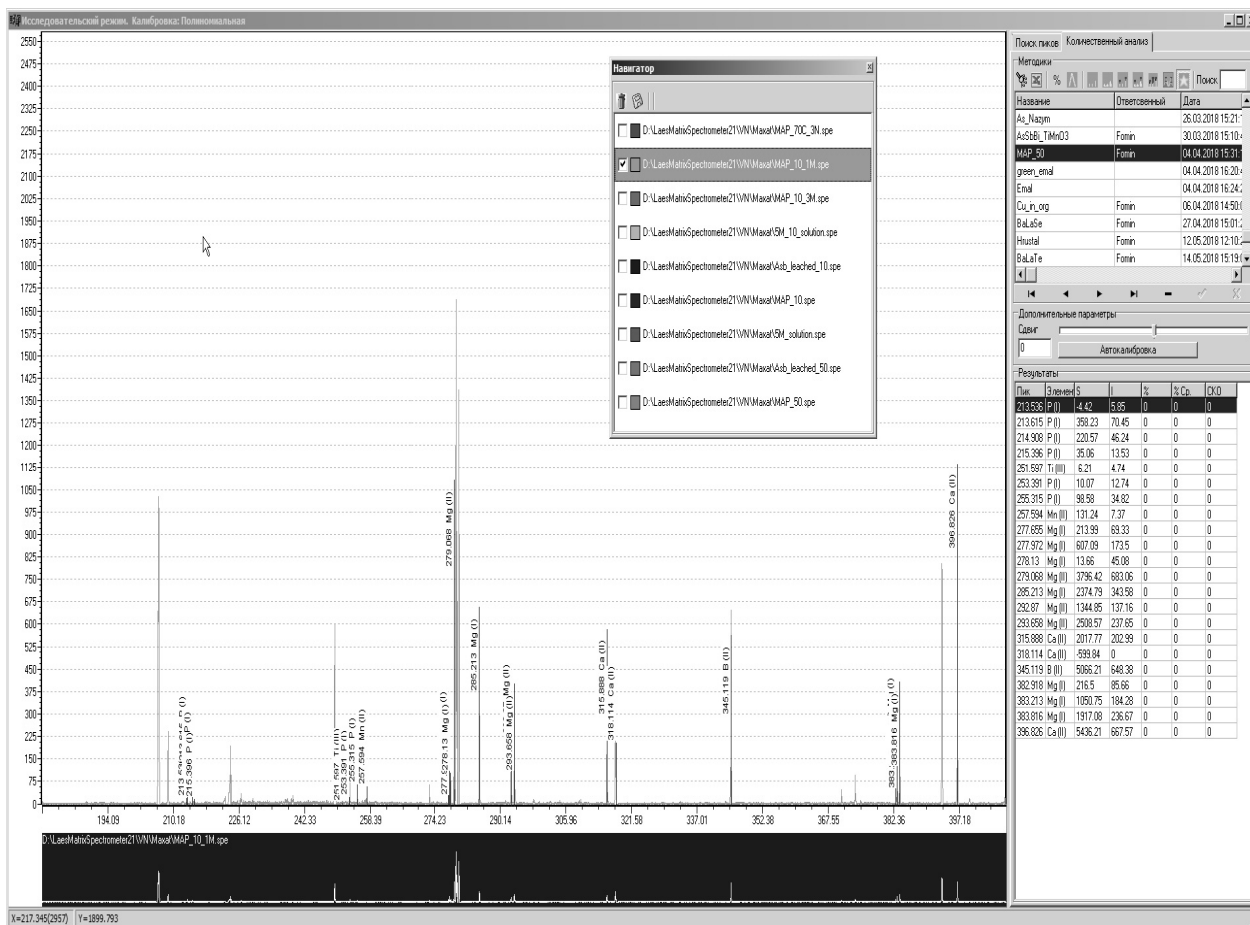


Figure 2. The metal content in the sludge studied during leaching with 1M ammonium chloride solution

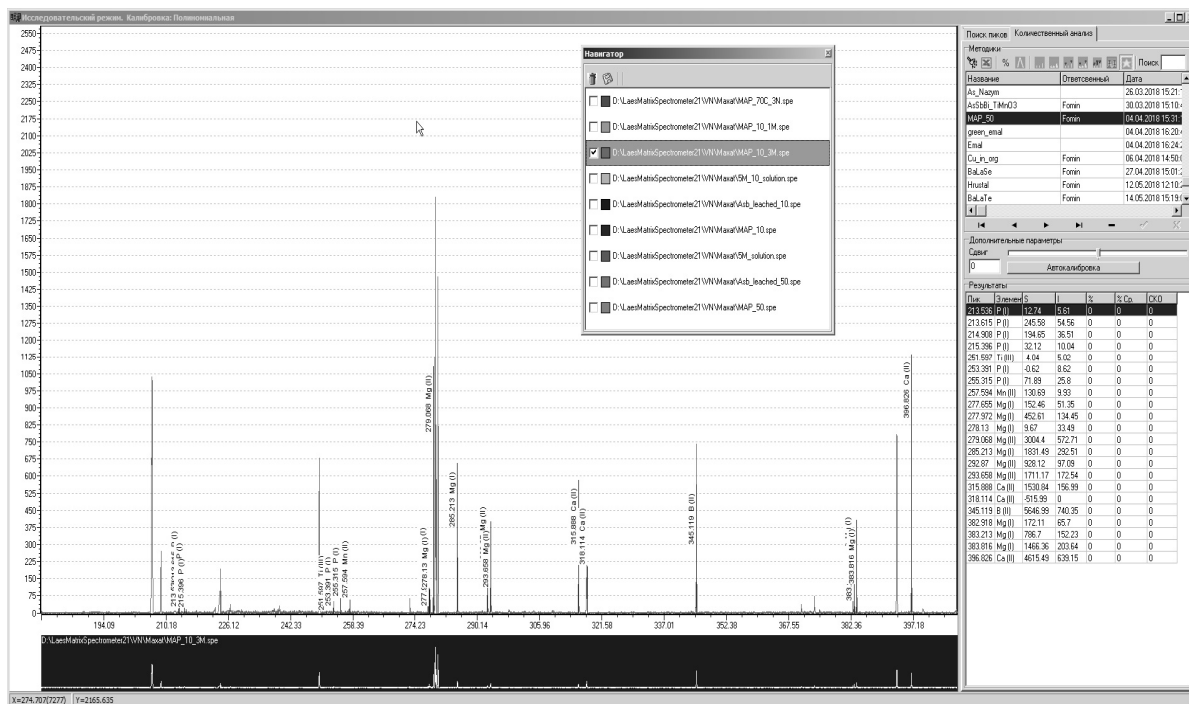


Figure 3. The metal content in the sludge studied during leaching with 3M ammonium chloride solution

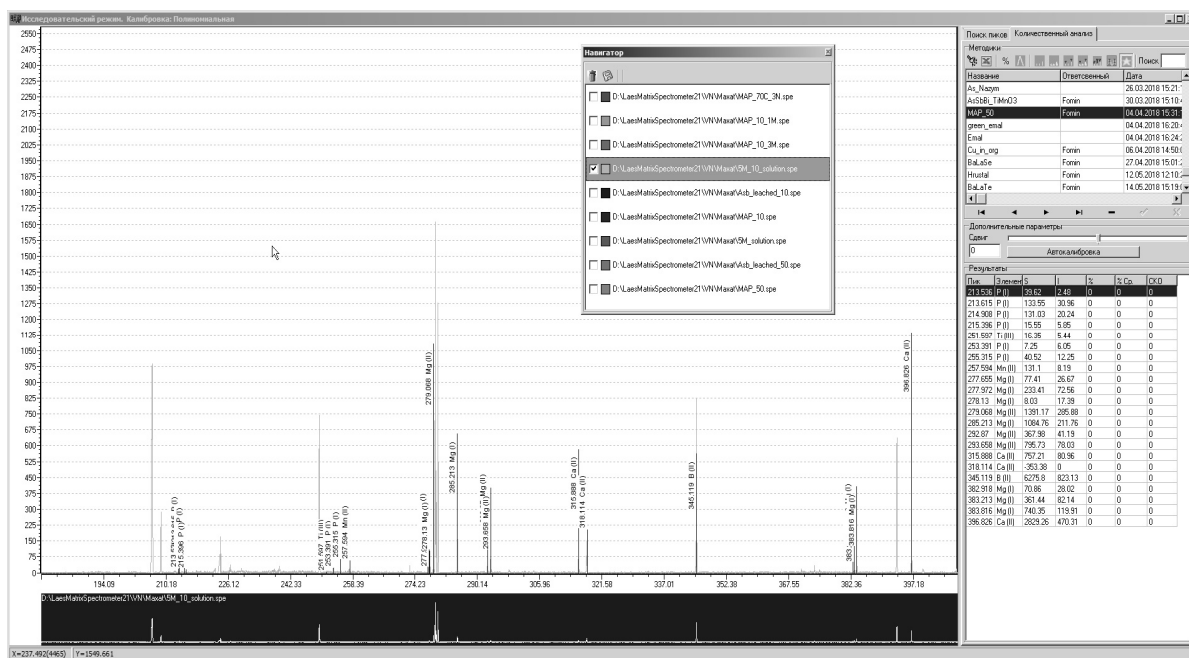


Figure 4. The metal content in the sludge studied during leaching with 5M ammonium chloride solution

It can be noted that the reaction rate increases with an increase in the concentration of ammonium chloride solution based on the results obtained. In this case, a certain period of time occurs when the saturation peak remains the same regardless of the concentration of the solvent. Thermodynamic parameters of the process are of interest for the production organization on the industrial scale. We carried out a series of experiments on the magnesium leaching with a 3 molar solution of ammonium chloride at different temperatures to study the thermodynamics of leaching. 300 mL of a 3 M solution of ammonium chloride was poured into a flask with 15 g of initial asbestos and thermostated at temperatures of 20, 40, 50, 60, 70 °C. Samples were

taken and titrated with Trilon B after a certain period of time. The results of the titration are shown in Table 4.

Table 4

**The concentration of magnesium in the reaction mixtures, mol/L**

$T, ^\circ\text{C}$	$\tau, \text{h}$								
	0.5	1.5	3	24	72	96	192	288	366
20	0.024	0.044	0.058	0.071	0.09	0.092	0.096	0.1	0.102
40	0.025	0.054	0.092	0.105	0.106	0.108	0.108	0.109	0.109
50	0.03	0.061	0.1	0.108	0.108	0.109	0.109	0.109	0.11
60	0.036	0.065	0.102	0.109	0.11	0.11	0.12	0.12	0.13
70	0.037	0.069	0.105	0.109	0.11	0.12	0.12	0.14	0.14

As a result of approximation of the experimental points the logarithmic curves are obtained in all cases that are shown in Figure 5. The accuracy of the approximation is 95–98 %.

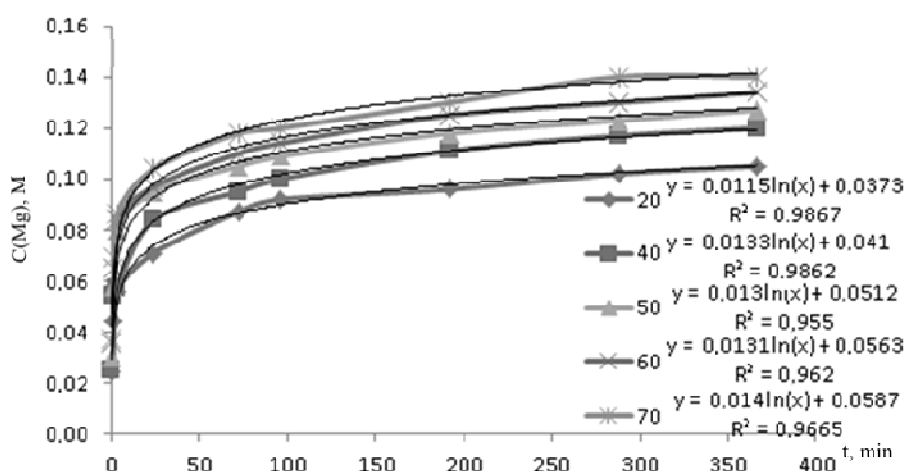


Figure 5. The dependence of the concentration of magnesium leached on the temperature of ammonium chloride solution

The activation energy was calculated with the help of the formula [4]:

$$E_a = R \times \ln \frac{\tau_2 \ln(1 - \alpha_1)}{\tau_1 \ln(1 - \alpha_2)} \left/ \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right.$$

The obtained data are given in Table 5. The value of the activation energy after statistical processing was  $43.815 \pm 8.973$  kJ/mol at a significance level of 95 % ( $p = 0.05$ ).

Table 5

**Reaction activation energy**

$T$	$\tau$	$\alpha$	$E_a, \text{J/mol}$
293.00	360.00	0.21	40941.50299
313.00	123.00	0.21	56236.10255
323.00	63.00	0.21	38413.44866
333.00	41.00	0.21	39668.83503
343.00	27.00	0.21	43814.97231

The obtained value of the activation energy is about 1.1–1.5 times exceeds the value obtained by the authors [7] for the magnesium leaching from calcium-containing magnesite ( $\sim 30$  kJ/mol). Apparently, this difference is due to the different chemical nature of the substrates studied.

### Conclusions

The selectivity of the process with respect to calcium is most likely explained by the kinetic parameters of the process and the somewhat higher activation energy of calcium leaching. Apparently, the reaction has the first order in ammonium chloride and a rate constant of  $\sim 1-5 \times 10^{-4}$ , while the velocity is controlled by diffusion. The experimentally determined value of the activation energy was  $43.815 \pm 8.973$  kJ/mol at a significance level of 95 % ( $p = 0.05$ ). Magnesium goes into solution, the pH of which is 9. This solution is convenient for precipitating magnesium ammonium phosphate. Magnesium ammonium phosphate is a valuable mineral fertilizer, as well as a profitable, marketable form for pure magnesium. Using ammonium phosphate and bringing the pH to 11, we got magnesium ammonium phosphate. The study of the precipitate obtained with LIBS showed that it contained a minor admixture of calcium and did not contain other metals except magnesium. Thus, the sediment is pure, and the calcium contained in a small amount does not interfere in any way for use in gardening.

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### Асбестқұрамды шикізаттан магнийді селективті бөліп алу әдісі

Мақалада хризотилді асбест қалдықтарын өңдеу бойынша іс жүзінде іске асырылған технологиялардың болмау себептерін анықтау және коммерциялық қызығушылық туғызатын магний мен басқа да пайдалы өнімдерді алу мақсатында қалдықтарды өңдеудің жаңа әдістері қарастырылды. Магний шаймалау кинетикасын зерттеу үшін түрлі концентрациядағы аммоний хлориді ерітінділері қатысында бірқатар тәжірибелер жүргізілді. Шаймаланған магнийдің концентрациясы  $NH_4Cl$  ерітіндісі концентрациясының ( $C_{Mg} = 0.092M$ ;  $C_{Mg} = 0.1M$ ;  $C_{Mg} = 0.102M$ ) жоғарлауымен сипатталды.  $3M$  және  $5M$   $NH_4Cl$  магний ерітінділерінің шаймалау жылдамдығы арасындағы айырмашылық айтарлықтай емес, ал  $1M$  және  $3M$  шешімдері үшін бұл өте үлкен. Магнийді шаймалаудың термодинамикасын зерттеу әртүрлі температурада аммоний хлоридінің  $3$  молярлық ерітіндісі қатысында жүргізілді. Алынған нәтижелер негізінде магний концентрациясының аммоний хлориді температурасы бойынша және зерттеуге алынған тұнбаның құрамындағы металл арасындағы тәуелділік графиктері жасалынды. Тәжірибелер нәтижесі асбест құрамынан магнийдің шаймалау дәрежесі температураның жоғарлауымен артатындығын көрсетті. Белсендіру энергиясы  $44$  кДж-ға тең. Тұнбаны анықтау лазерлік-атомдық эмиссионды спектрометрде жүргізілді. Тәжірибенің нәтижелері бойынша алынған тұнбаның құрамында белгілі бір мөлшерде магний, кальций және басқа да металдар кездесетінін көрсетті және кальций қоспасы алынған тұнбаның қасиеттеріне әсер

етпейтіндігі анықталды. Өртүрлі концентрациядағы аммоний хлоридін шаймалау арқылы жүргізілген тәжірибелер асбестің талшықты құрылымы жойылмағанын көрсетті.

*Кілт сөздер:* магнийді селективті бөліп алу әдісі, асбестқұрамды шикізат, кинетика, термодинамика, концентрация, магний-аммоний фосфаты, белсендіру энергиясы, шаймалау.

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### Селективное извлечение магния из асбестосодержащего сырья

В статье большое внимание уделено выявлению причин отсутствия практически реализуемых технологий переработки хризотил-асбестовых отходов и поиску новых методов обработки отходов с целью получения магния и других полезных продуктов, представляющих коммерческий интерес. Проведены серии опытов с растворами хлорида аммония разной концентрации для изучения кинетики выщелачивания магния. Концентрация выщелачиваемого магния растет с увеличением концентрации раствора  $\text{NH}_4\text{Cl}$  ( $C_{\text{Mg}} = 0.092\text{M}$ ;  $C_{\text{Mg}} = 0.1\text{M}$ ;  $C_{\text{Mg}} = 0.102\text{M}$ ), а также с увеличением времени самого процесса. Показано, что разница между скоростями выщелачивания магния 3М и 5М растворами  $\text{NH}_4\text{Cl}$  незначительна, а для 1М и 3М растворов — довольно велика. Исследование термодинамики выщелачивания магния проводили 3М раствором хлорида аммония при различных значениях температуры. На основании полученных результатов были построены графики зависимости концентрации выщелоченного магния от времени выщелачивания при разных температурах раствора хлорида аммония. Результаты экспериментов показали, что степень выщелачивания магния из асбеста возрастает с увеличением температуры. Вычислена энергия активации, которая составила 44 кДж. Идентификация осадка проводилась на лазерно-атомном эмиссионном спектрометре. Было установлено, что в полученных осадках содержится определенное количество магния, кальция и незначительное количество других металлов. Примесь кальция не влияет на свойства полученного осадка. Испытания, проведенные с применением раствора хлорида аммония различной концентрации, показали, что волокнистая структура асбеста не подвержена разрушению.

*Ключевые слова:* селективное извлечение магния, асбестосодержащее сырье, кинетика, термодинамика, концентрация, магний-аммоний фосфат, энергия активации, выщелачивание.

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### **Inhibitory activity investigation of a new nitrogen-containing surfactant in an acid medium**

In this paper, the results of testing a new nonionic surfactant as a corrosion inhibitor in a 0.5M hydrochloric acid solution are given. The corrosion inhibitor was synthesized by catalytic esterification of maleic anhydride with polyoxyethylene sorbitan and further amidating of the ether with diethanolamine. The structure and composition of the developed inhibitor were characterized by the methods of FT-IR and <sup>1</sup>H NMR spectroscopy. Results showed that the reagent MA/Tween-DEA effectively inhibited the corrosion of carbon steel in hydrochloric solution with an optimal inhibition efficiency of 94 % (100 ppm) at 303 K from weight loss test. Thermodynamic parameters such as adsorption heat ( $\Delta H_a$ ), adsorption entropy ( $\Delta S_a$ ) and adsorption free energy ( $\Delta G_{ads}$ ) were obtained from experimental data of the temperature studies of the inhibition process at five temperatures ranging from 303 to 343 K. The thermodynamic parameters of the corrosion process were calculated in the absence and presence of inhibitor and discussed. The mechanism of action of inhibitor protection of a steel plate by a synthesized inhibitor has been studied. Adsorption of MA/Tween-DEA on the carbon surface in 0.5 M HCl follows the Langmuir isotherm model.

*Keywords:* nonionic surfactant, inhibitor, corrosion protection, inhibition efficiency, temperature, adsorption, thermodynamic, carbon steel.

#### *Introduction*

The problem of corrosion and protection of oil and gas equipment in Kazakhstan is becoming actual, which is primarily due to an increasing number of developing oil, gas and gas condensate fields, containing aggressive components, secondly, with increasing work intensity of oilfield equipment. The use of corrosion inhibitors in the oil and gas industry makes it possible to extend the life of equipment and pipelines transporting oil and gas. Nowadays, the oil and gas industry around the world are the largest consumers of corrosion inhibitors [1].

The authors of [2–4] note that organic and polymeric compounds containing polar functional groups, such as nitrogen, sulfur and / or oxygen in the conjugate system, are effective corrosion inhibitors for steel structures. The inhibitory capacity of these substances is associated with the presence of cyclic rings in them and heteroatoms, which are the main active centers of adsorption [5–7]. Adsorption centers help to form complexes with metal ions. The formed complexes are adsorbed on the metal surface to form a barrier film that separates the metal surface from the corrosive agents present in the aggressive solution [8–11]. The purpose of this work is to study the kinetics parameters, inhibition efficiency and mechanism of corrosion in 0.5M HCl solution of carbon steel plates by a new MA/Tween-DEA reagent by weight loss method at various temperatures (303–343 K).

*Experimental**Materials*

Maleic anhydride (MA), diethanolamine (DEA), polyoxyethylene sorbitan trioleate (Tween-85), pyridine, N,N-dimethylformamide obtained from Sigma Aldrich and used without further purification.

*Solutions*

The aggressive solutions of 0.5M HCl were prepared by dilution of analytical grade 37 % HCl with distilled water.

*FT-IR, NMR analysis*

The structure of the synthesized organic inhibitor was confirmed by FT-IR spectrometry on an Agilent Cary 660 spectrometer; by <sup>1</sup>H NMR spectroscopy in dimethylsulfoxide on a Bruker Avance 300 Mhz NMR spectrometer; by HPLC with H<sub>2</sub>O / CH<sub>3</sub>CN / 0.1 % TFA, column: Nucleodur RP C18 10 μm, buffer races: A = 5 % CH<sub>3</sub>CN / H<sub>2</sub>O / 0.1 HCOOH, B = 100 % CH<sub>3</sub>CN / 0.1 HCOOH. Flow rate — 1 ml/min; Pressure — 68 bar; Electrospray — positive ionization (150–900).

*Synthesis*

Synthesis of a corrosion inhibitor was carried out in two stages. In the first stage, the reaction product was obtained by the catalytic esterification of maleic anhydride and polyoxyethylene sorbitan trioleate. In the second stage, amidation of the ester with diethanolamine was carried out.

A two-necked round bottom flask (50 ml) equipped with a magnetic stirrer and a reflux condenser was charged with maleic anhydride (0.5 g, 0.005 mol) and 5 ml of solvent (DMF). After the maleic anhydride is completely dissolved, Tween-85 (6.5 g, 0.005 mol) and pyridine (0.4 g, 0.005 mol) dissolved in 7.5 ml of DMF are added dropwise. The reaction mixture is heated to 115 °C and left with stirring and reflux for 5 h. Diethanolamine (0.8 g, 0.005 mol) is added to the mixture and the reaction is continued for another 5 h. After that, the process was stopped, cooled to room temperature and the solvent was removed on a rotary evaporator. The yield of the desired product was 80–85 %.

*Weight loss measurements*

Chemical composition of the steel St3. is given in Table 1. Carbon steel samples (5×2.5×0.2 cm) were abraded with a series of emery papers (grade 500–800–1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 250 mL beaker containing 250 mL 0.5M HCl solution with and without addition of different concentrations of MA/Tween-DEA. After 5 h the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility experiments were carried out in triplicate. The average weight loss of three parallel sheets was obtained. The tests were repeated at different temperatures.

The corrosion rate  $V_{cor}$  (mg/cm<sup>2</sup>×h) is calculated by the formula:

$$V_{cor} = \frac{W}{S \cdot \tau},$$

where  $W$  — is the average weight loss of three parallel St3 sheets;  $S$  — is the total area of one specimen and  $\tau$  — is the immersion time.

The inhibition efficiency (IE) was calculated as follows:

$$IE\% = \frac{V_0 - V_1}{V_0} \cdot 100,$$

where  $V_0$  and  $V_1$  — are the values of the corrosion rate without and with addition of the inhibitor, respectively.

Table 1

**Chemical composition of the steel (%)**

C	Si	Mn	Ni	S	P	Cr	N	Cu	As	Fe
0.14	0.15	0.4	0.3	0.05	0.04	0.3	0.0008	0.3	0.08	other

*Results and discussion*

A new chemical compound was prepared by the catalytic esterification of maleic anhydride with Tween-85 and further amidation of the ester acid with diethanolamine. IR and NMR spectroscopy methods were used to study the composition.

Figure 1 shows the FT-IR spectra of MA/Tween-DEA, in which the band at  $3382\text{ cm}^{-1}$  refers to the vibrations of the OH group, bands at  $2921$  and  $2878\text{ cm}^{-1}$ , respectively, to aliphatic  $-\text{CH}_2$  asymmetric and symmetrical vibrations, a band in the region of  $1724\text{ cm}^{-1}$  to the stretching vibrations of the  $\text{C}=\text{O}$  bond of the ester,  $1640\text{ cm}^{-1}$  refers to the amide bond ( $\text{N}-\text{C}=\text{O}$ , amide I). The band at  $1168\text{ cm}^{-1}$  can be attributed to the asymmetric vibration of  $\text{C}-\text{O}-\text{C}$  in the ester bond ( $\text{O}-\text{C}=\text{O}$ ).

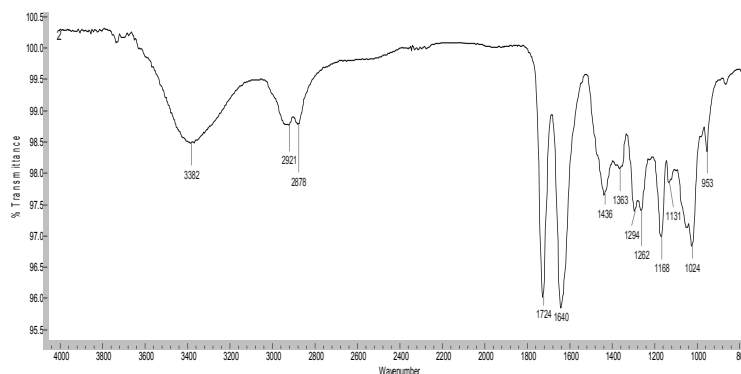


Figure 1. The FT-IR spectra of MA/Tween-DEA

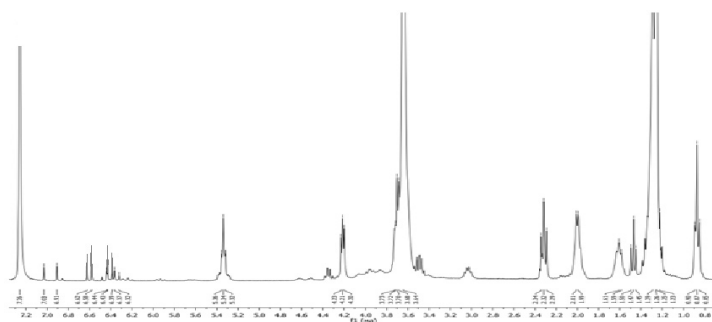
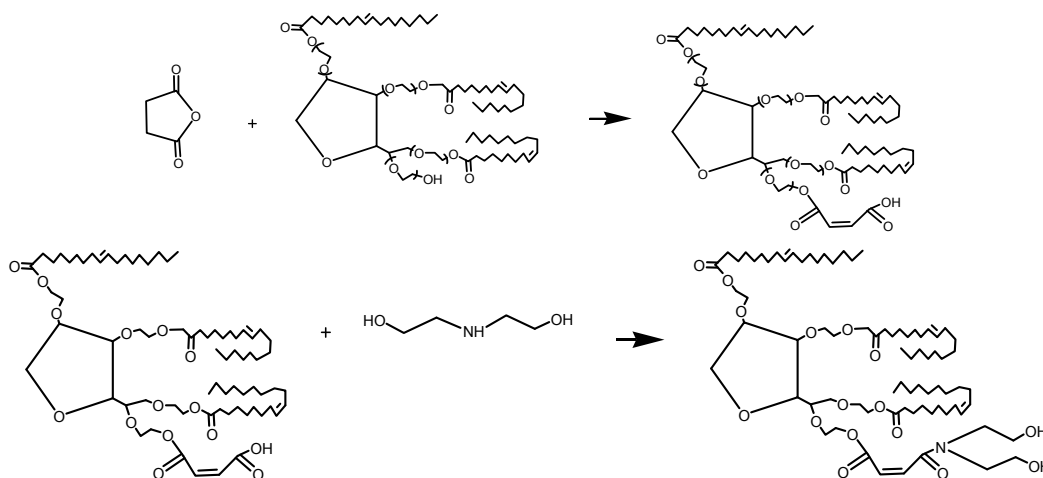


Figure 2. The  $^1\text{H}$  NMR spectrum of MA/Tween-DEA

Figure 2 shows the NMR spectrum of the MA / Tween-DEA reagent.  $^1\text{H}$ -NMR (300 MHz,  $\text{D}_2\text{O}$ , ppm):  $\delta = 0.85\text{--}0.9$  (t, 6 H,  $-2 \times \text{CH}_3$ , alkyl chain),  $1.1\text{--}1.4$  (m, 36 H,  $-2 \times (\text{CH}_2)_{14}$ , alkyl chain),  $1.51\text{--}1.71$  (m, 4 H,  $-2 \times \text{NCH}_2\text{CH}_2-$ ),  $3.01$  (s, 12 H,  $-2 \times \text{N}+(\text{CH}_3)_2$ ),  $3.61$  (s, 4 H,  $-2 \times \text{CH}_2\text{O}$ ),  $4.21$  (s, 4 H,  $-2 \times \text{N}+\text{CH}_2$ ),  $6.39\text{--}6.67$  (m,  $\text{CH}=\text{CH}$ ).

Based on the results obtained by FT-IR and NMR spectroscopy, the structure of the new compound was presented as follows:



Analyzing the structure of the synthesized compound, it is assumed that the new reagent can exhibit the properties of a corrosion inhibitor. The corrosion rate and inhibition efficiency for St3 steel in 0.5M hydro-

chloric solution at 30, 40, 50, 60 and 70 °C in the absence and presence of MA/Tween-DEA are given in Table 2. The study of the temperature range on the inhibition effectiveness is important for clarifying the mechanism and kinetics of their action and, ultimately, for the correct selection of these inhibitors for specific practical purposes.

Table 2

**Corrosion parameters obtained from weight loss of carbon steel in 0.5 M HCl solution containing various concentrations of MA/Tween-DEA at different temperatures**

Temperature, K	Concentration, ppm	Inhibition efficiency (IE), %	Corrosion rate ( $V_{cor}$ ), (mg/cm <sup>2</sup> ×h)
303	Blank		0.3870
	50	60	0.1548
	100	72	0.1084
	150	85	0.0581
	200	94	0.0232
313	Blank		0.4310
	50	58	0.1810
	100	67	0.1422
	150	79	0.0905
	200	89	0.0474
323	Blank		0.5220
	50	54	0.2401
	100	61	0.2036
	150	73	0.1409
	200	89	0.0574
333	Blank		0.6130
	50	51	0.3004
	100	58	0.2575
	150	69	0.1900
	200	79	0.1287
343	Blank		0.6750
	50	49	0.3443
	100	53	0.3173
	150	61	0.2633
	200	75	0.1688

Data analysis on temperature effect on corrosion rate show that with increasing temperature from 303 K to 343 K corrosion rate increases, which corresponds to the regularity of the temperature effect from the Arrhenius equation. Thus, at the temperature of 303 K, the corrosion rate of the uninhibited medium is 0.3870 mg/cm<sup>2</sup>×h, and the introduction of the inhibitor, even in a minimum amount of 50 ppm decrease the corrosion rate by two times and a half and  $V_{cor}$  is 0.1548 mg/cm<sup>2</sup>×h, 200 ppm decreases  $V_{cor}$  in 16 times to 0.0232 mg/cm<sup>2</sup>×h. A similar pattern was found for the temperature range studied from 313 to 343 K. The effectiveness of inhibitory protection in the temperature range under study increases with increasing consumption of the inhibitor, but decreases with increasing temperature. Thus, at the temperature of 303 K, the effectiveness of inhibitor protection increases from 60 % at a reactant consumption of 50 ppm to 94 % at 200 ppm. However, with an increase in temperature to 343 K, inhibitor protection achieves lower values from 49 % at a reagent consumption of 50 ppm to 75 % at 200 ppm.

The relationship between the corrosion rate (mg/cm<sup>2</sup>×h) of the steel plate in a neutral medium and the temperature can be described using the *Arrhenius* equation [9]:

$$V_{cor} = \lambda \exp\left(-\frac{E_a}{RT}\right),$$

where  $E_a$  — is activation energy, kJ/mol;  $\lambda$  — is pre-exponential factor;  $R$  — is universal gas constant, J/mol×K;  $T$  — is the absolute temperature, K.

Figure 3 shows plots of  $\ln V_{cor}$  from  $1/T$  at various concentrations of the reagent and without the introduction of an inhibitor, where extrapolation to the y-axis gives  $\ln \lambda$ , and extrapolation to the abscissa value ( $-E_a/R$ ).

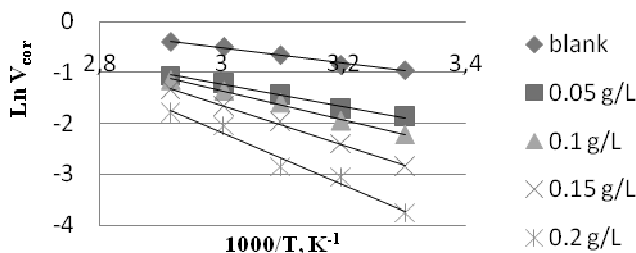


Figure 3. Arrhenius plot for St3 steel in the absence and presence of different concentrations of MA/Tween-DEA

Thermodynamic parameters such as enthalpy and entropy of corrosion process were calculated using the alternative Arrhenius equation [9].

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^0}{R}\right) \exp\left(-\frac{\Delta H_a^0}{R}\right),$$

where  $h$  — is the Planck’s constant  $6.6261 \times 10^{-34}$  Js;  $N$  — is the Avogadro’s number  $6.0225 \times 10^{23}$  mol<sup>-1</sup>.

Figure 4 shows a plot of  $\ln V_{cor}/T$  versus  $1/T$  at different inhibitor’s concentration, where extrapolation to the y-axis yields  $\Delta S_a/R$ , and extrapolation to the abscissa axis ( $-\Delta H_a/R$ ) [12, 13].

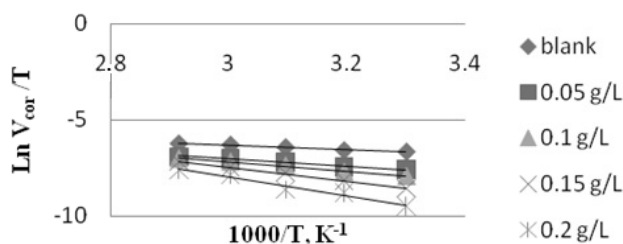


Figure 4. Transition state plot for St3 steel in 0.5M HCl solution in the absence and presence of different concentrations of MA/Tween-DEA

Using the data of the effect of temperature on the corrosion rate, the activation energy was calculated in the presence and absence of an inhibitor. From the obtained values of the activation energy, we can assume the mechanism of action of corrosion inhibition. Calculated values of the activation energy and enthalpy from Figures 3 and 4 are shown in Table 3. As can be seen from Table 3, for the corrosion process at a reactant concentration of 50 ppm  $E_a$  is 12.66 kJ / mol and it increases with an increase in the amount of added inhibitor to 42.97 kJ / mol. An increase in the enthalpy with an increase in the amount of inhibitor introduced is explained by the fact that the decrease in the corrosion rate of steel is mainly controlled by kinetic activation parameters [14].

Table 3

**The values of the parameters  $E_a$ ,  $\Delta H_a$ ,  $\Delta S_a$  in the absence and presence of corrosion inhibitor**

Concentration, g/l	$E_a$ , kJ/mol	$\Delta H_a$ , kJ/mol <sup>-1</sup>	$\Delta S_a$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
Blank	12.66	9.98	-22.59
0.05	18.20	15.52	-11.96
0.1	23.74	21.06	3.55
0.15	32.59	29.92	27.82
0.2	42.97	40.29	54.47

Positive values of the enthalpy of  $\Delta H_a$  indicate the endothermic nature of the corrosion process. The effectiveness of organic substances as corrosion inhibitors can be attributed to the adsorption of molecules of

reagents with the help of polar groups on a metallic surface [15]. Based on the data of thermodynamic calculations, it was shown that, by the mechanism of action, the inhibitor is prone to physical adsorption on the metal surface. The choice of the adsorption isotherm equation depends on the convergence of the obtained data with the trend line. In this paper, we used the equation of the Langmuir adsorption isotherm:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh},$$

where  $K_{ads}$  — is adsorption constant;  $\theta$  — is the fraction of steel surface covered by the adsorbed molecules.

The diagram of the dependence of  $C_{inh}/\theta$  on  $C_{inh}$  is shown in Figure 5, where the value of  $K_{ads}$  was obtained by extrapolation to the axis ordinate.

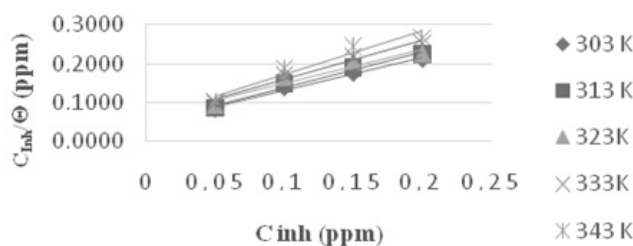


Figure 5. Langmuir adsorption isotherm plots for carbon steel in 0.5M HCl with different concentrations of MA/Tween-DEA

Calculated values of  $K_{ads}$  are given in Table 4. Values of the  $K_{ads}$  indicate that at temperatures of 303–313 K the system practically stays in equilibrium ( $K_{ads} \approx 1.0$ ). A further increase in temperature from 323 to 343 K leads to an increase of desorption process and decrease in the effectiveness of inhibitory protection. Standard free energy of adsorption  $\Delta G_{ads}$  was calculated by equation:

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}),$$

where  $\Delta G_{ads}$  — is free energy of adsorption, 55.5 — is the water concentration of the solution mL/L.

Table 4 shows the values of the equilibrium constant of adsorption-desorption  $K_{ads}$  and free Gibbs energy  $\Delta G_{ads}$ .

Table 4

**Values of the adsorption-desorption equilibrium constant  $K_{ads}$  and the summary Gibbs energy  $\Delta G_{ads}$**

Temperature, K	$K_{ads} \times 10^3, \text{ mol}^{-1}$	$\Delta G_{ads}, \text{ kJ/mol}$
303	1.1022	-10.4
313	1.0207	-10.5
323	0.9123	-10.7
333	0.8758	-10.9
343	0.8518	-11.3

Negative values of  $\Delta G_{ads}$  prove [16] the stability of the adsorbed film on the surface of the steel plate. A decrease in  $\Delta G_{ads}$  (more negative values) with increasing temperature indicates the presence of an endothermic process, which also confirms the mechanism of physical adsorption of the reagent.

### Conclusions

MA/Tween-DEA is a good inhibitor for carbon steel in 0.5M HCl solution. The adsorption of reagent on St.3 steel follows the Langmuir adsorption isotherm. Inhibition efficiency increases with increasing inhibition concentration but decreases with increase of temperature. Gibb's free energy, enthalpy and entropy of adsorption indicate that adsorption process is endothermic and inhibitor adsorbed on surface of carbon steel samples through physical adsorption.

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### **Қышқыл ортада жаңа құрамында азоты бар беттік-белсенді заттардың коррозия ингибиторларының қорғауға температураның әсері**

Мақалада жаңа бейорганикалық беттік-белсенді заттың тұз қышқылының 0,5М ерітіндісіндегі коррозия ингибиторы ретінде қолдану нәтижелері келтірілген. Коррозия ингибиторы малеинді ангидридi мен полиоксидиленсорбитанның каталитикалық этерификациясы және одан әрі дизтаноламин эфирімен амидтеу арқылы синтезделді. Ингибиторлардың құрылымы мен құрамы ИҚ және <sup>1</sup>H ЯМР-спектроскопия әдістерімен сипатталды. Нәтижелер МА/Tween-DEA реагенті гидрохлорлы ерітіндідегі көміртекті болаттың коррозиясын 303 К температурада салмақ жоғалту сынағынан 94 % (100 ppm) оңтайлы тежеу тиімділігін көрсетті. 303-тен 343 К-ге дейін бес температура аралығында ингиблеу үрдісінің температуралық зерттеудің тәжірибелік деректері нәтижесінде энтальпия ( $\Delta H_a$ ), энтропия ( $\Delta S_a$ ) және Гиббстің бос энергиясы ( $\Delta G_{ads}$ ) сияқты термодинамикалық параметрлері алынды. Коррозияның термодинамикалық параметрлері ингибитор қатысында және ингибиторсыз есептеліп, талқыланды. Өзірленген ингибитормен болат пластинаның ингибиторлы қорғау әрекетінің механизмі зерттелді. 0,5М HCl-дегі МА/Tween-DEA көміртегілік бетіндегі адсорбциясы Ленгмюр изотермиялық моделіне сәйкес келеді.

*Кілт сөздер:* ионды емес ББЗ, ингибитор, коррозиядан қорғау, ингибиторлы қорғау тиімділігі, температура, адсорбция, термодинамика, көміртегілік болат.

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## **Исследование ингибиторной активности нового азотсодержащего ПАВ в кислой среде**

В статье приведены результаты испытаний нового неионогенного поверхностно-активного вещества в качестве ингибитора коррозии в 0,5М растворе соляной кислоты. Ингибитор коррозии синтезировали каталитической этерификацией малеинового ангидрида с полиоксиэтиленсорбитаном и дальнейшим амидированием эфира диэтаноламином. Структура и состав разработанного ингибитора были охарактеризованы методами ИК- и  $^1\text{H}$  ЯМР-спектроскопии. Результаты показали, что реагент МА/Tween-DEA эффективно ингибирует коррозию углеродистой стали в растворе соляной кислоты с оптимальной степенью ингибиторной защиты 94 % (100 ppm) при 303 К гравиметрическим методом. Термодинамические параметры, такие как энтальпия ( $\Delta H_a$ ), энтропия ( $\Delta S_a$ ) и свободная энергия Гиббса ( $\Delta G_{ads}$ ), были получены из экспериментальных данных температурных исследований процесса ингибирования при пяти температурах в диапазоне от 303 до 343 К. Термодинамические параметры коррозии рассчитывали в отсутствие и присутствии ингибитора и обсуждали. Изучен механизм действия ингибиторной защиты стальной пластины синтезированным ингибитором. Адсорбция МА/Tween-DEA ингибитора на углеродной поверхности в 0,5М HCl соответствует модели изотермы Ленгмюра.

*Ключевые слова:* неионогенный ПАВ, ингибитор, защита от коррозии, эффективность ингибиторной защиты, температура, адсорбция, термодинамика, углеродистая сталь.



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## Catalytic wet peroxide oxidation of 4-nitrophenol with new pillared clays prepared from the natural material extracted in deposits of Kazakhstan

Natural resources are among the main wealth of the Republic of Kazakhstan, including abundant and cheap natural clays in the southern and northern region of the country. The chemical industry in Kazakhstan has been developing well in recent years and there is an urgent need to find solutions for the treatment of the wastewaters they generate. Composite adsorbents based on natural and pillared clays modified with metal ions have significant prospects for practical use in various fields, such as wastewater treatment, oxidation of organic pollutants, and adsorption of light organic gases. Development of destructive methods based on deep transformations of organic pollutants is considered as a promising direction. Oxidation-reduction reactions activated by various physicochemical reagents allow ensuring complete destruction of hardly oxidizable organic substances and transferring them to safe low-molecular compounds. This work aims to explore natural clays in the synthesis of low-cost pillared clays to be used as catalysts in oxidation technologies for the treatment of wastewaters. Pillared clays with Zn/Fe cations have been prepared from natural clays of Kazakhstan deposits and assessed as catalysts for the catalytic wet peroxide oxidation of 4-nitrophenol that was followed by measuring 4-nitrophenol, H<sub>2</sub>O<sub>2</sub> and the total organic carbon at 398 K. The degradation efficiency of 4-nitrophenol was 100 % with Karatau and Kokshetau Zn-Fe pillared clays and total organic carbon removal was 66 % with Karatau Zn-Fe pillared clay after 2h, considering reaction runs carried out with 5 g/L of pillared clays and at a temperature of 50 °C.

*Keywords:* natural clays, pillared clays, catalytic oxidation, 4-nitrophenol, wastewater, TOC, CWPO, degradation.

### Introduction

The products of the modern industry are becoming increasingly important for the health of the ever-growing population of the planet. In Kazakhstan, a lot of industry has been developing well in recent years, but there is the need to solve the problem of cleaning their drains. One solution passes through the study of wastewater treatment by catalytic wet peroxide oxidation (CWPO) [1]. CWPO is a technology that relies on the oxidation of organic pollutants contained in wastewaters by the action of hydroxyl radicals generated from the catalytic decomposition of hydrogen peroxide. The years of independence in Kazakhstan have become the year's of formation of a completely new state system for ensuring environmental safety, environmental management and nature management, a well-organized and territorially ramified system of executive bodies in the field of environmental protection in the Republic of Kazakhstan. The most contaminated rivers are Nura, Syrdarya, Ili, Lake Balkhash [2, 3]. Ground water is also contaminated, which is the main source of drinking water supply for the population [3]. 4-Nitrophenol (4-NP) is widely used in the production of medicines, fungicides, dyes and dark leather products [4]. Also, it is dangerously toxic, non-biodegradable industrial pollutant, discharged by various enterprises. The oxidation of 4-NP by techniques, such as photo catalysis, Fenton and intensified Fenton, involves the occurrence of oxidized intermediates, namely catechin, hydroquinone and benzoquinone [5, 6]. In this work [7], experiments were done on the photo oxidation of 4-NP in water by UV/H<sub>2</sub>O<sub>2</sub> and the results showed that 4-NP in photo degradation almost completely degraded. Pillared clays (PILCs) have received increased interest due to their texture and catalytic activity for various reactions [8] and they can be an interesting type of porous material used as a sorbent and catalyst.

In this work, we report results of 4-NP oxidation as a model pollutant by CWPO with pillared clays modified by Fe-Zn cations from natural clays of Karatau and Kokshetau deposits.

## Experimental

### Material and Solid Synthesis

Two natural clays with different characteristics from locations in South and North of Kazakhstan of regions Karatau and Kokshetau deposits were used as raw material to prepare the pillared clays. Clays were washed with water several times at 50 °C. The wash with HCl (37 wt.%) was also assessed at 50 °C in order to eliminate residual content inside of the clays. Pillared clays were prepared from natural clay with acid washed. Pillared clays were synthesized with zirconium tetrachloride as a source of zirconium polycations. The pillaring solution was prepared by slow addition of NaOH (0.2M) to the solution containing Zr at room temperature until pH = 2.8 was obtained. The resultant solution was aged for 24 h at room temperature. The clay pillaring process keeps a ratio of 10 mmol of total metal per gram of washed clay. The final material was dried at 350 K for 24 h and calcinated during 2 h at 823 K considering a heating rate of 275 K min<sup>-1</sup>. The X-ray spectral analysis method was used to determine the physico-chemical characteristics of the natural clays. An electron probe microprobe of the brand Superprobe 733 (Super Probe 733) from JEOL (Jael), Japan, was used to determine the angular position and intensity of reflexes. Analyzes of the elemental composition of samples and photography in various types of radiation were performed using an Inca Energy with adispersive spectrometer from Oxford Instruments, England. UV-Vis absorption spectra were obtained using a T70 Spectrophotometer (PG Instruments, Ltd.) in the wavelength range of 200–660 nm, with a scan interval of 1 nm. SEM was performed on a FEIQuanta 400FEG ESEM/EDAX Genesis X4M instrument equipped with an Energy Dispersive Spectrometer (EDS). Transmission electron microscopy (TEM) was performed by LEO 906E instrument operating at 120 kV equipped with a 4 Mpixel 28×28 mm CCD camera from TRS.

### Results and discussion

The results of elemental composition of pillared clays were obtained using EMP analysis. Table presents the content of elements in the catalyts.

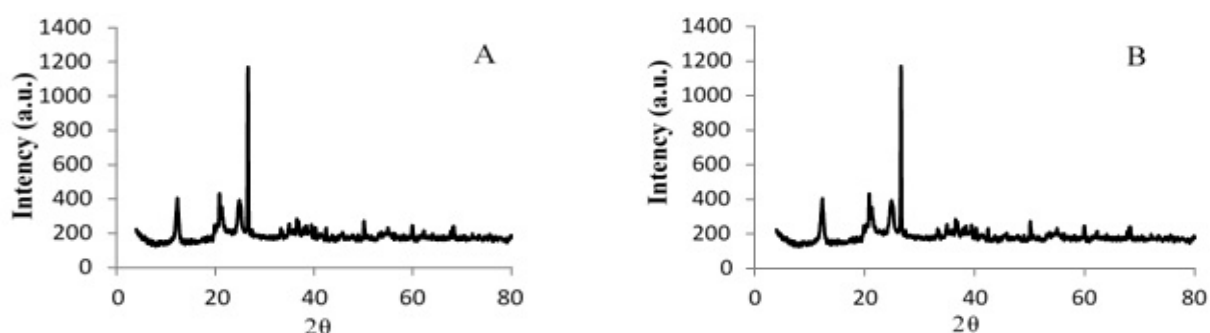
Table

The results of elemental analysis

Pillared clays	Mass of the element (%)										
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	Zr
Fe-Zn (Karatau)	47.02	1.79	1.80	7.11	24.99	2.92	1.90	0.62	14.06	1.85	0.31
Fe-Zn (Kokshetau)	51.29	n.d.	0.24	13.51	24.29	0.36	0.15	1.35	22.85	0.18	n.d.

After pillaring treatment of clays with FeSO<sub>4</sub> and ZnCl<sub>2</sub> solutions the amount of iron in a sample obtained on the Karatau Fe-Zn pillared clay was 14.06 %, and based on the Kokshetau clay was 22.85 %. The chemical composition analysis shows that Si content is higher than other metal elements (see Table). The amount of aluminum absorbed by Kokshetau clay is larger than by Karatau one. The Ca content for Karatau and Kokshetau pillared clays is 1.90 % and 0.15 %, respectively. These results prove a modification of the Fe-Zn pillared clays by hydrolysis and polymerization [9].

The spectra obtained by X-Ray Diffraction (XRD) for natural clays from Karatau and Kokshetau are depicted in Figure 1.



A — Karatau; B — Kokshetau

Figure 1. X-ray diffraction spectra of natural clays by EMP

Our attention was attracted by widespread and cheap mineral clays, which are traditionally used as sorbents for various purposes. The direct use of natural clays for wastewater treatment from organic pollutants is limited due to their chemical and structural features. But they are promising materials for the preparation of carriers for active metals on their basis. The mineralogical composition of Karatau clay is a representative of polymineral clay. Clay samples were subjected to X-ray diffractometric analysis and polymineral composition was confirmed by the appearance of the corresponding signals on the X-ray patterns: montmorillonite ( $d = 14.73\text{--}14.56, 4.254\text{--}2.60 \text{ \AA}$ ), muscovite ( $d = 2.38 \text{ \AA}$ ), kaolinite ( $d = 7.09\text{--}7.04, 2.56 \text{ \AA}$ ) with the formula  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$ . Kokshetau clay showed the presence of kaolinite ( $d = 7.18 \text{ \AA}$ ) and muscovite ( $d = 4.45 \text{ \AA}$ ).

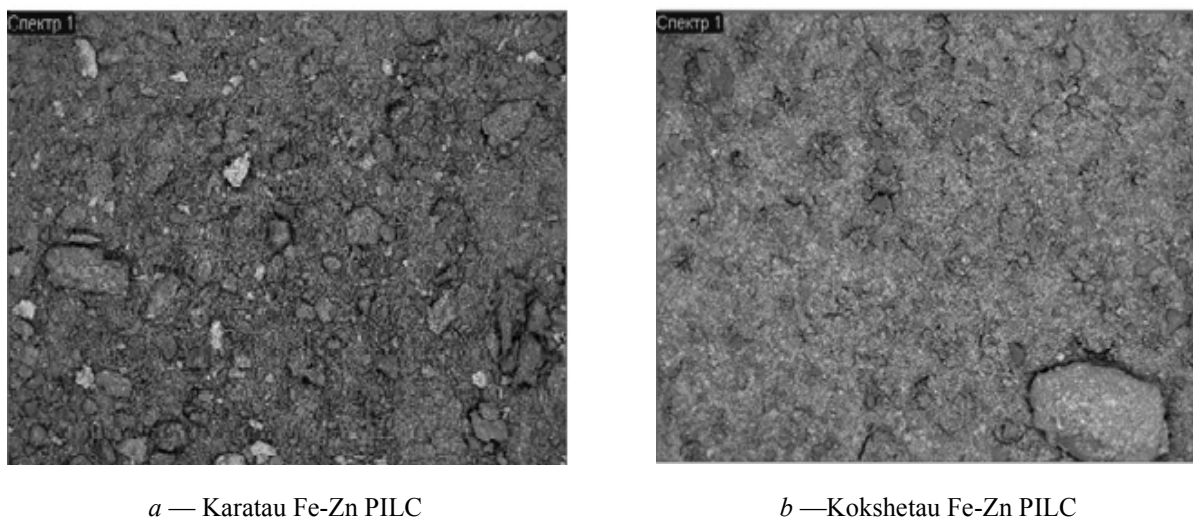
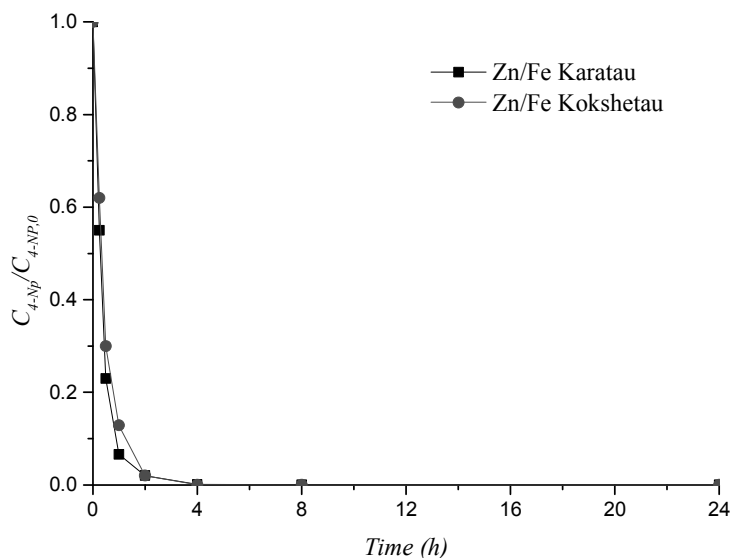


Figure 2. SEM images

The surface morphologies of PILCs are shown in Figure 2. After pillaring the clay the surface of PILCs became rough and porous. The rough surface of PILCs indicated the increase in active sites which made the catalyst more active [10].

The catalytic oxidation of 4-NP in a diluted aqueous medium was carried out in a 250 mL well-stirred glass reactor and thermostated at 323 K. The reactor was loaded with 100 mL of a 4-NP aqueous solution ( $5.0 \text{ g} \times \text{L}^{-1}$ ), the initial pH of solution was adjusted to 3 by adding  $\text{H}_2\text{SO}_4$  and NaOH solutions (not buffer). The stoichiometric quantity of hydrogen peroxide for mineralization was added. The catalyst was loaded ( $2.5 \text{ g/L}$ ) after homogenization of the resulting solution, that moment being considered as  $t_0 = 0 \text{ min}$ . All experiments were carried out for 24 h. Several samples were withdrawn from the medium of reaction at previously selected times to take the course of the 4-NP conversion and the appearance of the intermediate compounds that were measured by high-performance liquid chromatography (HPLC). For that purpose, a Jasco HPLC system equipped with a UV-Vis detector (UV-2075 Plus), a quaternary gradient pump (PU-2089 Plus) for solvent delivery ( $1 \text{ mL min}^{-1}$ ) and a Kromasil 100-5-C18 column ( $15 \text{ cm} \times 4.6 \text{ mm}$ ;  $5 \mu\text{m}$  particle size; reversed-phase) was employed. Total organic carbon (TOC) and  $\text{H}_2\text{O}_2$  were also measured during experiments by using a Shimadzu TOC-L. The pillared clays modified with iron and zinc cations showed excellent catalytic activity in the 4-NP oxidation reaction, with the best results obtained for the modified pillared clay of the Karatau deposit after washing with an acid solution (Fig. 3).

The resulting pillared clays showed very high catalytic activity for the removal of 4-NP. 100 % oxidation of 4-NP with Karatau Zn-Fe catalyst was achieved after 4 h of reaction. Kokshetau pillared clay gives the removal of the contaminant only after 4 hours of reaction. The catalyzer of Karatau Zn-Fe showed a higher activity. In this case, the oxidation process takes no more than 2 hours, which is also the best result in comparison with the known analogues.



4-NP — 5 g/L;  $H_2O_2$  — 17.8 g/L; 2.5 g clays; pH = 3.0, 50 °C

Figure 3. Catalytic peroxide oxidation of 4-NP with Zn-Fe Karatau and Kokshetau PILCs

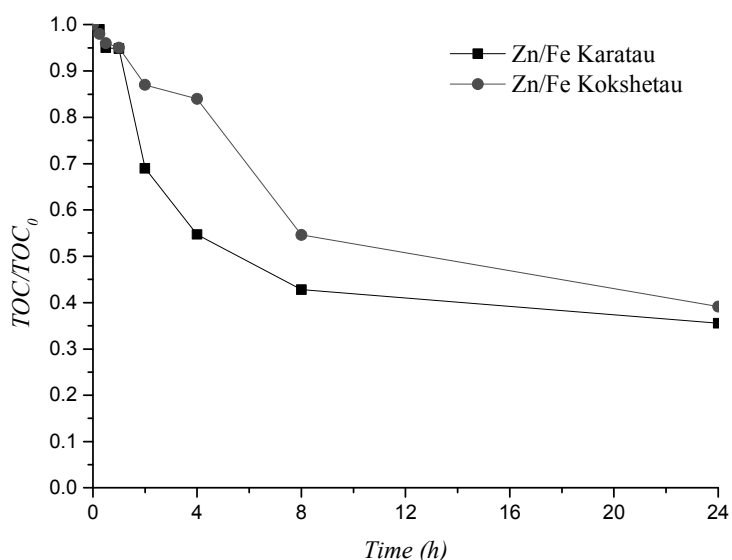


Figure 4. Conversion of TOC in the removal of 4-nitrophenol by CWPO with natural and pillared clays from Karatau and Kokshetau catalyst at 24 hours of reaction time

In the catalytic oxidation experiments, the total removal of the pollutant is reached after 8 h when Karatau and Kokshetau Zn-Fe pillared clays are used as a catalyst. The conversions of TOC after 24 h, with each material, are shown in Figure 4. The high activity for mineralization of the Karatau and Kokshetau Zn-Fe pillared clays obtained with more than 66 % TOC removal after 8 h of reaction.

### Conclusions

Natural clays from the Kokshetau and Karatau regions of the Republic of Kazakhstan can be used as catalysts in the catalytic oxidation of organic pollutants with  $H_2O_2$ . Their catalytic activity can be increased significantly by pillaring processes. The pillaring process of these natural clays is possible when using  $Fe^{2+}$  and  $Zn^{2+}$  cations, increasing the catalytic activity of the materials. The conversion of TOC (66 %) and conversion of 4-NP (100 %) was obtained with the Karatau Zn-Fe pillared clay. Pillared clays showed higher catalytic activity in the oxidation of 4-NP.

### Acknowledgement

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### Қазақстандағы елді мекендеріндегі табиғи материалдан алынған жаңа бағаналы сазбалшықтардың көмегімен 4-нитрофенолды ылғалды каталитикалық сутегі асқынтотықпен тотықтыру

Қазақстан Республикасының негізгі байлықтарының бірі табиғи ресурстар, соның ішінде Оңтүстік және Солтүстік өңіріндегі арзан және бай табиғи сазбалшықтар болып табылады. Соңғы жылдары Қазақстанда химия өнеркәсібі қарқынды дамып, ағынды сулардан өндіріс қалдықтарын тазартудың шешу жолдарын қарастыру қажеттілігі бар. Металл иондарымен модифицирленген бағаналы және табиғи сазбалшық негізіндегі композициондық адсорбенттер әртүрлі тәжірибелік аймақтарда қолдану маңыздылығы бар, соның ішінде ағынды суларды тазарту, органикалық ластауыштарды тотықтыру, жеңіл органикалық газдарды адсорбциялау. Органикалық ластауыштардың терең қайта құруына негізделген деструктивтік әдістердің дамуы перспективалық бағыт ретінде қарастырылды. Әртүрлі физика-химиялық реагенттермен активтелген тотығу-тотықсыздану реакциялары қиын тотығатын органикалық заттарды толық жоюына және қауіпсіз төменмолекулалық қосылыстарға айналуға мүмкіндік береді. Бұл жұмыс ағынды суларды тотықтыру технологияларында катализатор ретінде қолданылатын қымбат емес бағаналы сазбалшықтарды синтездеу үшін алынған табиғи сазбалшықтарды зерттеуге бағытталған. Zn/Fe катиондарымен модифицирленген сазбалшықтар Қазақстанның елді мекендердегі табиғи сазбалшықтардан синтезделіп және катализатор ретінде сутегі асқын тотығы қатысында 4-нитрофенолдың каталитикалық белсенділігі тексеріліп, 398 К көрсеткішінде 4-нитрофенолдың, H<sub>2</sub>O<sub>2</sub> және жалпы органикалық көміртек конверсиясы өлшенді. Zn–Fe Қаратау және Көкшетау бағаналы сазбалшықтарымен 4-нитрофенол деградация тиімділігі 100 %

болып, 5 г/л концентрациясы бойынша 2 сағ аралығында Zn–Fe Каратау бағаналы сазбалшығы 66 % жалпы органикалық көміртек нәтижесін құрды.

*Кілт сөздер:* табиғи сазбалшық, бағаналы сазбалшық, каталитикалық тотығу, 4-нитрофенол, ағынды су, ТОС, CWPO, деградация.

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### **Каталитическое мокрое пероксидное окисление 4-нитрофенола с новыми столбчатыми глинами, полученными из природного материала, добытого на месторождениях Казахстана**

Природные ресурсы являются одним из основных богатств Республики Казахстан, в том числе богаты и дешевые природные глины в Южном и Северном регионах страны. Химическая промышленность Казахстана в последние годы быстро развивается, и существует настоятельная необходимость найти решения для очистки сточных вод. Композиционные адсорбенты на основе природных и столбчатых глин, модифицированных ионами металлов, имеют значительные перспективы для практического использования в различных областях, таких как очистка сточных вод, окисление органических загрязнителей, адсорбция легких органических газов. Разработка деструктивных методов, основанных на глубоких превращениях органических загрязнителей, рассмотрена как перспективное направление. Окислительно-восстановительные реакции, активируемые различными физико-химическими реагентами, позволяют обеспечить полное разрушение трудно окисляемых органических веществ и превращение их в безопасные низкомолекулярные соединения. Эта работа направлена на изучение природных глин в синтезе недорогих столбчатых глин, которые будут использоваться в качестве катализаторов в технологиях окисления для очистки сточных вод. Модифицированные глины с катионами Zn-Fe были синтезированы из природных глин месторождений Казахстана и исследованы как катализаторы при каталитическом окислении 4-нитрофенола с пероксидом водорода, после чего были измерены конверсия 4-нитрофенола,  $H_2O_2$  и общий органический углерод при 398 К. Эффективность деградации 4-нитрофенола составила 100 % со столбчатыми глинами Zn-Fe Каратау и Кокшетау, а общий органический углерод — 66 % со столбчатой глиной Zn-Fe Каратау при концентрации 5 г/л и температуре 50 °С при длительности процесса 2 ч.

*Ключевые слова:* природные глины, столбчатые глины, каталитическое окисление, 4-нитрофенол, сточные воды, ТОС, CWPO, деградация.

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## Influence of coal heat treatment parameters on physical-chemical properties of smokeless fuel

A series of experiments on coking long-flame coals by high-speed thermooxidative pyrolysis was carried out as a part of smokeless fuel technology development from domestic energy coals. The objective of experiments was to determine the influence of basic technological parameters of the coking process (heating rate, coking temperature) on the final physical-chemical properties of the semi-coke, which is an initial material for briquetted smokeless fuel manufacture. The experiments were carried out in a Tamman resistance furnace at 600–1100 °C imitating the coking process in industrial shaft furnace. The rate of heating and the final temperature of coking were found the most important control factors ensuring the production of lump coke with sufficient strength. In the mentioned temperature interval, the reactivity of semi-coke changes by a complicated pattern varying from 3.5 to 9.7 ml/g·s. Along with coking temperature and heating rate, the structural strength of semi-coke grows monotonically, reaching 80 % at heating rate of 90 degrees per minute and a temperature of 1100 °C. Thus, the results of this work allow us to conclude that the most rational temperature range for smokeless fuel production by means of high-speed pyrolysis of young high-volatile coal is found within 600–700 °C (the temperature interval of semi-coking). To ensure sufficient structural strength of semi-coke the rate of coal heating should be at least 30 °C/min. A highly active material with a reactivity of over 9 ml/g·s and a sufficiently high strength and a residual volatiles content of about 8–11 % can be obtained using this method.

*Keywords:* smokeless fuel, thermo-oxidative pyrolysis, energy coals, semi-coke, coking temperature, structural strength, reactivity, volatile substances.

Long flame coal from the Shubarkol coal field was used as a raw material for smokeless fuel making. Shubarkol deposit with overall reserves of over 1.8 billion tons [1, 2] is located in Tengiz area of Karaganda region. The coal is related to long flame (free-burning) coal type, is petrographically homogeneous and vitrinitized. By reflectance, the coal is related to grade D (candle type) [3]. Coals are low-ash, low-sulfur with low phosphorus content, easy and medium-enriching. The content of vitrinite is over 80 % of the organic mass. The reflection is 0.6 %. The quality of coals according to exploration data is as follows:  $W^p$  — 15 %;  $A^d$  — 5÷15 %;  $V^{daf}$  — 40 %;  $S_t^d$  — 0.5 %;  $C^{daf}$  — 76 %;  $H^{daf}$  — 5.5 %;  $Q_s^{daf}$  — 26 MJ/kg;  $Q_i^r$  — 22 MJ/kg. It can be seen that for Shubarkol coal has distinctively low ash content. In separate parts of the coal bed, the ash level has extreme values of 1.4 and 31.0 %. At the same time, the bulk of coal contains 6.0 % ash and below.

The method of high-speed thermooxidizing coking was used to obtain durable lump material from sieved Shubarkol coal based on the rapid heating of coal particles by heat released during the combustion of volatile products of thermal destruction [4–6]. In this process, the formation of the coke structure goes through a series of reactions of coal matter decomposition and the synthesis of new compounds with the formation of semi-coke. Further transformations of the latter lead to the formation of a carburized coke material [7].

To simulate coal heating conditions of high-speed thermooxidizing coking, we used the Tamman resistance furnace, into which a crucible of heat-resistant steel with a coal sample inside was introduced. The crucible has high walls to provide access of air oxygen into the reaction zone. The electric supply of the heater is provided by a power transformer of 80 kVA with thyristor regulation of voltage and current, which allows maintaining the set temperature with an accuracy of 10 °C. A portion of the coal charge was prepared from the 10–20 mm Shubarkol coal. The temperature in the furnace and in the coal layer was constantly measured during the experiment. After the experiment, the residue was weighted to determine the mass loss.

The studies were carried out at a strictly fixed temperature, which was varied from 600 to 1100 °C with the interval of 100 °C. A sample of coal in a heat-resistant steel reactor was loaded into a preheated furnace. During the experiment, a continuous measurement of the temperature in the coal bed was made and, after

reaching a predetermined level of heating, an exposure was held for 5 minutes. After that, the reactor was removed from the furnace and cooled in a sealed container to room temperature. The coking gas evolved in the process of pyrolysis was burned down outside the furnace.

In order to eliminate the influence of heat loss by moisture evaporation, the beginning of recording the temperature in the layer is attributed to the dry state of the material. The zero test time corresponds to coal sample temperature of 180–250 °C, at which point the physical moisture is completely removed from the sample (Fig. 1).

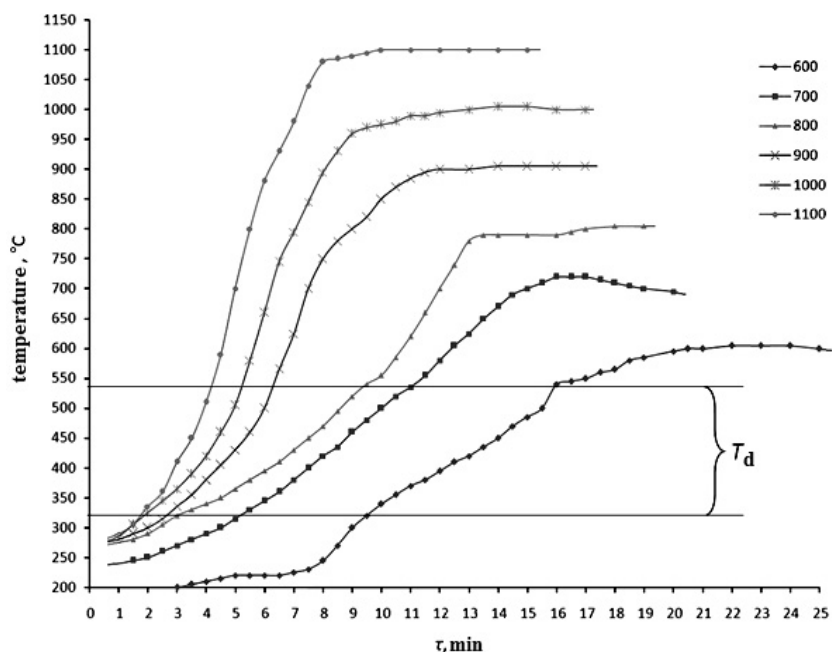


Figure 1. Dynamics of temperature changes in the coal layer at various initial temperatures in the furnace

The influence of temperature and coal heating rate on the structure and properties of the coking product was studied experimentally. The process of high-speed pyrolysis of coal was imitated by pre-heating the furnace to certain degree, which allowed heating the coal samples with varying temperature gradients [8]. The dynamics of the temperature change in the coal layer is shown in Figure 1 as a function of time and the initial temperature level in the furnace.

The data in Figure 1 show that in the temperature range of 320–540 °C corresponding to coal matter destruction processes the rate of coal heating depends on the preset temperature gradient and amounts to 29.4–90.9 degrees per min (Fig. 2), which is sufficient for the formation of a stable structure of the coke residue (semi-coke).

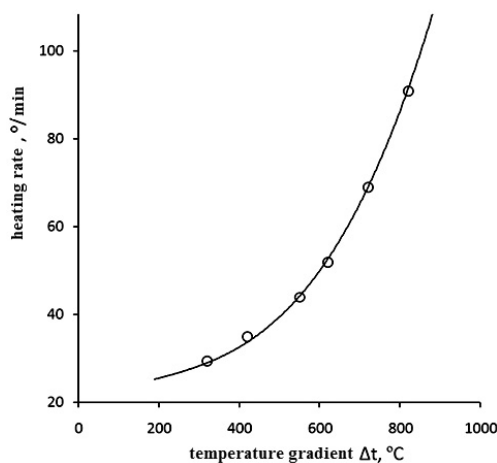


Figure 2. Effect of the temperature gradient on the coal heating rate



Table represents the data on the heating rate and the numerical values of coal mass loss and the results of the proximate analysis of semi-coke samples obtained in interval of 600–1100 °C and heating rates of 29.4–90.9 degrees per minute.

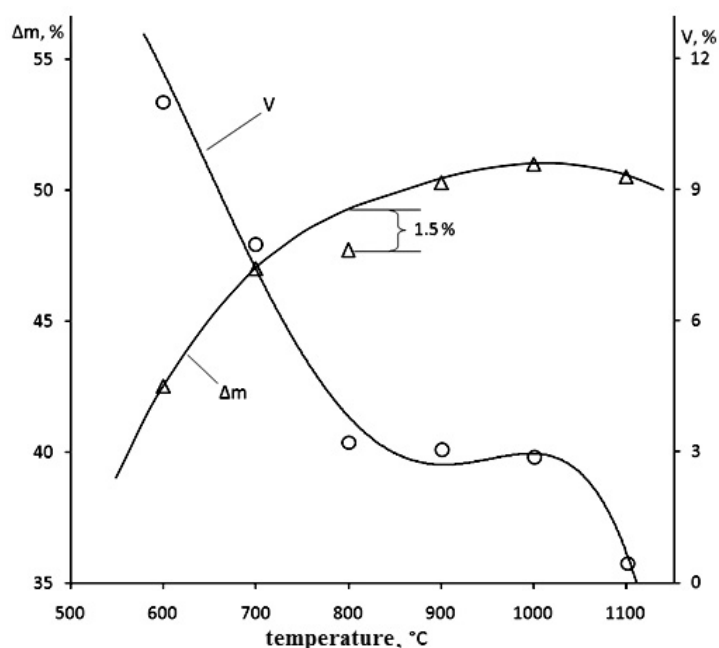
Table

Parameters of high-speed coking process and proximate composition of semi-coke

Temperature, °C	Heating rate, °/min	Mass loss, %	Proximate composition of the product, %		
			A <sup>c</sup>	V <sup>d</sup>	W <sup>r</sup>
600	29.41	42.5	3.01	11.02	2.76
700	35.7	47.0	3.23	7.74	3.54
800	45.45	47.8	3.48	3.22	4.17
900	53.57	50.3	3.61	3.04	4.31
1000	65.22	51.0	3.80	2.86	3.16
1100	90.90	49.8	3.95	0.45	3.37

As we can see, the residual amount of volatiles in the semi-coke (see Table) is in full compliance with coal mass loss (Fig. 3). It can be seen that the most intensive loss of coal mass is observed at low temperatures of 600–800 °C where the greatest decrease of volatiles level takes place. The level of volatile substances stabilizes after 800 °C and varies insignificantly from 3.22 to 2.86 % up to 1000 °C. It is only above 1100 °C, that the volatiles level sharply decreases, reaching 0.45 %. At a temperature of 950–1000 °C the structure of the semi-coke begins to decompose with the release of heavy resins containing hydrogen.

Evaluation of structural strength and reactivity of semi-coke samples obtained at different heating rate and temperature was carried out in accordance with State Standards, namely, «State Standard 9521–74» and «State Standard 10089–89». Evaluation results are shown in the Figure 4. The structural strength of the semi-coke is minimal (no more than 50 %) in the low temperature range of 600–700 °C and at a heating rate below 40 degrees per min. The most noticeable increase in the structural strength occurs in the interval of 700–800 °C and the heating rate range of 40–60 degrees per minute, where structural strength reaches 72 %.

Figure 3. Dependence of mass loss ( $\Delta m$ ) and residual volatiles level ( $V$ ) from the coking temperature

The monotonous growth of the structural strength up to 80 % is observed at a heating rate of 90° degrees per minute and a temperature of 1100 °C. The rate of heating and the final temperature of coking are, therefore, the most important control factors ensuring the production of lump coke with sufficient strength, as follows from the experimental data.

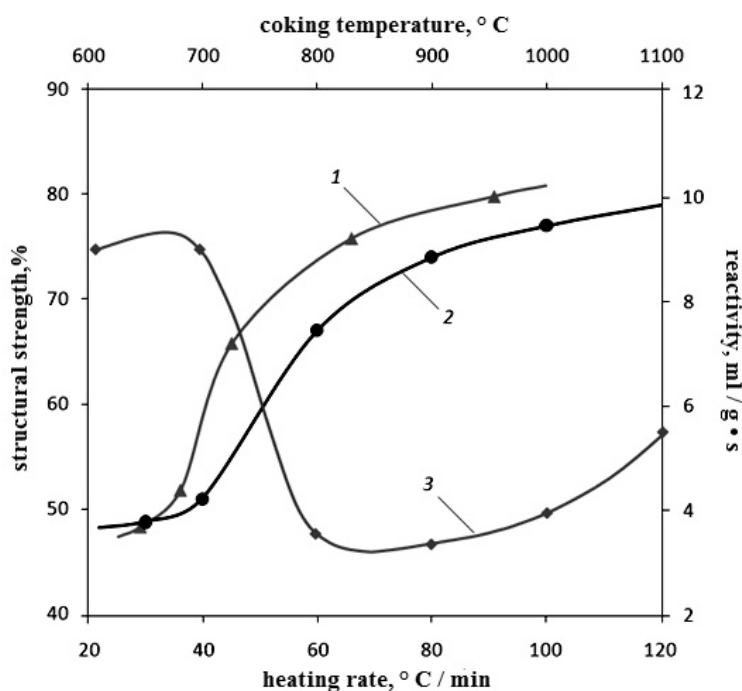


Figure 4. Influence of heating rate (1) and temperature (2) on structural strength and temperature (3) on the reactivity of semi-coke

It follows from the data in Figure 4 that the level of reactivity of semi-coke varies within 3.5–9.7 ml/g·s in the investigated temperature range, and, while the coking temperature grows monotonically, the reactivity variation follows more complicated pattern. Semi-coke has greatest reactivity, which reaches 9.7 ml/g·s, at 600–700 °C. Growth of coking temperature from 600 to 700 °C has very slight influence on overall reactivity. However, the latter sharply decreases to 3.5 ml/g·s in the interval of 700–800 °C and remains practically unchanged up to 900 °C, after which point it begins to increase faster to reach 5.6 ml/g·s at 1100 °C.

#### Conclusion

Thus, the results of this work allow us to conclude that the most rational temperature range for smokeless fuel production by means of high-speed pyrolysis of young high-volatile coal is found within 600–700 °C (the temperature interval of semi-coking). The production of the most reactive material, with a sufficiently high strength and a residual volatile content of about 8–11 %, is ensured under these conditions. This semi-coke considering its basic physical-chemical and technological properties can be proposed as a high-quality intermediate material for further production of smokeless fuel.

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### Көмірді термиялық өңдеу режимдерінің түтінсіз отынның физика-химиялық қасиеттеріне әсерін зерттеу

Отандық энергетикалық көмірлерден түтінсіз отынды өндіру технологиясын жасау шарасында жоғары жылдамдықты термототықтырғыш пиролиз тәсілімен ұзын жалынды көмірлерді кокстау бойынша зерттеу жұмыстары жүргізілді. Кокстау процесінің негізгі технологиялық параметрлерінің (қыздыру жылдамдығы, кокстау температурасы) жартылай кокстың — брекettelген түтінсіз отынды алуға арналған бастапқы материалдың соңғы физика-химиялық қасиеттеріне әсері орнатылды. Зерттеу өндірістік шахталы пештердегі көмірді кокстау процестерін келтіретін, 600–1100 °С температурада Таммана кедергілі пешінде жүргізілді. Зерттеу мәліметтерінің талдауы кокстаудың қыздыру жылдамдығы және соңғы жылдамдығы кесекті және берік жартылай коксты алуына ықпал ететін анықтағыш негізгі фактор болып есептеледі. Зерттелген температура аралығында жартылай кокстың реакциялық қабілеті күрделі заңдылық бойынша өзгереді және 3,5–9,7 мл/г·с шамасы аралығында ауытқиды. Қыздыру жылдамдығын және температурасын жоғарылату барысында қыздыру температурасы 90 град/мин және температурасы 1100 °С кезінде 80 % жететін жартылай кокстың монотонды құрылымдылық өсуі байқалады. Зерттеу шешімі бойынша бастапқы ұшқыш заттардың жоғары мөлшеріне ие жас көмірлерден жоғары жылдамдықты пиролиз тәсілімен алынатын түтінсіз отынды термиялық өңдеу температурасы 600–700 °С (жартылай кокстау және жартылай коксты алу температурасы интервалы) неғұрлым ұтымды болып келеді. Жартылай кокстың жеткілікті құрылымдық беріктігін қамтамасыз ету үшін көмірді қыздыру жылдамдығы 30 °С/мин кем болмауы керек. Бұнын өзінде жоғары белсенді материал, реакциялық қабілеті 9 мл/г·с кем емес, жеткілікті беріктікке ие және қалдық ұшқыш заттар мөлшері 8–11 % болатын алу қамтамасыз етіледі.

*Кілт сөздер:* түтінсіз отын, термототықтырғыш пиролиз, энергетикалық көмір, жартылай кокс, кокстау температурасы, құрылымдық беріктік, реакцияға қабілеттілік, ұшқыш заттар шығыны.

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### Влияние режимов термообработки угля на физико-химические свойства бездымного топлива

В рамках создания технологии производства бездымного топлива из отечественных энергетических углей проведена серия экспериментов по коксованию длиннопламенных углей методом высокоскоростного термоокислительного пиролиза. Установлено влияние основных технологических параметров процесса коксования (скорости нагрева, температуры коксования) на конечные физико-химические свойства полукокса — исходного материала для получения брикетированного бездымного топлива. Опыты проводили в печи сопротивления Таммана при температуре 600–1100 °С в условиях, имитирующих процесс коксования угля в промышленной шахтной печи. Анализ экспериментальных данных указывает на то, что скорость нагрева и конечная температура коксования являются определяющими, наиболее важными факторами, влияющими на получение кускового и прочного полукокса. В исследованном диапазоне температур величина реакционной способности полукокса изменяется по сложной закономерности и колеблется в пределах 3,5–9,7 мл/г·с. При повышении температуры и скорости нагрева наблюдается монотонный рост структурной прочности полукокса, достигающей 80 % при скорости нагрева 90 град/мин и температуре 1100 °С. По результатам исследований определено, что для бездымного топлива, получаемого методом высокоскоростного пиролиза из молодых углей с высоким исходным содержанием летучих веществ, температура термообработки 600–700 °С (температурный интервал полукокса и получения полукокса) является наиболее рациональной. Для обеспечения достаточной структурной прочности полукокса скорость нагрева угля должна быть не менее 30 °С/мин. При этом обеспечивается получение высокоактивного материала с реакционной способностью не менее 9 мл/г·с, с достаточно высокой прочностью и содержанием остаточных летучих веществ около 8–11 %.

*Ключевые слова:* бездымное топливо, термоокислительный пиролиз, энергетические угли, полукокс, температура коксования, структурная прочность, реакционная способность, выход летучих веществ.

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## **Comparison of the chemical flood recovery efficiency via experimental studies on the Pre-Caspian Basin core samples**

This article examines the polymer and ASP flooding effects on the X field. Experimental studies were carried out on core material from heavy oil to compare the effectiveness of these methods. Core data as a sampling depth, porosity, permeability and core volume, as well as properties of reservoir oil and water were determined before filtration tests. At early stage of the study, an optimum composition of alkali-surfactant system for combined flooding has selected. At the second stage, type of the polymer and its optimum concentration has been determined, both for the polymer and for the ASP flooding methods. The one-concentration values have been used for a comparative analysis of the both flooding methods. At the final stage, the filtration tests have been performed on the PLS-200 unit for the comparative evaluation of polymer or ASP flooding efficiency. The studies represent increased displacement coefficient through both recovery methods. For this field, the maximum total displacement coefficient with a value of 0.68 unit fraction is achieved when a solution of both the polymer and the polymer in combination with surfactant and alkali solutions affect. However, the maximum displacement with coefficient 0.19 has been achieved by the ASP method.

*Keywords:* core samples, polymer flooding, ASP flooding, heavy oil, surfactant, alkali, concentration, displacement coefficient.

### *Introduction*

Nowadays the hydrocarbon resource can be characterized by a significant increase in hard-to-recover heavy oil reserves. The Pre-Caspian Basin remained highly concentrated on reserves of heavy oil and natural bitumen; there is an increasing tendency due to the depletion of light fraction. The yields are currently low; the water breakthroughs are more rapid in more permeable layers and inter-layers, the field development becomes less profitable.

Oil reserves of such fields can be recovered with the use of tertiary recovery, for example, chemical flooding method. These methods are not an innovation and have used around the world for more than 30 years. However, due to the development of technology and chemical industry, oil companies again turned their attention to chemical methods. The main Chemical Enhanced Oil Recovery (EOR) includes technologies based on injection of surfactants, alkalis, gel and sedimentation reagents, and polymer solutions [1, 2]. Such flooding methods are widely used in countries such as Russia and China. For example, 80 % of applied tertiary methods refer specifically to chemical EOR in Russia [3]. Also, there are successful examples of polymer flooding in the Daqing and Shengli oil fields in China, where in 2004, oil production increased to 14 % due to the polymer injection and increased to 25 % due to surfactant / alkali / polymer injection [4].

It was agreed to carry out a laboratory test at one of the local oilfields based on such successful chemical methods abroad. The polymer and polymer / surfactant/ alkali systems are the most acceptable in order to remove highly water cut heavy oil. The polymer greatly influences the water viscosity, because of which the solution mobility ratio was reduced and displacement efficiency was increased [5, 6]. The use of water-soluble polymers allows improving the front of oil/water displacement, to extent the water-free operation, which as a result contributes to the increased oil recovery [7, 8]. The combination includes surfactant solutions to reduce the interfacial tension between oil and water, which leads to improved rheological and filtration properties of the oil and microemulsions stabilized by surfactants.

In many websites and articles, both a polymer and ASP flooding methods are applied at various fields with theoretical justification, the field and experimental data [9–15]. Based on the review results, both methods have demonstrated good oil displacement properties, suitable for heavy oil located at the West Kazakhstan field. Therefore, in order to identify an effective flooding method, the laboratory tests have been carried out on core samples from Pre-Caspian Basin. When selecting test samples, factors such as reservoir type, average porosity and the permeability, reservoir temperature and water salinity have been taken into account [16]. Based on the above, the laboratory tests have been carried out on X field chosen as comparative study

for heavy oil displacement and identification of an effective method. Data on core samples from his field is presented in Table 3 and the parameters of the reservoir water are presented in Table 1.

### Experimental

Experience with late stage development project has shown the high water cut and high level of viscosity. The field has several productive horizons, which has represented by sandy siltstone with the medium- and high-permeable layers having average porosity of 34 %. The net pay thickness reaches up to 10 meters and has a reservoir temperature of about 24–30 °C, which are acceptable indicators for polymer flooding.

Cretaceous deposits were selected for the study; core samples with a diameter of 3.8 cm and 5.8 cm have been used. The studies were carried out on four core models with porosity about 33 %. To determine the effect of permeability the cores were selected varying within the range of 400–2300 mD. Core sampling was made manually with subsequent laying out. Upon selection, all samples have been sent for the extraction from mineral oils, water and salts [17, 18]. After core preparation, the next step was to prepare oil and reservoir water. Oil sample was selected manually from the field; water was prepared under laboratory conditions. The reservoir water was prepared based on its chemical composition using the salt types specified in Table 2 [19].

Table 1

Reservoir water parameters (initial data)

Horizon	Ion content (mg/L)					
	HCO <sub>3</sub> '	Br	Cl'	Na'+K'	Ca''	Mg''
M-II	268.0	8.22	71672.0	41069.0	2405.0	1459.0

Table 2

Necessary salt amounts to create reservoir water

No.	Salts	M-II g/L
1	Sodium bicarbonate (NaHCO <sub>3</sub> )	0.369
2	Sodium bromide (NaBr)	0.011
3	Magnesium chloride (MgCl <sub>2</sub> ·6H <sub>2</sub> O)	12.204
4	Calcium chloride (CaCl <sub>2</sub> )	6.660
5	Sodium chloride (NaCl)	78.047
6	Potassium chloride (KCl)	19.571
	Total mineralization	116.861

The next step was the selection of the surfactant / alkali / polymer systems. The lauryl sulfate was used as a surfactant; the sodium hydroxide was used as an alkali. These reagents were prepared in the reservoir waters in the desired concentrations and mixed until complete dissolution has occurred. A phase behavior study of the surfactants and alkali at the oil/water interface was made for the selection of a suitable ASP solution. The following factors have been taken into account for selecting the most suitable polymer for this field:

- high water solubility;
- high viscosity at a given concentration;
- emulsion stability;
- economic parameters.

Based on the above characteristics a FloPaam 5205 VHM polymer having a concentration of 2500 ppm has been selected for the study. Then the main experiment has implemented on the filtration unit. PLS-200 system with four hydrostatic core holders was used for filtration tests. Core samples have been initially saturated with water, and then inserted into the hydrostatic core holders of the equipment [20].

The saturation process of the water samples was performed on an automatic saturator (AST-600), which allows selecting the time of air extraction and saturation pressure in an automated manner for fast and complete saturation of the core samples. The studies were carried out on four core samples. The filtration tests were carried out using two-cylinder high-pressure syringe pumps and piston displacement cylindrical tanks

for the supply of reservoir water and polymer solutions. All experimental studies were carried out at the lack of back pressure, since the liquid volumes were calculated by the method of material balance. The experiment was carried out in the following sequence:

1. Samples were saturated 100 % with water, which then was displaced by oil to create reservoir conditions.

2. The stage of water/oil displacement was carried out to determine the displacement coefficient. In this regard, measuring tubes were installed at the core holder outlet to count the recovered oil. The water/oil displacement coefficient was determined by the ratio of the displaced oil  $V_o$  to the initial oil volume and was calculated by the following formula:

$$\beta = \frac{V_o}{V_{init o}}$$

3. After the injection of 6–8 pore volume and bringing the water cut to the 95–99 %, a selected alkali / surfactant system was injected at a 1–1.5 of the pore volume (only for ASP flooding).

4. Then 2500 ppm polymer solution was injected. Polymer injection continued until the water cut reached 99 % when the pressure was stable.

### Results and discussion

Filtration studies on the effectiveness of polymer systems (polymer and ASP flooding) were carried out on four core samples. Table 3 represents the investigation data indicating the sampling intervals and the typical parameters.

Table 3

#### Core samples and results

Name	Value			
<i>Core data</i>				
Model number	No.1	No.2	No.3	No.4
Depth, m	258.75	258.75	258.85	260.8
Diameter, cm	3.82	3.83	3.81	3.8
Cross section area, cm <sup>2</sup>	11.47	11.52	11.42	11.34
Pore volume, cm <sup>3</sup>	24.69	24.68	21.58	27.05
Air permeability, mD	724.1	1460	393.5	2370
Porosity, %	37.27	36.76	32.87	37.27
<i>Experiment data</i>				
Flooding method	ASP		Polymer	
Temperature, °C	20			
Oil viscosity in the experiment, mPa·s	407.4			
Water viscosity in the experiment, mPa·s	1.05			
Polymer concentration, ppm	2500			
Alkali/Surfactant concentration, gram	0.02/0.6	0.02/0.8	0	0
<i>Experiment results</i>				
Displacement coefficient in water injection, unit fraction	0.51	0.49	0.412	0.58
Residual oil saturation after water injection, unit fraction	0.265	0.315	0.476	0.343
Displacement coefficient in polymer injection, unit fraction	0.60	0.68	0.51	0.68
Residual oil saturation after polymer injection, unit fraction	0.22	0.20	0.416	0.275

For the filtration studies on ASP flooding it was necessary to predict the phase behavior of all the injected liquids. For this purpose, the different alkali/surfactant solutions were prepared in the reservoir water. According to the experiment the following results were achieved:

- the surfactant concentration of 0.02 % reacts without sedimentation,
- the alkali concentration of 0.6 % and 0.8 % demonstrates the low sedimentation at the Cretaceous horizon. Therefore, the following concentrations were chosen for filtration studies:

- a) 0.02/0.6;  
b) 0.02/0.8.

Surfactants and alkalis should not be used for polymer flooding. The results of the filtration studies are shown in Figure 1.

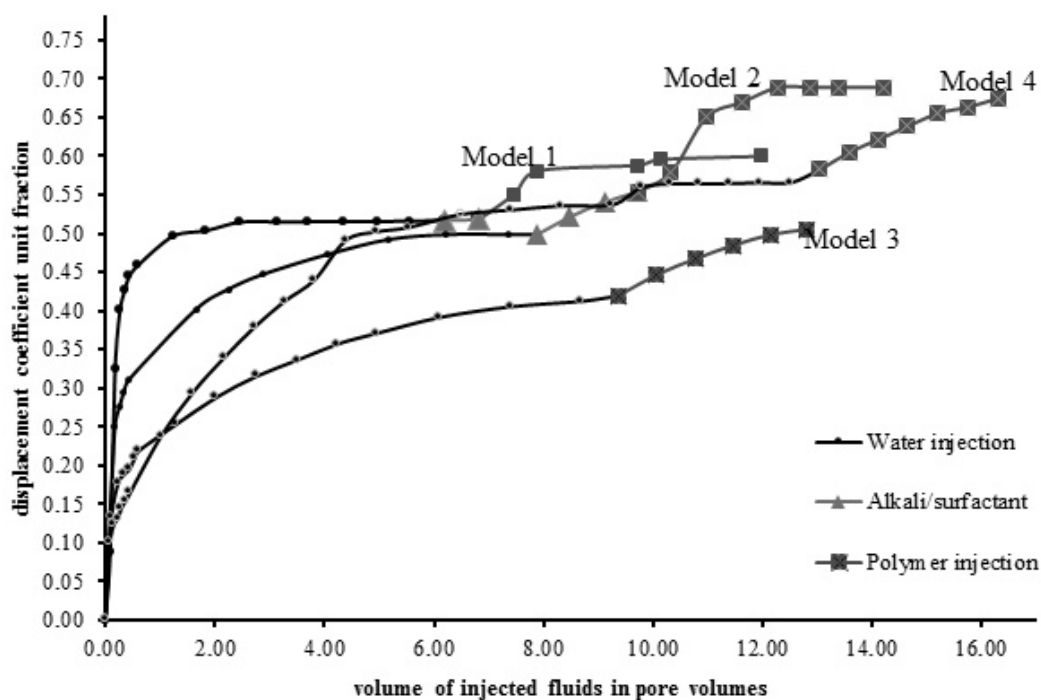


Figure 1. The values of displacements at a polymer and an ASP flooding method

In the Figure above, models 1 and 2 are related to ASP flooding method. Oil displacement by water injection reaches 0.51 unit fraction for the first model and is 0.49 unit fraction for the second model. Then remained oil is displaced by surfactants / alkali solutions, which gave absolutely different results for the both model. For example, the first model, which has a surfactant concentration of 0.02 and alkali concentration of 0.6, does not provide additional extraction. However, an increase in alkali concentration to 0.8 for the second model showed an increase in displacement coefficient for 5%. Models 3 and 4 demonstrate only polymer flooding, where oil initially displaced by reservoir water then by polymer solution. Based on the results of all four models, a polymer flooding has shown the low displacement equal to 0.51 unit fraction, and both polymer and an ASP flooding have shown the maximum displacement equal to 0.68 unit fraction. In addition, there were signs of increase in displacement coefficient when increase the permeability. The relationship between the displacement coefficient and permeability has shown in Figure 2.

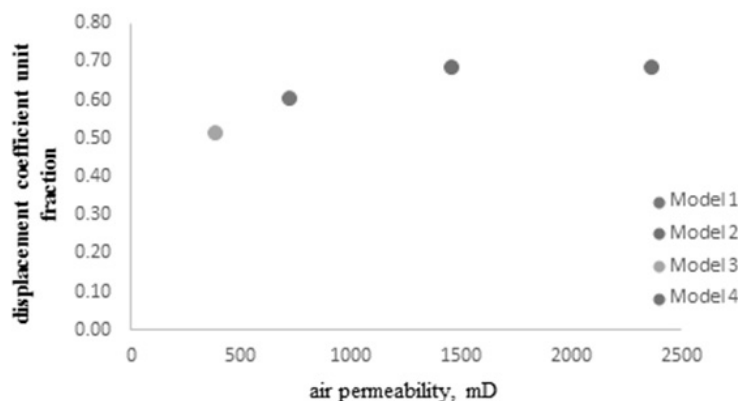


Figure 2. Dependence of displacement coefficient on core sample permeability



### Conclusion

The following results have been obtained during the experimental studies. Firstly, when choosing a surfactant/alkali system, it is not enough to study only the phase behavior of polymer solution at the oil/water interfaces; the key element to achieve the effectiveness of solutions is to carry out filtration tests. Secondly, filtration tests with polymer concentration 2500 ppm have shown an equally high displacement coefficient for both flooding methods. However, this value of 0.68 unit fraction was achieved by polymer and water injection. To obtain more accurate data on the effect of chemicals, the displacement coefficient was calculated only for injected solutions without effect of water displacement and study showed the following results:

a) for model 1, the displacement coefficient increases by 9 % for polymer flooding; there is no displacement due to combined surfactant/alkali flooding;

b) for model 2, the displacement coefficient increases by 5 % in surfactant and alkali injections and increases by 14 % in polymer flooding and showed 19 % increase due to the chemical flooding;

c) for models 3 and 4, the displacement coefficient increases by 10 % in polymer flooding.

Based on these results, the maximum incremental production of 19 % has achieved only with ASP flooding. Undoubtedly, the oil/water displacement also depends on the permeability, which has shown in Figure 2. However, the incremental production for the first core model reached 9–10 % at a lower permeability of 724 mD within ASP flooding and at a higher permeability of 2370 mD within polymer flooding. This is another proof of effectiveness of the ASP flooding method. The laboratory results prove that an ASP flooding is more developed and effective oil recovery method compared to polymer flooding.

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### **Мұнай беруді арттырудың химиялық әдістерінің тиімділігін Каспий маңы ойпаты тау жыныс үлгілерінде эксперименттік зерттеулерді жүргізу арқылы салыстыру**

Мақалада физика-химиялық әдістермен Х кен орынында қойнау қатқа әсер етуде полимерлі және аралас су тоғытуды қолдану қарастырылды. Осы әдістердің тиімділігін салыстыру мақсатында тұтқырлығы жоғары мұнайлы керн үлгілерінде эксперименталды зерттеулер жүргізілді. Керн деректері: кернді іріктеу интервалы, керннің кеуектілігі, өтімділігі және көлемі, сондай-ақ қабаттық мұнай мен судың қасиеттері фильтрациялық зерттеулер өткізілгенге дейін анықталды. Зерттеудің бірінші кезеңінде аралас су тоғыту үшін БА3 және сілті ерітінділерінің оңтайлы арақатынасы таңдалды. Екінші кезеңде полимерлік және аралас әдістер үшін полимердің түрі таңдалды және оңтайлы концентрациясы анықталды. Су тоғытудың екі тәсілін салыстырмалы талдау үшін концентрациясының бір мәнін пайдалану шешілді. Қорытынды кезеңде полимерлік және аралас су тоғыту әдістерінің тиімділігін салыстырмалы бағалау үшін фильтрациялық зерттеулер PLS-200 қондырғысында орындалды. Жүргізілген зерттеулер нәтижесінде анықталғандай, осы екі әдіспен қойнау қатқа әсер ету кезінде ығыстыру коэффициентінің өсуі байқалды. Осы кен орнында полимер ерітіндісімен мен полимердің БА3-бен және сілті мен комбинациядағы ерітінділері мен қойнау қатқа әсері кезінде ең жоғарғы жиынтық ығыстыру коэффициентінің мәніне 0,68 үлестік бірлік қолжеткізілді. Алайда егер қойнау қатқа тек химиялық әсерді ескерсек, онда ығыстыру коэффициенті сәйкесінше 0.1 және 0.19 тең болады, бұл аралас әдіс тиімділігін көрсетеді.

*Кілт сөздер:* тау жыны сұлгілері, полимермен су тоғыту, комбинациялық су тоғыту әдісі, тұтқырлығы жоғары мұнай, БА3, сілті, концентрация, ығыстыру коэффициенті.

А.Ж. Наукенова, Ж.Б. Куатов, Б.Е. Бекбауов, Р.Б. Мербаев

### **Сравнение эффективности физико-химических методов увеличения нефтеотдачи путем экспериментальных исследований на керновых образцах месторождений Прикаспийской впадины**

В статье рассмотрено полимерное и комбинированное заводнение для физико-химического воздействия на пласт месторождения Х. Для сравнения эффективности данных методов были проведены экспериментальные исследования на керновых образцах, содержащих высоковязкие нефти. Данные керны (интервал отбора, пористость, проницаемость, объем, а также свойства пластовой нефти и воды) были определены до проведения фильтрационных исследований. На первом этапе исследований было подобрано оптимальное соотношение растворов ПАВ и щелочей для комбинированного заводнения, на втором этапе были выбраны тип полимера и оптимальная концентрация как для полимерного, так и для комбинированного метода. Для сравнительного анализа двух способов заводнения было решено использовать одно значение концентрации. На заключительном этапе для сравнительной оценки эффективности полимерного и комбинированного заводнения были выполнены фильтрационные исследования на установке PLS-200. В результате проведенных исследований установлено, что при обоих методах воздействия на пласт наблюдалось увеличение коэффициента вытеснения. Для данного месторождения максимальный суммарный коэффициент вытеснения со значением 0,68 доли ед. достигается при воздействии раствором как полимера, так и полимера в комбинации с растворами ПАВ и щелочи. Однако если учесть только химическое воздействие на пласт, то коэффициент вытеснения будет равным 0,1 и 0,19 соответственно, что показывает эффективность комбинированного метода.

*Ключевые слова:* керн, полимерное заводнение, комбинированный метод заводнения, высоковязкая нефть, ПАВ, щелочь, концентрация, коэффициент вытеснения.

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## **Analysis of oil sludge and selection of solvents for the extraction method of petroleum products recovery**

Analysis of oil sludge formed in a storage tank for straight-run fuel oil of «Pavlodar Oil Chemistry Refinery» LLP was carried out in this work. Content of water, oil products and mechanical impurities was 12.4 %, 17.6 % and 70 %, respectively. A sample of oil separated from the sludge was analyzed for the content of silica gel resins, paraffins and asphaltenes, and their group composition was studied using the IR spectrometry method. It was revealed that the oil sludge stabilizers belonged to the paraffin type. TG/DSC analysis was used to obtain information on the initial and final temperature of the thermal decomposition of the oil sludge. It was shown that oil products are completely burned to a temperature of 600 °C. This temperature was used for calcining oil sludge. The phase composition of mechanical impurities isolated from the oil sludge was determined by X-ray diffraction analysis. According to the data obtained from X-ray diffraction analysis, main constituents of the mineral part of the oil sludge were quartz sand (63.1 %) and albite (16.5 %). The most optimal mixture of solvents (white spirit: hexane) for extracting petroleum products from the oil sludge was obtained using the extraction method.

*Keywords:* oil sludge, mechanical impurities, solvent, extraction, paraffins, resins, asphaltenes, TG/DSC analysis.

### *Introduction*

Oil sludge is a complex physico-chemical mixture consisting of water, oil products and mechanical impurities (clay, sand, metal oxides). These components are well mixed and stabilized. The oil phase primarily consists of saturated and aromatic hydrocarbons, asphaltenes and resins [1–4]. A significant amount of oil sludge is produced by the oil industry during production, transportation, storage and refinery. In oil refineries, sludge is formed during processes of fluid catalytic cracking, visbreaking, air flotation and wastewater treatment. Oil sludge accumulates in sedimentation tanks and at the bottom of storage tanks, occupying a working volume [3, 5–7]. Storage of oil sludge causes complex environmental problems, while the oil part of it is a valuable organic raw material. As a result of utilization it is possible to obtain such commodity products as hydrocarbon gas, commercial fuel components, lubricants, bitumen etc., as well as recycling products such as uncultivated soil, ash, soot, gaseous components.

Several methods of processing oil sludges are known with the aim of reducing toxicity, minimizing the volume of oil sludge and extracting petroleum products. Flotation, pyrolysis, combustion, biodegradation, freezing/thawing, ultrasonic treatment, electrical processing, microwave radiation and solvent extraction are among them [3, 4]. Their effectiveness depends on the properties of specific oil sludge such as macrostructure and chemical composition [8]. However, most of the methods are expensive, requiring a long time and even causing secondary pollution of the environment [6]. Based on the analysis of literature data extraction of sludge by a solvent is the most effective method of extracting petroleum among the listed methods, which is characterized by low energy costs [7]. In connection with the foregoing the authors of this paper had aim to analyze the oil sludge and offer the most effective solvent or solvent system for recovering petroleum products by the extraction method based on the data obtained. A sample of oil sludge taken from the storage tank of straight-run heavy fuel oil of «Pavlodar Oil Chemistry Refinery» LLP was selected as a research object of this work.

### *Experimental*

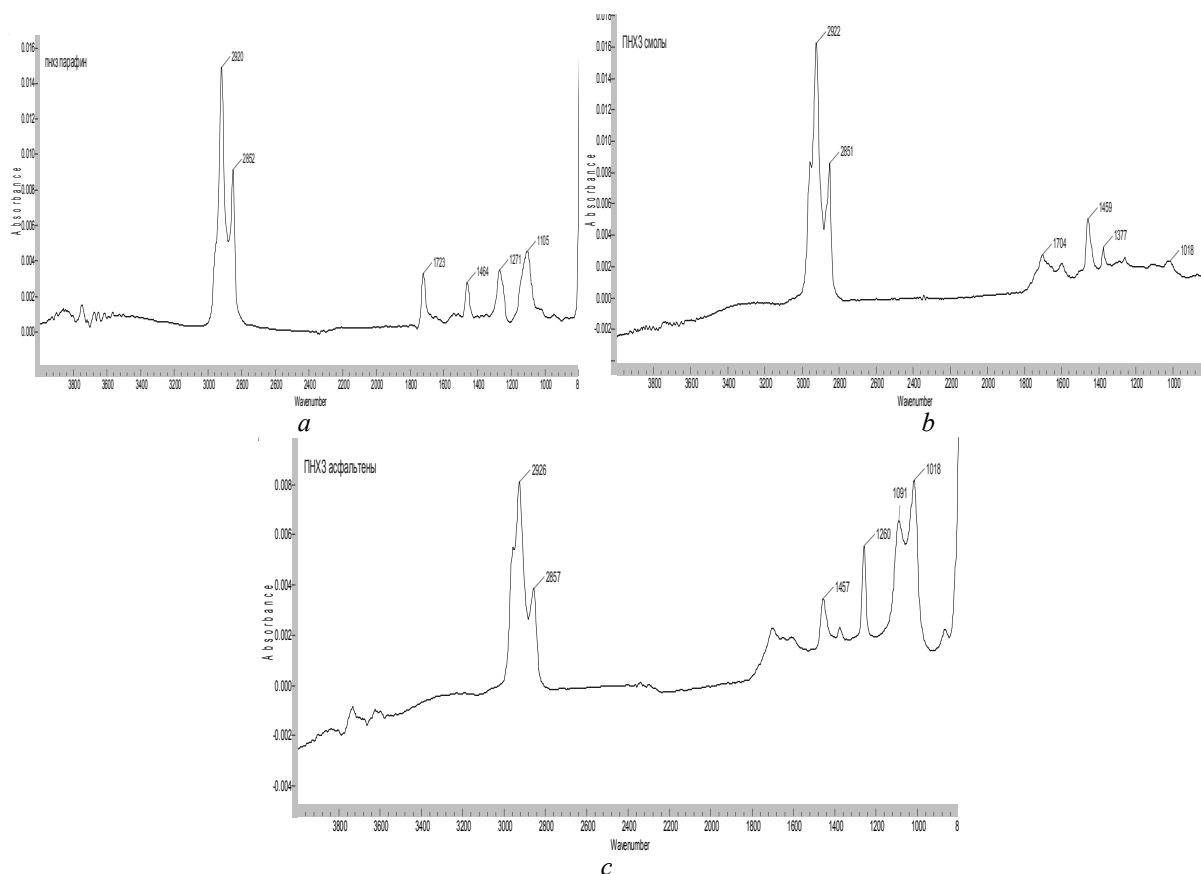
The composition of the sludge was determined by the gravimetric method. A sample of oil sludge (10 g) was dried to constant mass in a thermal oven at 105 °C. The weight loss of the sample was corresponded to the water content of the sludge. The water content determined by the described method corresponds to the water content obtained by the Dean-Stark Method (State standard 2477–65). The content of

petroleum products in the sludge was calculated from the weight loss of the sludge sample subjected to heat treatment in a muffle furnace at 600 °C. A sample of oil extracted from the sludge was analyzed for the content of silica gels (State standard 11858–66), paraffins (State standard 11851–85), resins and asphaltenes (State standard 11858–66\*).

### Results and discussion

It was noted that oil from the sludge is characterized by a relatively large content of silica gel resins (R) and paraffins (P) 4.67 wt. % and 6.88 wt. % respectively. The content of asphaltenes (A) 1.98 wt. %. It is known that, depending on the ratio  $(R + A) / P$ , oil sludge stabilizers can be subdivided into the following types, namely, asphaltene  $((R + A) / P \geq 1.0)$ ; paraffin  $((R + A) / P \leq 1.0)$ ; mixed  $((R + A) / P \approx 1.0)$ . The stabilizers of the sludge investigated were assigned to the paraffin type based on the data obtained.

The group composition of isolated paraffins, resins and asphaltenes were studied by IR spectroscopy at 20 °C on a Cary 660 FT-IR spectrometer (Fig. 1). From the IR spectrum of paraffin (Fig. 1a) it can be seen that its composition contains an intense set of absorption bands in the 2920 and 2852  $\text{cm}^{-1}$  region that corresponds to stretching vibrations of C–H bonds of methyl and methylene groups. The absorption bands in the 1464  $\text{cm}^{-1}$  region are due to bending vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  groups. The absorption band in the region of 1271  $\text{cm}^{-1}$  indicates the presence of unbranched paraffin chains [9]. It follows from Figure 1 that the resin is characterized by a high content of C–H bonds of saturated hydrocarbons in the regions of the absorption bands 1377, 1459, 2861, 2922  $\text{cm}^{-1}$ . The absorption bands in the IR spectra of 1018 and 1704  $\text{cm}^{-1}$  indicate the presence in the samples of both aromatic structures and carbonyl groups. Asymmetric and symmetrical oscillations of  $-\text{CH}_3$  and  $-\text{CH}_2$  groups at 2926, 2857  $\text{cm}^{-1}$  are observed in the spectrum of asphaltenes (Fig. 1c). The absorption bands around 1700  $\text{cm}^{-1}$  are due to the presence of carbonyl groups.

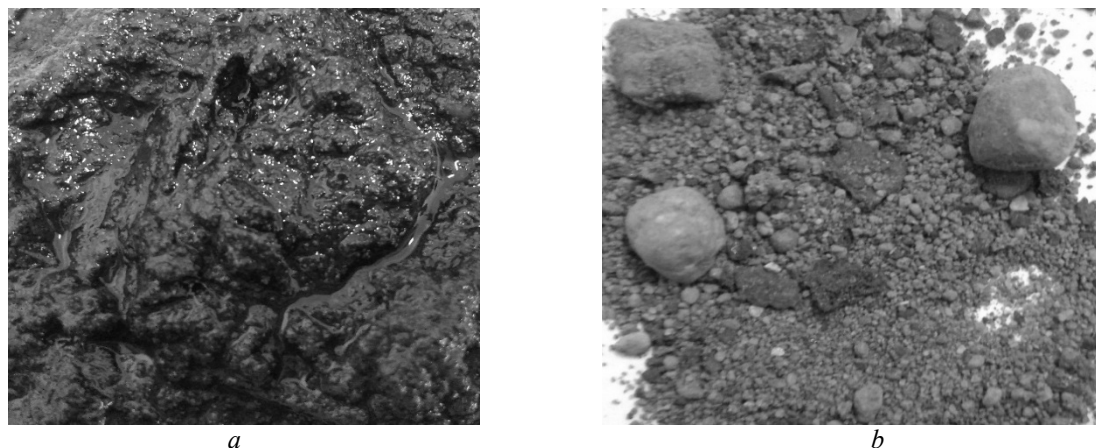


*a* — paraffins; *b* — resins; *c* — asphaltenes

Figure 1. FT-IR spectra of components of oil sludge

Figure 2 presents photographs of samples of oil sludge before and after calcination. Figure 2a shows that oil sludge is a mass of black color. The sample acquired a ginger color and became crumbly after calci-

nation at 600 °C (Fig. 2b). Thus, it can be concluded that all petroleum products are oxidized and burned during calcination at temperature of 600 °C.



*a* — a sample of the original oil sludge; *b* — a sample of oil sludge after calcination at 600 °C

Figure 2. Photographs of oil sludge before and after calcination

Oil sludge investigated was analyzed on TG/DSC to obtain information on the initial and final temperature of thermal decomposition. The studies were performed on a differential scanning calorimeter DSC 131 evo from Setaram at a temperature range from 25 °C to 900 °C. The scanning was performed at a velocity of 20 °C/min. The results of the analysis are shown in Figure 3.

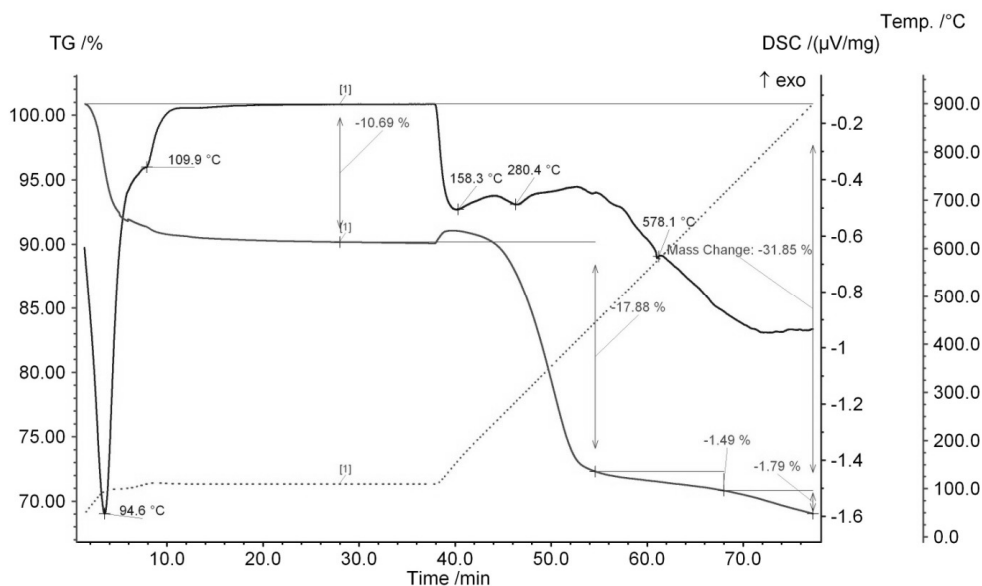


Figure 3. Thermogram of the oil sludge

Several stages of mass loss can be observed from the curves of TG and DSC of oil sludge shown in Figure 3 at temperatures below 160 °C, the mass loss on the TG curves corresponds to the evaporation of moisture and light components whose boiling points are below 160 °C [6]. The thermogram shows the boiling range of the aqueous phase at a temperature of 94.6 °C. The mass loss during the evaporation of light-boiling components was 10.69 %. The largest loss of mass (17.88 %) is observed at temperatures from 158.3 °C to 578 °C. The exothermic peak (280–578 °C) with a maximum at 450 °C, according to the literature [9], refers to the oxidative cracking of hydrocarbons. The loss of mass observed above 600 °C is determined by the thermal decomposition of some inorganic mineral substances [10]. Using this method of research, it was shown that oil products are completely burned to a temperature of 600 °C. Thus, the calcination temperature was found to determine the content of petroleum products in the oil sludge.

Determination of the phase composition of mechanical impurities isolated from oil sludge calcined at 600 °C for 1 hour of oil sludge was carried out by X-ray diffraction analysis using a D8 Advance X-ray diffractometer (Bruker).

Table 1

**Results of X-ray phase analysis of mechanical impurities of oil sludge**

Name	Formula	Content, %
Silicon oxide	SiO <sub>2</sub>	63.1
Albite	NaAl(Si <sub>3</sub> O <sub>8</sub> )	16.5
Orthoclase	KAl(Si <sub>3</sub> O <sub>8</sub> )	6.9
Magnetite	FeO·Fe <sub>2</sub> O <sub>3</sub>	6.4
Muscovite	KAl <sub>2</sub> (Si <sub>3</sub> AlO <sub>10</sub> )(OH) <sub>2</sub>	4.1
Kaolinite	Al <sub>2</sub> O <sub>3</sub> ·2 (SiO <sub>2</sub> )·2 H <sub>2</sub> O	2.9

According to the data obtained (Table 1), the main constituents of the mineral part of the oil sludge are quartz sand (63.1 %) and albite (16.5 %), silicates (6.9 %), magnetite (6.4 %), muscovite (4.1 %), kaolin (2.9 %). The mineral part of the oil sludge investigated, according to the results of the study, is suitable for use as components of building materials.

Thus, on the basis of a complex analysis of oil sludge, it was determined that the water content in the oil sludge under investigation was 12.4 wt.%, the content of oil products was 17.6 wt.% and mechanical impurities was 70 wt.%. As it is known from the literature [3] oil recovery is the most preferred option for the processing of oil sludge, it is noted that it is economically feasible to process sludge containing more than 10 mass% of oil. Extraction-gravimetric method for oil sludge was used to select solvents that have an optimal ratio of dissolving power and the ability to break conglomerates of sparingly soluble components into small fragments.

Table 2

**Results of experiments on the selection of solvents by extraction-gravimetric method at the boiling point of solvents**

Solvent/mixture of solvents	Solvent ratio, vol. %	Extraction rate of oil products, %
Petroleum ether	100	63.13
White Spirit	100	71.02
Benzene	100	74.60
Petrol	100	82.95
Hexane	100	89.60
Thinner 646	100	96.99
Gasoline: hexene	95:5	88.30
Hexane : hexene	95:5	92.05
White spirit : hexene	95:5	97.44

According to the results obtained (Table 2), the most effective solution for dissolving the sludge is a mixture of solvents such as white spirit with hexene, the degree of recovery of petroleum products with this mixture was 97.44 % while in white spirit, which is a mixture of liquid aliphatic and aromatic hydrocarbons the recovery rate does not exceed 71 %. Good results were obtained using a solvent 646, in which toluene, butyl acetate, acetone, butanol, ethyl alcohol are present. The recovery rate of oil products was 96.99 %. Petroleum ether was the least effective solvent as it is a mixture of light aliphatic hydrocarbons; the content of dissolved petroleum products in it was 63.13 %. It can be noted that an increase in the efficiency of solvents is observed when an unsaturated hydrocarbon (hexene) is added to them.

A series of experiments were carried out to select the optimal ratio of hydrocarbons in white spirit: hexene mixture in order to extract oil products from oil sludge efficiently. Mass ratio of oil sludge : solvent was held at 1:4 and the dissolution time was 1 hour. The maximum yield of petroleum products 17.15 % by weight was observed at a volume ratio of white spirit : hexene 95:5. In this connection, for a given ratio of a mixture of hydrocarbons, studies were carried out on the selection of the oil sludge: solvent optimal ratio.

The data indicate that for the oil sludge and solvent mixture of white spirit : hexene (95:5) the ratio 1:4 is optimal.

### Conclusions

Thus, an analysis of oil sludge from a storage tank for straight-run fuel oil was carried out. According to the TG/DSC analysis, it was found that water evaporation occurred at 94.6 °C, mass loss in the 158.1–578.3 °C region corresponds to the combustion of organic substances, and at a higher temperature, some inorganic mineral compounds are expected to decompose. It is established that the mineral part of the oil sludge was mainly represented by quartz. The most optimal mixture of solvents for extracting petroleum products from oil sludge was extracted using the extraction method. The best results were obtained by using a mixture of white spirit : hexene in a weight ratio of 95:5, the ratio of oil sludge : solvent 1:4. At this ratio, the recovery of oil from the sludge was almost 98 %.

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## Мұнай өнімдерін экстракциялық әдіспен бөліп алу үшін мұнай шламын талдау және еріткіштерді таңдау

Мақалада «Павлодар мұнай-химия зауыты» ЖШС мазутты сақтау резервуарынан алынған мұнай шламына талдау жүргізілді. Су, мұнай өнімдері мен механикалық қоспалардың мөлшері сәйкесінше 12,4 %, 17,6 % және 70 % құрады. Шламнан бөлініп алынған мұнайдың сынамасы құрамында силикагель шайырлары, парафиндер және асфальтендер мөлшерін анықтау үшін талданды, сонымен қатар олардың топтық құрамы ИҚ спектрометриясы арқылы зерттелді. Мұнай-шламының тұрақтандырғыштары парафинді түріне жататындығы анықталды. Мұнай шламының термиялық ыдырауының бастапқы және соңғы температуралары жайлы ақпарат алу үшін ТГ/ДСК талдауы пайдаланылды. Мұнай өнімдері 600 °C температурада толығымен жанып кететіндігі байқалды. Сондықтан аталған температура мұнай шламын күйдіру үшін пайдаланылды. Мұнай шламынан бөлініп алынған механикалық қоспалардың фазалық құрамы D8 Advance (Bruker) рентген-фазалық дифрактометр көмегімен рентген-фазалық талдау әдісімен анықталды. Алынған мәліметтер бойынша, кварц құмы (63,1 %) және альбит (16,5 %) мұнай шламының минералды бөлігінің негізгі құраушысы болып табылатындығы көрсетілді. Мұнай шламынан экстракция әдісімен мұнай өнімдерін бөліп алу



үшін еріткіштердің ең оңтайлы қоспасы таңдалды. Ең жақсы нәтиже уайт-спирит : гексен қоспасы арқылы алынды.

*Кілт сөздер:* мұнай шламы, механикалық қоспалар, еріткіш, экстракция, парафиндер, шайырлар, асфальтендер, ТГ/ДСК талдау.

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## Анализ нефтяного шлама и подбор растворителей для экстракционного метода извлечения нефтепродуктов

В статье проведен анализ нефтяного шлама ТОО «ПНХЗ», отобранного из резервуара хранения прямогонного мазута. Содержание воды, нефтепродуктов и механических примесей составило 12,4 %, 17,6 % и 70 % соответственно. Образец нефти, выделенный из шлама, был проанализирован на содержание силикагелевых смол, парафинов и асфальтенов, а также был изучен их групповой состав с помощью метода ИК-спектроскопии. Выявлено, что стабилизаторы нефтешлама относятся к парафиновому типу. Для получения информации о начальной и конечной температурах термического разложения исследуемого нефтешлама был использован ТГ/ДСК анализ. Было показано, что нефтепродукты полностью сгорают до температуры 600 °С. Данная температура используется для проведения обжига нефтешлама. Определен фазовый состав механических примесей, выделенных из нефтешлама, методом рентгенофазового анализа на рентгенофазовом дифрактометре D8 Advance (Bruker). По полученным данным выявлено, что основными составляющими минеральной части нефтешлама являются кварцевый песок (63,1 %) и альбит (16,5 %). Была подобрана наиболее оптимальная смесь растворителей для извлечения нефтепродуктов из нефтешлама экстракционным методом. Лучшие результаты были получены при применении смеси уайт-спирит : гексен.

*Ключевые слова:* нефтяной шлам, механические примеси, растворитель, экстракция, парафины, смолы, асфальтены, ТГ/ДСК анализ.

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# ХИМИЯНЫ ОҚЫТУ ӘДІСТЕМЕСІ МЕТОДИКА ОБУЧЕНИЯ ХИМИИ METHODS OF TEACHING CHEMISTRY

UDC 501:543.061

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## **Application of educational games in the teaching of chemistry**

The authors of the article consider the possibilities of using the game method of instruction in the study of chemistry. Correctly selected game and tasks allow activating both the learning process itself and creating conditions for the multilateral development of students. The article presents two games «Electronic formula» and «Guess the compound». The main rule of the game «Electronic formula» which guides the players is the strictly consistent construction of electronic formulas of the currently selected elements. As a result, students learn the knowledge of electronic constitution of elements and the ability to build them. The second game «Guess the compound» is based on the question-and-answer principle and ends at the moment when one of the players (or a group of players) with the help of their guiding indirect questions will guess what this substance is. Questions can be asked in different ways, but in general, based only on the chemical and physical properties of the substance being determined. The content and form of the organization of game training contribute to the formation of skills and practical skills, the disclosure of the creative abilities of students. The opportunity is shown to awaken and strengthen interest in chemistry, a sense of collectivism and mutual assistance in solving difficult problems. The possibilities of mutual enrichment with information and skills in the process of the game, the development of the ability to generalize and control the acquired knowledge, confirmed by the long-term use of the game method of learning in the study of chemistry in secondary schools and in higher education institutions are revealed.

*Keywords:* education, educational chemical games, electronic formula, analysis of substance composition.

The use of new technologies in teaching and upbringing is the most priority in the modern educational process. One of the most effective methods for developing and improving cognitive activity, intellectual and creative abilities of students is the use of gaming technologies. As practice has shown, they contribute to the activation of attention, thinking and quick reaction in solving set tasks. A great contribution to the development of the theory and practice of gaming technologies was made by many foreign and domestic authors, for example [1–7].

As a result of the use of game training methods: 1) cognitive activity is stimulated; 2) mental activity is activated; 3) associative thinking and memorization is formed; 4) develops the ability to solve problematic issues; 5) personality traits are manifested; 6) the motivation to study the subject increases. Game technologies in the chemistry lesson contribute to the acquisition of specific practical skills, consolidating them, turning knowledge into experience. Of course, any learning games should have a great content and cognitive saturation, a scientific content that generates interest in cognition. This strategy can be used to arouse and strengthen interest in the study of the fundamentals of natural sciences, and in particular the subject of chemistry [8]. When using gaming technologies in training, it is necessary to use such methodical procedures that would activate the thought of students, stimulate them to independently acquire knowledge.

It is necessary for the pupil to work actively and enthusiastically in the lessons, to use this as a starting point for the emergence and development of curiosity, deep. The process of the game allows to form the qualities of an active participant in the game process, learns to find and make decisions, develop abilities that can be found in other conditions and situations, to learn consciousness, non-ordinary behavior, the ability to

adapt in the existing conditions set by the game. To learn the ability to communicate, establish contacts, get pleasure from communicating with partners, learn to create a special emotional environment, attractive for students. Game forms can be used both in school and in higher educational institutions, as well as used in conducting non-traditional lessons.

A feature of educational games in the natural sciences is the need for a game form to teach students the laws of a particular science. At the same time, it is necessary to link the educational material with the corresponding teaching game, which is quite a difficult task, since the creation and use of such games require the consideration of a large number of conditions. For training in higher education, there are few such educational games. Therefore, the creation of such games for the natural sciences, in particular for chemistry, is an independent scientific, pedagogical and methodical interest.

One of the first examples of such games in chemistry was presented in [9]. Almost at the same time in [10; 12–65], similar games were shown for use in chemistry classes at higher educational institutions.

It should be noted that the use of educational games in chemistry classes has made it possible to intensify the process of chemistry teaching itself, and therefore, as a first example consider the game called «Electronic formula» which is based on the building of electronic formulas of different chemical elements. The game offered for learning makes it easier by the students to obtain the knowledge they need for understanding the principles of formation of the electron configuration of the chemical elements. The second game given as an example is called «Guess the compound», which allows the determination of the substance, asking the least number of questions about the properties of the ions which compose this compound.

#### *Educational game «Electronic formula»*

As is known from the textbooks, the distribution of electrons in the atom by levels and sublevels is represented by the electronic formulas of the elements. For example, the electronic formula of zinc will look like this:  $Zn — 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ .

In the learning process, students need knowledge of the electronic structures of elements and the ability to build them. In the educational game «Electronic formula» use the cards, which show the individual components of the electronic formula of the element (see Fig. 1):

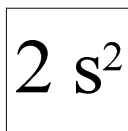


Figure 1. Card of the educational game «Electronic formula»

All cards have the same size, for example, with cards that are widely known to us for the card game. The game continues until one of the students-player gets rid of their cards. The main rule that guides players is the rule of strictly sequential construction of electronic formulas of the currently selected elements (naturally, in the order of the sequence of student moves). For example, the teacher decides to check the students' knowledge of electronic carbon, chlorine and scandium formulas. To do this, they prepare cards for the components of the electronic structures of these elements. In the case of carbon having the electronic formula  $1s^2 2s^2 2p^2$ , make 4 cards (see Fig. 2).

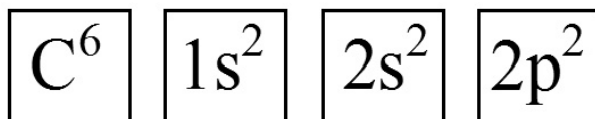
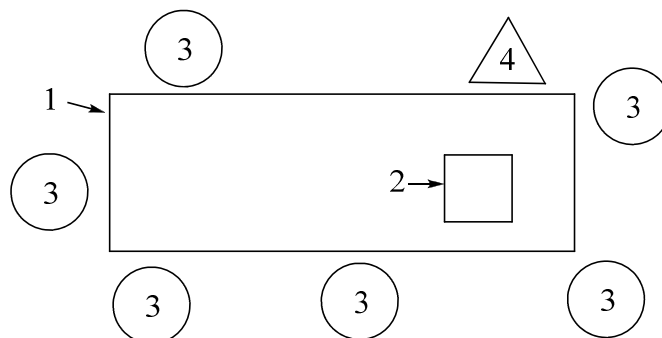


Figure 2. A set of cards for the carbon atom in the game «Electronic formula»

Correspondingly, 6 and 8 cards are prepared for chlorine and scandium having electronic structures:  $1s^2 2s^2 2p^6 3s^2 3p^5$  and  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ . Then the cards are mixed and distributed to the playing students. Since the number of cards in this example will be equal to 18 and each player is given at least 4–5 cards, the optimal number of players will be 3–4 players. The sequence and direction of the moves of the participants in the game are agreed in advance. As a rule, the game goes along the clock hand and the first student begins it, sitting in this direction immediately after the person who distributes cards. The distribution

of cards to students performs in turn. The scheme for students' location and the course of the game «Electronic formula» is presented in Figure 3.



1 — table; 2 — frame of the periodic table; 3 — students; 4 — teacher

Figure 3. Location of the game participants

You must strictly follow the rule of compulsory course for each student. In one move, only one card is laid out from the number of cards of chemical elements or the electronic formulas that make up them. The game «Electronic formula» is carried out using the Table shown in Figure 4.


Figure 4. Table of the educational game «Electronic formula»

Cards with components of electronic structures can be laid out only after the card with the chemical symbol of the corresponding element is put. For example, proceeding analysis of the task described above, let's say that when distributing cards our student got the following ones (see Fig. 5).

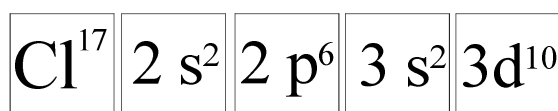


Figure 5. Cards received for the game by the student-player

To his first move, we can assume that the following game situation will appear on Table, shown in Figure 6.

$\text{C}^6$	$1s^2$	$2s^2$				
$\text{Sc}^{21}$	$1s^2$					

Figure 6. The situation of the educational game «Electronic formula» at the moment of the student's possible move

Our player can make, according to the rules of the game, two possible moves. The first is to go with a card of chlorine, while opening up opportunities for other players, allowing them to get rid of other cards, the second — with a  $2s^2$  or  $3s^2$  card, continuing the already begun series of respectively carbon or scandium. The

second move seems naturally more profitable for the player because he has a card  $3d^1$ , which he can lay out, sending the game in the direction of building the corresponding for the scandium series. This is also correct in that he can use the  $2p^6$  card in this row. And chlorine cards also allow other players to orientate the game in a direction more advantageous for them.

Thus, the educational game «Electronic formula» gives students the specific subject knowledge and has a direct impact on the formation of such qualities of students as the system approach, flexibility, and understanding of the basic law of chemistry.

#### *Educational game «Guess the compound»*

The «Guess the compound» educational game is simple both in design and by the rules. Any number of students can take part in it in any quantitative ratio. The basic principle of the game is the question-and-answer, and it ends at the moment when one of the players (or a group of players) using his leading questions will guess the substance hidden from him (her). The opposite side, respectively, selects the substance, in the literal sense of the word or theoretically, and answers the questions of the requesting side. The answers can only be unambiguous «yes» or «no». Questions should be as clear and simple as possible. That player (or team) wins, who will determine the substance, asking the least number of questions. The game is more convenient to carry out, thus, when one student stands on the board, and the rest, having chosen up the substance, answer the questions. Then there is a change of players in order of priority. The game ends when all students already had have been in the role of guessing player. If the number of players in the group is large, then it is recommended to play with teams. For a more complete understanding of the game, let's analyze the corresponding example. It deals with the chemical properties of selected compounds from the cations and anions. Suppose that for the game the group has offered a solution of the silver nitrate salt. How can the student guess this problem? For this, one of the possible variants of questions and answers with comments to them is supplemented then.

Question: Is it a solution?

Answer: Yes.

Question: Is it colored?

Answer: No.

Two of these questions make it possible to determine whether a solubilized unknown substance is well dissolved in water (or some other solvent, which it is desirable to specify by asking an additional question: is the solvent the water?). And whether there are colored anions or cations in solution. If they are available, it is recommended to find out their color, giving additional information. In our case, this is not the case, and further questions can be asked in different ways, but in general, based only on the chemical and physical properties of the substance being determined. Asking questions like this: the substance cation is in the first group of the periodic table? — is not allowed, because such generalizations do not give a more complete picture of the game, so further questions can continue in the following order:

Question: Is the cation of substance monovalent?

Answer: Yes.

Knowledge of the valence of the cation sharply narrows the circle of cation search. Anion ions reacting with the cation can also act. In our case, the cation circle is limited, and therefore the greatest effect can be given by the question concerning anions that can precipitate a number of related cations.

Question: Does the substance cation form a precipitate in an ammonia solution with a carbonate ion?

Answer: No.

Question: Does the substance cation form a precipitate with the chlorine anion?

Answer: Yes.

Thus, using the leading questions given above, it was possible to find out that the required cation is precipitated with hydrochloric acid. Further determination of the cation does not cause difficulties. The cation is monovalent, so, it can be  $Hg^{2+}$  or  $Ag^+$ . We will know the cation by asking the question: «Does the molecule of the chloride precipitate contain two anion atoms?» Having determined the silver ion, we proceed to find the nature of the anion. This process is simplified since we know that not all anions give a colorless solution with  $Ag^+$ . The determination of the anion is carried out, in the main, already disassembled above. So, one of the recommended questions can be:

Question: Is the anion of substance monovalent?

Answer: Yes.

Question: Does the combination of this anion with the hydrogen ion form a very common acid?

Answer: Yes.

Question: Is it a complex anion consisting of several atoms of two elements?

Answer: Yes.

After these questions and answers, students almost always become clear that the anion which needed to guess is silver nitrate.

In future, the order of the game does not change much. After determining the substance, the total number of questions is recorded for the following comparison with the results of other students. The teacher during the training game «Guess the compound» serves as a referee and consultant.

Thus, from the material discussed above, it is clear that the game «Guess the compound» forces students to use not only all their knowledge but also develops such valuable qualities for specialists as logic, initiative, ingenuity, non-standard thinking and much more. It is also important that the game can be used from the very first steps and until the end of training course, up to the exam. Recommend only to take into account the preparedness of students for the subject in the compilation and selection of tasks for the game. It is usually better to give for guessing the problem, consisting only of one substance, element, which is especially valuable for the first periods of training of students in chemistry.

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### **Химиядан білім беру барысында ойын арқылы оқыту әдісін қолдану**

Мақала авторлары химиядан білім беру барысында ойын арқылы оқыту әдісін пайдалану мүмкіндіктерін қарастырды. Дұрыс таңдалып алынған ойындар мен тапсырмалар оқу процесі барысындағы білім алушылардың белсенділігін арттыруға және олардың жан-жақты дамуына мүмкіндік берді. Мақалада «Электрондық формула» және «Қосылысты тап» ойындарын қарастыру

ұсынылған. Ойыншылардың «Электрондық формула» ойыны бойынша ұстанатын басты ережесі таңдап алған элементтің электронды формуласын катаң түрде біртіндеп құрастыру болып табылады. Нәтижесінде оқушы элементтің электронды құрылымын біліп, оны құрастыруды үйренеді. Екінші ойын «Қосылысты тап» сұрақ-жауап принципі бойынша жүргізіледі және ойыншылардың бірі (немесе ойыншылар тобы) олардың жанама сұрақтарының көмегімен осы заттың қандай екенін білген сәтте аяқталады. Ойын арқылы оқытуды ұйымдастырудың мазмұны мен формасы білім алушының шығармашылық қабілеттерін ашып, практикалық дағдылары мен біліктілігін қалыптастыруға ықпал етеді. Химияға қызығушылығын оятуға және арттыруға, қиын мәселелерді шешуде ұжымдық және өзара қол ұшын беруге деген мүмкіндіктерін қалыптастыру көрсетілген. Ойын процесі барысында білім алушының ақпарат пен дағдыларының қалыптасуы, алған білімдерін жалпылау және бақылау мүмкіндіктерінің жетілуі жалпы білім беретін мектептерде және жоғары оқу орындарында ойын әдісін ұзақ уақыт бойы қолдану дәлелдеп отыр.

*Кілт сөздер:* білім беру, оқу-химиялық ойындар, электрондық формула, заттардың құрамын талдау.

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## Применение учебных игр в преподавании химии

В статье рассмотрены возможности применения игрового метода обучения при изучении химии. Правильно подобранная игра и задания позволяют активизировать как сам процесс обучения, так и создать условия для многостороннего развития учащихся. Авторами представлены на рассмотрение две игры «Электронная формула» и «Угадай соединение». Главным правилом игры «Электронная формула», которым руководствуются игроки, является строго последовательное построение электронных формул выбранных в данный момент элементов. В результате у обучающихся формируется знание электронных структур элементов и умение их построить. Вторая игра «Угадай соединение» ведется по принципу вопрос – ответ и заканчивается в тот момент, когда один из играющих (или группа играющих) с помощью своих наводящих косвенных вопросов догадается, что это за вещество. Вопросы могут задаваться по-разному, но в целом основываясь только на химических и физических свойствах определяемого вещества. Содержание и форма организации игрового обучения способствуют формированию умений и практических навыков, раскрытию творческих способностей учащихся. Показана возможность пробудить и укрепить интерес к химии, чувство коллективизма и взаимовыручки в решении трудных проблем. Раскрыты возможности взаимообогащения информацией и умениями в процессе игры, развития способности к обобщению и контролю полученных знаний, подтвержденные многолетним применением игрового метода обучения при изучении химии в средней школе и в высших учебных заведениях.

*Ключевые слова:* образование, обучающие химические игры, электронная формула, анализ состава вещества.

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