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MEMORABLE DATES

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Congratulations on the anniversary of Professor S.E. Kudaibergenov

The article is dedicated to the 70th anniversary of Sarkyt Elekenovich Kudaibergenov, a prominent Kazakh scientist-chemist. His career and the most significant events of his scientific life are briefly described here. The contribution of Professor S.E. Kudaibergenov to the development of physical chemistry of polymers and his participation in the internationalization of the polymer scientific school are shown.

This article is devoted to the 70th anniversary of Sarkyt Elekenovich Kudaibergenov, a prominent Kazakh scientist-chemist. S.E. Kudaibergenov is an internationally recognized expert in the field of physical chemistry of polymers, Doctor of Chemical Sciences (1991), Professor (1994), Laureate of the Kazakh SSR State Prize in Science and Technology (1987).

Professor S.E. Kudaibergenov is an enthusiastic person who has been inspiring his colleagues and a large number of young researchers working in the field of polymer science for several decades. His fundamental scientific works mainly devoted to the physical chemistry of hydrophilic polymers, stimulated significant progress in this field [1–6].

After graduating from the Faculty of Chemistry at Kazakh State University named after Kirov (now Al-Farabi Kazakh National University) in 1973, Sarkyt Kudaibergenov remained at this university as an engineer and then as a research intern. His academic career continued at the Institute of Chemical Sciences of the Academy of Sciences of the Republic of Kazakhstan in the Laboratory of Physical Chemistry of Polymers led by Academician E.A. Bekturov, a distinguished chemist. A truly important milestone in the career of Professor S.E. Kudaibergenov was the work on a candidate dissertation on the topic "Hydrodynamic properties of polyelectrolytes based on vinylethylpiperidoles-4", which he successfully defended in 1980. This work anticipated his innovative research on the development of the physical chemistry of polyelectrolytes [7, 8]. Studies of polymer complexation reactions were one of the many contributions that S.E. Kudaiberegenov made for the development of polymer science.

One of his first co-authored monographs "Polymer Complexes and Catalysts" describes the interaction of macromolecules with metal ions, explains the mechanisms and conditions of formation of polymer-metal complexes, which have great theoretical interest and practical application [9]. In this book the catalytic properties of some macromolecular compounds in solutions, which are models of biocatalyst-enzymes, are also described. These works formed the basis of the author's further research [10–12]. In 1991 S.E. Kudaibergenov defended his Doctoral Thesis "Complex formation reactions with participation of synthetic polyampholytes" at Lomonosov Moscow State University, in 1994 he has received a title of Professor. After productive work at the Institute of Chemical Sciences, Sarkyt Elekenovich works at responsible positions in the scientific structures of the Ministry of Education and the National Academy of Sciences of the Republic of Kazakhstan. In 1996 S.E. Kudaibergenov was invited to the position of Professor at al-Farabi Kazakh National University,

where he organized a scientific group for the production and research of "smart" polymeric materials based on hydrogels and interpolymer complexes. In 1999 Professor S.E. Kudaiberegenov founded a private research organization "Institute of Polymer Materials and Technologies", which successfully operates today and contributes to the development of polymer science in Kazakhstan. The special connection of the scientist with his small motherland is expressed in his cooperation with Semipalatinsk Shakarim State University, where he was a professor of the Department of Chemistry from 2005 to 2019. S.E. Kudaibergenov made a great contribution to the organization of scientific work of Kazakh National Technical University named after K.I. Satpayev, where he permanently headed the Laboratory of Engineering Profile (2008–2020).

As a famous scientist in the field of fundamental science Professor S.E. Kudaibergenov was able to apply the results of theoretical research to solve important practical problems, in particular to increase the efficiency of oil production. The scientist had experience as the head of scientific subdivisions of oil producing companies "KazTransOil" and "KazMunayGas" (2001–2004), headed the commercialization project "Development and implementation of polymer flooding technology to increase oil recovery". These works are important for the development of the economy of Kazakhstan.

In the early days of his scientific career, in 1995, S.E. Kudaibergenov completed a three-month internship at the National Science Foundation in the USA, where he became acquainted with the system of science funding in that country. Then in 1998, as a visiting professor, he researched at Waseda University (Japan) in the research group of Professor E. Tsuchida.

In 2002–2003 Professor S.E. Kudaibergenov was invited as a professor at Kwangju Institute of Science and Technology (South Korea), where he researched and shared his experience with young scientists. He is one of the first scientists in Kazakhstan who received several grants from international foundations, including Soros Fund (1994), INTAS-Kazakhstan (1997, 1999, 2001), INTAS-Aral (2003), NATO (2011–2014), projects with China (2015–2016, 2018–2019), EU Horizon-2020 (2019–2022). Professor S.E. Kudaibergenov is a member of the editorial board of several national English-language scientific journals and was also a guest editor of the special issue "Advanced Technologies in Polymer-Protected and Gel-Immobilized Nanocomposites" for the Polymers journal (MDPI, 2020). He is a regular guest lecturer at international scientific conferences and symposia and a member of the organizing committee of several prestigious scientific forums, including the IUPAC International Symposium on Macromolecule-Metal Complexes (MMC) and the International Symposium on Macro- and Supramolecular Architectures and Materials (MAM). S.E. Kudaibergenov initiated 8 International workshops on polymer specialty that were held in Almaty, Semey and Issyk-Kul (Kyrgyzstan). The last workshop was held at Karagandy University of the name of academician E.A. Buketov in 2019, sponsored by the International Science and Technology Center (ISTC). Invited by S.E. Kudaibergenov, well-known national and international scientists such as Hiroyuki Nishide (Waseda University, Tokyo), Sayora Rashidova (Institute of Physics and Chemistry of Polymers, Uzbekistan), Gulzhian Dzhardimalieva (Institute of Chemical Physics of RAS, Russia), Vladimir Lozinsky (Institute of Elementoorganic Compounds of RAS, Russia), Oguz Okay (Istanbul Technical University, Turkey), Hekki Tenhu (University of Helsinki, Finland), Vitaliy Khutoryanskiy (University of Reading, UK) made plenary reports at the VIII International Symposium on Specialty Polymers. The above mentioned demonstrates that Professor S.E. Kudaibergenov is a scientist of world renown, and the results of his research are recognized in the scientific community. He is also distinguished by his great desire to help young scientists choose their scientific direction, find foreign partners, and use the results for the benefit of the national scientific school.

Professor S.E. Kudaibergenov individually and in collaboration published 19 monographs in Russian, Polish and English languages, he has more than 400 scientific publications, including 17 review articles, 11 book chapters and more than 130 scientific articles published in English in international peer-reviewed journals with a high impact factor. In 2002 and 2021 he published fundamental monographs "Polyampholytes: Synthesis, Characterization and Application" in Springer and "Polyampholytes: Past, Present, Perspectives" in Kazakhstan publishing house. According to the Web of Science, Clarivate Analytics database, S.E. Kudaibergenov is the world's leader in the number of publications in the field of Polyampholytes [13–16]. The annual citation index of his works reaches up to 200 citations. His Hirsch index is 20.

As a member of the editorial board of the journal "Bulletin of the Karaganda university. Chemistry series" Professor S.E. Kudaibergenov contributes to the further promotion of our publication in international scientific bases, his articles and reviews published in the journal are the most demanded among readers. On behalf of the editorial board of the journal we congratulate Professor S.E. Kudaibergenov with his 70th anniversary! We wish you great success in scientific work, good students and followers, new scientific works.

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Е.М. Тажбаев, М.Ж. Бүркеев

Профессор С.Е. Құдайбергеновті мерейтойымен құттықтау

Мақала қазақтың көрнекті ғалым-химигі — Сарқыт Елекенұлы Құдайбергеновтің 70 жылдық мерейтойына арналған. Оның еңбек жолы және ғылыми қызметіндегі маңызды кезеңдері қысқа түрде сипатталған. Профессор С.Е. Құдайбергеновтің полимерлердің физикалық химиясын дамытуға және полимерлер ғылыми мектебін интернационалдандыруға қосқан үлесі көрсетілген.

Е.М. Тажбаев, М.Ж. Буркеев

Поздравление с юбилеем профессора С.Е. Кудайбергенова

Статья посвящена 70-летнему юбилею выдающегося казахстанского ученого-химика — Кудайбергенова Сарқыта Елекеновича. В краткой форме описаны его трудовой путь и наиболее значимые события научной карьеры. Показан вклад профессора С.Е. Кудайбергенова в развитие физической химии полимеров и его участие в интернационализации полимерной научной школы.

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ORGANIC CHEMISTRY

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The use of Lewis acid AlCl3 as a promoter in the Pd-complex catalytic system of the cyclohexene hydroethoxycarbonylation reaction

This paper presents the results of detailed studies of the possibility of using Lewis acid AlCl3 as a promoter of the catalytic three-component system PdCl2(PPh3)2–PPh3–AlCl3 in the hydroethoxycarbonylation reaction of cyclohexene at low carbon monoxide pressures (2.5 MPa). As a result a high catalytic activity of the three-component system was established and the reaction proceeds regioselectively with the formation of ethyl ether of cyclohexanecarboxylic acid. The optimal conditions of the process have been elaborated (molar ratio of the starting reagents [Cyclohexene]:[Ethanol] = 1:1; molar ratio of the components of the catalytic system = = [PdCl2(PPh3)2]:[PPh3]:[AlCl3] = 1:6:9; carbon monoxide pressure $P_{CO} = 2.5$ MPa; process temperature $T = 120$ °C and reaction time $\tau = 5$ h) at which the target product yield reaches 80.7 %. To identify the obtained ethyl ester of cyclohexane carboxylic acid gas chromatographic analysis and mass- and IR- spectra were carried out. Based on the data obtained, a possible mechanism of the reaction route of cyclohexene carbonylation with carbon monoxide and ethanol in the presence of the three-component system PdCl2(PPh3)2–PPh3–AlCl3 is proposed and discussed.

Keywords: cyclohexene, carbon monoxide, Pd-complex catalysts, phosphine ligands, aluminium (III) chloride, hydroalkoxycarbonylation, ethyl ester of cyclohexanecarboxylic acid, "Hydride" mechanism.

Introduction

Production technologies based on the use of carbon oxides are being developed recently throughout the world. Development of processes based on carbon monoxide use is motivated by a number of reasons. One of key reasons is the need to use alternative sources of raw materials. Starting from 40's of XIX century oil was the main source of raw material for chemical production, and petrochemicals production on its basis developed fast. However, a trend of crude production slowdown is observed today and effective processes that will be able to replace it are being searched for [1–3].

The carbonylation method is used, on an industrial scale, in the synthesis of carboxylic acids, hydroxy-acids, acid anhydrides, lactones, alcohols, ethers and esters, aldehydes and ketones. Many of these reactions have been well-studied and developed but a number of processes still undergo the search for catalyst systems with relatively high activity and selectivity.

It is possible to synthesize compounds with a large number of carbonyl groups having practical importance by carbonylation of unsaturated compounds. Interest to this reaction is preconditioned by the possibility of recovery of unsaturated compounds from non-petroleum raw material (natural gas, coal) [1–4].

The interaction of olefins with CO and H_2O leads to the formation of linear or branched carboxylic acids. Esters of carboxylic acids are obtained by replacing water with alcohol. The structure of the obtained esters depends primarily on the nature of the catalysts used, as well as the conditions of their use. Derivatives of

esters of carboxylic acids are mainly linear and α-branched, and synthesized with the participation of catalysts based on metals of group VIII of the Periodic Table [5, 6].

$$RHC{=}CH_2 + CO + R'OH \xrightarrow{\text{Cat.}} \begin{cases} RCH_2CH_2COOR' \\ \\ \underset{\underset{CH_3}{|}}{RCH}{-}COOR' \end{cases}$$

R= H, Alk, Ar   Cat. = metal complex catalysts
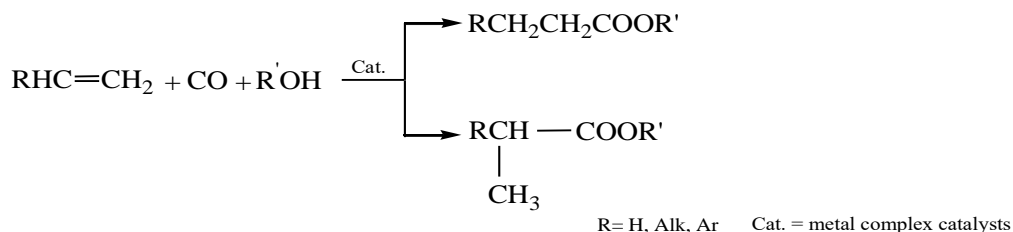
Currently, many studies have been carried out in the field of hydroesterification of alkenes [7–20] and the degree of their transformation and sensitivity has been studied. Works [3, 17] have studied the influence of various factors on carbonylation processes (at 70–95 °C, 1–4 MPa, for 3 hours) of primary alkenes, such as propene, isobutylene, pentene-1, hexene-1, heptene-1, octene-1, and other terminal alkenes in the presence of $(PPh_3)_2PdCl_2$–$SnCl_2$ catalysts. Output of obtained esters varies within limits of 70–95, depending on structure of the used catalyst system.

Most of recent researches are focused on the processes of carbonylation of hexane-1, octane-1, decene-1, and dodecene-1. In particular, hexene-1 was carbonylated in the presence of the $PdCl_2$-6PPh₃-5p-TsOH system at 125 °C and a pressure of 0.8 MPa [18, 19] as well as in the presence of the $PdCl_2(PPh_3)_2$-PPh₃-AlCl₃ system at 120 °C and a pressure of 2.5 MPa for 5 hours [12]. As a result, 84–93.8 % of the product was obtained with a selectivity of 98 %. In order to increase the selectivity with respect to linear esters, the systems $PdCl_2$–mono-phosphine ligand–LiCl–Lewis acid were used in the reaction of hydromethoxycarbonylation of alkenes [20]. The process was found to be influenced by parameters such as CO pressure, solvents and the nature of the catalyst. 1-Dodecene was hydromethoxycarbonylated with a $PdCl_2$–$P(p\text{-}C_6H_4\text{-}OCH_3)_3$–LiCl–SnCl₂ catalyst ($T = 110$ °C, $P_{CO} = 2.4$ MPa, 22 h) in a high yield (93 %). The results of the carbonylation of octene-1 and tetradecene-1 in the presence of the same catalytic system were obtained with high efficiency (96 %) within 22 hours. Previous works on the carbonylation of octene-1 together with methanol and CO in the presence of the $Pd(CH_3COO)_2$–PPh₃–p-TsOH system at 80 °C and a pressure of 2.1 MPa showed a yield of 74 %, and the conversion of the substrate was achieved in 3.5 hours [12]. Most of the studies mentioned above aimed at increasing the yields of linear isomers, which is the main problem in the carbonylation of alkenes, since the practical value of the resulting linear isomer of the product is very high.

Currently, cyclic carboxylic acids and their esters obtained from cycloolefins with carbon monoxide and alcohols or phenols are an important raw material for the synthesis of pharmaceuticals and flavorings. Therefore, more work is underway to find effective catalysts and optimal parameters for their preparation, as well as research on kinetics and thermodynamics [6, 21–29].

R= H, Alk, Ar   Cat. = metal complex catalysts
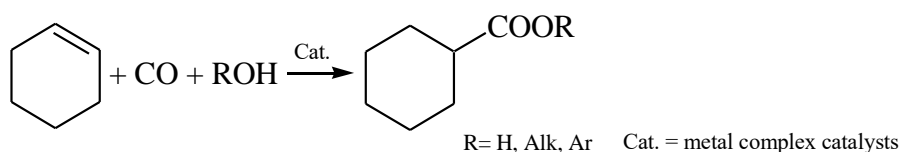
Esters of carboxylic acids are widely used in practice as pesticides, solvents in varnishes, dyes, flavours in perfume compositions, additives to various types of fuel, additives to polymeric materials, etc. [30–31]. One of the most important qualities is their use as semi-finished products in chemical and pharmaceutical synthesis [5, 6]. Some esters are components of pharmaceuticals.

Based on the studies of the above literature, it is possible to conclude that the processes of carbonylation of unsaturated compounds, especially olefins, is the most effective method for the synthesis of various organic compounds of great practical importance. Compared to other methods for the production of carboxylic acid esters, hydroalkoxycarbonylation of olefins has a number of advantages, such as single-stage processes, the availability of raw materials, the possibility of influencing the reaction by changing the nature of the metal-complex catalyst and the conditions of the process, which determines that the conduct on an industrial scale is in all respects advantageous.

Experimental

Primary reagents, features and methods of their study. Reagents produced by SIGMA-ALDRICH (bis(triphenylphosphine)palladium (II) dichloride, cyclohexene (purity 99 %), triphenylphosphine, aluminium trichloride), absolute ethyl alcohol, carbon monoxide reagent without superrefining (CO) were used as primary reagents.

Equipments. Experiments were conducted in a steel laboratory autoclave reactor (capacity 100 ml) equipped with a mixer and heater. The target product (ethyl ester of cyclohexanecarboxylic acid) was identified by gas chromatography on an Agilent 7890A/5975C mass-spectrometer (USA). Chromatography conditions were as follows: gas chromatograph 7890A with mass-selective detector 5975C produced by Agilent, helium mobile phase (gas carrier), evaporation temperature 300 ºC, flow shift (Split) 1000:1. Also, column heating with initial oven temperature 40 °C (1 min), temperature increase 5 ºC per minute and final value 250 ºC that is maintained for 1 minute were used. Total analysis time was 44 minutes and mass detector ionization was carried out by electron impact method. A capillary chromatographic column HP-FFAP was also used; the column length was 30 m, the inner diameter was 0.25 mm, the stationary phase was nitrophthalic acid modified with polyethylene glycol.

Hydroethoxycarbonylation of cyclohexene. 0.08 g (1.14×10^{-4} mol) PdCl$_2$(PPh$_3$)$_2$, 0.180 g (6.84×10^{-4} mol) PPh$_3$, 0.122 g (9.12×10^{-4} mol) AlCl$_3$, 2.289 g (4.96×10^{-2} mol) ethanol and 4.067 g (4.96×10^{-2} mol) of cyclohexene were placed into a steel autoclave reactor (100 ml) equipped with a mixer and carbon monoxide injection device. Ratio of primary reagents and components of catalyst system was [C$_6$H$_{10}$]:[C$_2$H$_5$OH]:[PdCl$_2$(PPh$_3$)$_2$]:[PPh$_3$]:[AlCl$_3$] = 435:435:1:6:9. The reactor was sealed. To remove air inside of it, it is blown through with carbon monoxide three times and filled with carbon monoxide until pressure reaches 1.5 MPa. Then, mixer and heater are turned on and within 1 hour temperature is increased up to 120 °C, and carbon monoxide pressure grew up to 2.5 MPa. At a given temperature and pressure the reaction mixture is intensively stirred for 5 hours. Then it is cooled to room temperature and reaction mixture fractionation is carried out at atmospheric pressure. As a result of distillation, 6.244 g (80.7 %) of ethyl ester of cyclohexanecarboxylic acid was obtained.

Results and discussion

The reaction of cyclohexene hydroethoxycarbonylation in the presence of PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ catalyst system has the following form:
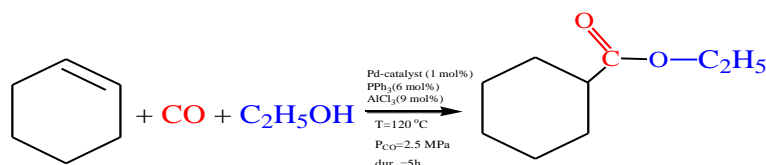
The activity of the three-component catalytic system PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$, which contains AlCl$_3$ as a promoter, was studied in the hydroethoxycarbonylation of cyclohexene at low pressure (P$_{CO}$ = 2.5 MPa) of carbon monoxide. A high catalytic activity of the catalytic system with respect to this reaction was found. Cyclohexanecarboxylic acid ethyl ester formation reaction was confirmed by reference data for such characteristics as GC/MS analysis, boiling point, and refractive index.

The effect of the reaction conditions (temperature, CO pressure, molar ratio of primary reagents, ratio of the components of the catalytic system and reaction time) on the yield of the target product has been established (Table 1).

Table 1 shows the results of the influence of various conditions on the yield of ethyl ester of cyclohexanecarboxylic acid as the target product of the reaction of hydroethoxycarbonylation of cyclohexene in the presence of the system PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$. Temperature, pressure of carbon monoxide, reaction time, and the amount of AlCl$_3$ in the PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ catalytic system were the main factors determining the outcome of the process. An increase in the reaction temperature from 110 to 130 °C led to an increase in the yield of target products from 65.8 to 80.7 %. A further increase in temperature reduces the yield of target products due to catalyst deactivation (formation of palladium on carbon). The graphs of the yield of the target products depending on the pressure of carbon monoxide and the duration of the reaction also have an extreme form. Optimal conditions are P$_{CO}$ = 2.5 MPa, τ = 5 h. A further increase in the pressure of carbon monoxide to 3.0 MPa sharply reduces the yield of the target products. Apparently, that is due to competition between the

olefin and carbon monoxide behind the center of the palladium focal point. The molar ratio of AlCl$_3$ in the catalytic system also strongly affects on the yield of the target products. An increase in the PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ ratio from 1:8 to 1:9 led to an increase in the yield of target products from 72.6 to 80.7 %; a further increase in the excess of AlCl$_3$ reduces the yield of the target product. No solvents were used in this reaction, and the ratio of the starting reagents affected the product yield. With the ratio [C$_8$H$_{10}$]:[C$_2$H$_5$OH] = 661:435, the product yield is 72.3 %; further reduction to [C$_8$H$_{10}$]:[C$_2$H$_5$OH] = 435:435 gives the highest product yield of 80.7 %, but further reduction to [C$_8$H$_{10}$]:[C$_2$H$_5$OH] = 217.5:435 reduces the yield of the target product.

Table 1

Hydroethoxycarbonylation of cyclohexene in the presence of the PdCl₂(PPh₃)₂–PPh₃–AlCl₃ system

Exp. no.	[C$_8$H$_{10}$]:[C$_2$H$_5$OH]	[PdCl$_2$(PPh$_3$)$_2$]:[PPh$_3$]:[AlCl$_3$]	T, °C	P_{CO}, MPa	τ, h	Product yield, %
1	661:435	1:6:9	120	2.5	5	72.3
2	435:435	1:6:9	120	2.5	5	80.7
3	217.5:435	1:6:9	120	2.5	5	55.6
4	435:435	1:6:8	120	2.5	5	72.6
5	435:435	1:6:10	120	2.5	5	74.2
6	435:435	1:6:9	130	2.5	5	66.7
7	435:435	1:6:9	110	2.5	5	65.8
8	435:435	1:6:9	120	3.0	5	68.0
9	435:435	1:6:9	120	2.0	5	43.4
10	435:435	1:6:9	120	2.5	4	68.5
11	435:435	1:6:9	120	2.5	6	77.2

Thus, it was found that the three-component catalytic system PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$, which contains AlCl$_3$ as a promoter in the carbonylation reaction of cyclohexene at a low carbon monoxide pressure (2.5 MPa), exhibits high catalytic activity. As a result, the following effective parameters were identified: [C$_6$H$_{10}$]:[C$_2$H$_5$OH]:[Pd]:[PPh$_3$]:[AlCl$_3$] = 435:435:1:6:9, P_{CO} = 2.5 MPa, T = 120 ºC, τ = 5 h. Under the developed optimal reaction conditions, the yield of ethyl ester of cyclohexanecarboxylic acid was 80.7%.

The study and identification of the fractionated product was carried out as mentioned above (experimental part), by gas chromatography method (shown in Figure 1). On the chromatogram we can observe a change in the value of the total ion current at the 19th minute of exposure, which, in turn, indicates the presence of the target product – ethyl ester of cyclohexanecarboxylic acid (at the 1st minute — unreacted ethanol; at the 3rd minute — unreacted cyclohexene).
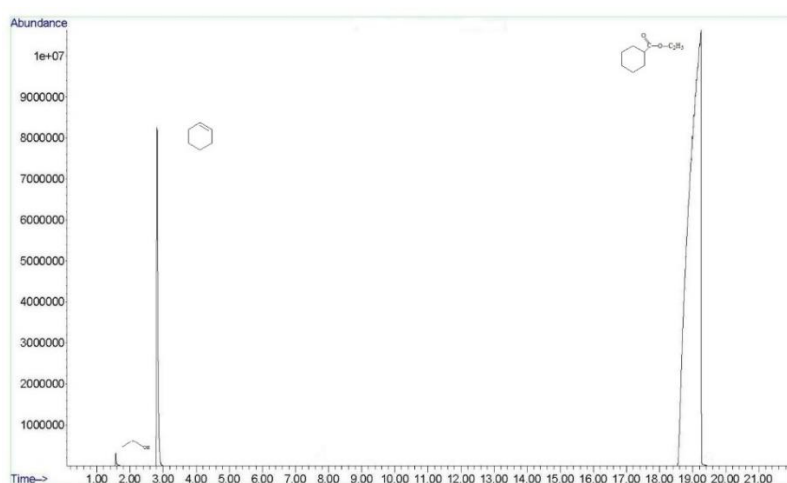
Figure 1. GC analysis of target product

Along with the hydroethoxycarbonylation of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter, there can also be a "hydride" mechanism, reminiscent of the carbonylation process, which occurs in the presence of strong hydrogen acids (p-TsOH, etc.).

The mechanism of the reaction of hydroethoxycarbonylation of cyclohexene can proceed in the same way as the mechanism of hydroethoxycarbonylation of octene-1 in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ [7].
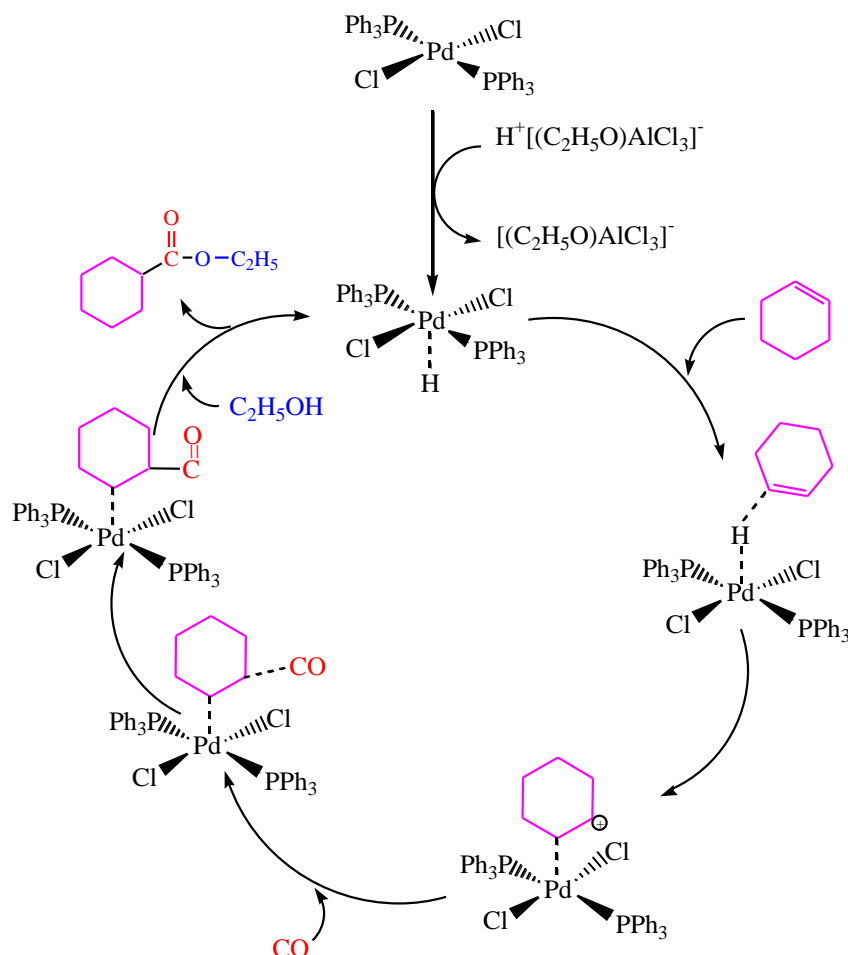
Figure 2. "Hydride" mechanism of cyclohexene hydroesterification reaction

The mechanism of cyclohexene hydroesterification in the presence of three-component $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalyst system is shown in Figure 2. The stage of HPd hydride complex formation is the main stage of the process. This complex gives the possibility of further catalytic cycle. When ethanol interacts with aluminum (III) chloride, which is a strong Lewis acid, it is possible to get the formation of $H^+[C_2H_5OAlCl_3]^-$ proton and $[C_2H_5OAlCl_3]^-$ of weakly coordinating anions complexes. The polarization of O-H bonds in alcohol under the action of strong Lewis acids allows the process to take place according to the hydride mechanism.

Conclusions

The activity of the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter in the carbonylation reaction of cyclohexene with carbon monoxide and ethanol was investigated. A high catalytic activity of this catalytic system was found. The effect of process conditions, such as components of catalyst system ratio and primary reagents mole ratio, temperature, CO pressure, reaction time on the result of the hydroethoxycarbonylation reaction of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ at low carbon monoxide pressure was studied. Optimal parameters were identified: $[C_6H_{10}]:[C_2H_5OH]:[Pd]:[PPh_3]:[AlCl_3] = 435:435:1:6:9$, $P_{CO} = 2.5$ MPa, $T = 120$ ºC, $\tau = 5$ h. The possibility of cyclohexanecarboxylic acid ethyl ester synthesizing at these parameters with a yield of 80.7 %

was investigated. Ethyl ether of cyclohexanecarboxylic acid is of great practical importance as flavoring agents, food additives in food, pharmaceutical and other industries.

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Циклогексенді гидроэтоксикарбонилдеу реакциясының Pd-комплексті каталитикалық жүйесінде AlCl₃ Льюис қышқылын промотор ретінде қолдану

Мақалада көміртек оксидінің төмен қысымында (2,5 МПа) циклогексенді гидроэтоксикарбонилдеу реакциясында үш компонентті PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ каталитикалық жүйесінің промоторы ретінде AlCl$_3$ Льюис қышқылын пайдалану мүмкіндігінің зерттеу нәтижелері келтірілген. Нәтижесінде үш компонентті жүйенің жоғары каталитикалық белсенділігі және реакция региоселективті циклогексанкарбон қышқылының этил эфирін түзе отырып жүретіндігі анықталды. Процестің оңтайлы шарттары табылып (бастапқы реагенттердің моль қатынасы [Циклогексен]:[Этанол] = 1:1; каталитикалық жүйе компоненттерінің молярлық қатынасы = [PdCl$_2$(PPh$_3$)$_2$]:[PPh$_3$]:[AlCl$_3$] = 1:6:9; Р$_{CO}$ көміртегі тотығының қысымы = 2,5 МПа; процесс температурасы T = 120 °C және реакция уақыты τ = 5 сағ), онда мақсатты өнімнің шығымы 80,7 % жетті. Алынған циклогексанкарбон қышқылының этил эфирін анықтау үшін газохроматографиялық талдау жүргізіліп, масс- және ИҚ-спектрлері түсірілді. Алынған мәліметтер негізінде үш компонентті PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ жүйесінің қатысуымен циклогексеннің көміртек оксиді және этанолмен карбонилдеу реакциясының мүмкін болатын механизмі ұсынылды және талқыланды.

Кілт сөздер: циклогексен, көміртек моноксиді, Pd-комплексті катализаторлар, фосфинді лигандтар, алюминий (III) хлориді, гидроалкоксикарбонилдеу, циклогексанкарбон қышқылының этил эфирі, «гидридтік» механизм.

Н.Ж. Кудайбергенов, К.М. Шалмагамбетов, А. Вавасори, Г.Ж. Жаксылыкова,
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Использование кислоты Льюиса AlCl₃ в качестве промотора в Pd-комплексной каталитической системе в реакции гидроэтоксикарбонилирования циклогексена

В статье представлены результаты детальных исследований возможности использования кислоты Льюиса AlCl₃ в качестве промотора каталитической трехкомпонентной системы PdCl₂(PPh₃)₂–PPh₃–AlCl₃ в реакции гидроэтоксикарбонилирования циклогексена при низких давлениях моноксида углерода (2,5 МПа). Установлены высокая каталитическая активность трехкомпонентной системы и региоселективное протекание реакции с образованием этилового эфира циклогексанкарбоновой кислоты. Разработаны оптимальные условия процесса (мольное соотношение исходных реагентов [циклогексен]:[этанол] = 1:1; молярное соотношение компонентов каталитической системы = [PdCl₂(PPh₃)₂]:[PPh₃]:[AlCl₃] = 1:6:9; давление моноксида углерода P$_{CO}$=2,5 МПа; температура процесса T = 120 °C и время реакции τ = 5 ч), при которых выход целевого продукта достигает 80,7 %. Для идентификации полученного этилового эфира циклогексанкарбоновой кислоты проведен газохроматографический анализ и сняты масс- и ИК- спектры. На основании полученных данных предложен и обсужден возможный механизм протекания реакции карбонилирования циклогексена моноксидом углерода и этанолом в присутствии трехкомпонентной системы PdCl₂(PPh₃)₂–PPh₃–AlCl₃.

Ключевые слова: циклогексен, моноксид углерода, Pd-комплексные катализаторы, фосфиновые лиганды, хлорид алюминия (III), гидроалкоксикарбонилирование, этиловый эфир циклогексанкарбоновой кислоты, гидридный механизм.

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Study of the phenolic compounds of the dry extract of *Thymus crebrifolius* using a combined HPLC–UV and HPLC-ESI-MS/MS method

In world practice interest in herbal medicines is noticeably increasing every year. From this point of view, plants of the *Thymus* L. genus of the *Lamiaceae* family are of undoubted interest. Previously we have obtained a dry extract from the aerial part of an endemic plant of the flora of Kazakhstan *Thymus crebrifolius Klokov* for the first time by double extraction of raw plant materials with 70% ethanol using ultrasound. Dry extract of *Thymus crebrifolius* has a wide spectrum of antimicrobial activity, including against *Helicobacter pylori*, while it is not toxic, and can be used as an antimicrobial agent. The article presents the results of a study of the composition of phenolic compounds of dry extract of *Thymus crebrifolius* using a combined HPLC-UV and HPLC-MS/MS method. 12 phenolic compounds have been identified and quantified in the dry extract of *Thymus crebrifolius*. Four of them are phenolic acids, and eight are flavonoids. The dominant phenolic compounds are luteolin-7-O-glucoside (109.00 mg g^{-1}), rosmarinic acid (30.98 mg g^{-1}), naringenin (24.84 mg g^{-1}), epicatechin (9.98 mg g^{-1}), myricetin (6.15 mg g^{-1}) and gallic acid (3.41 mg g^{-1}). The results of chromatographic analysis will be used to standardize drugs based on dry extract of *Thymus crebrifolius*.

Keywords: Thymus crebrifolius Klokov, dry extract, HPLC-UV, HPLC-ESI-MS/MS, phenolic acids, flavonoids, luteolin-7-O-glucoside, rosmarinic acid.

Introduction

In world practice, interest in herbal medicines is noticeably increasing every year. At the same time, special importance is attached to the study of wild-growing plants and their use both in the form of medicinal raw plant materials and for the production of new drugs.

From this point of view, plants of the *Thymus* L. genus of the *Lamiaceae* family are of undoubted interest. The attention of researchers has long been attracted by plants of the genus *Thymus* L., whose representatives are a source of medicinal plant materials with a wide spectrum of action.

The State Pharmacopoeia of the Republic of Kazakhstan includes the herb *Thymus serpyllum* L. and the herb *Thymus vulgaris* L. as medicinal plants [1]. In official medicine these herbs are used as a medicinal plant material with antibacterial, astringent, anti-inflammatory, sedative, anticonvulsant, expectorant, antispasmodic, choleretic, analgesic, diuretic, wound healing and anthelmintic effect. It is used in the form of decoctions and infusions [1].

At the same time, a possible reduction in stocks of medicinal raw plant materials leads to the need to expand the raw material base of official medicinal plants at the expense of additional plant sources and their complex use. The results of study of the distribution of the genus *Thymus* L. showed that 15 species grow on the territory of Central Kazakhstan, 5 of them are endemic, including *Thymus crebrifolius* Klokov. It should be noted that *Thymus vulgaris* L. does not grow in the Karaganda region. In Central Kazakhstan, the most common *Thymus serpyllum* L. *Thymus crebrifolius* form large thickets in certain geographical areas, for example, in the Ulytau mountains [2]. According to the results of a survey of raw materials on the territory of the Karaganda region, *Thymus crebrifolius* has sufficient general operational reserves and possible volumes of annual procurements for use in pharmacy and medicine. However, the composition and biological properties of *Thymus crebrifolius* remain largely unexplored.

Previously we have obtained a dry extract from the aerial part of *Thymus crebrifolius* Klokov for the first time by double extraction of plant raw materials with 70% ethanol using ultrasound. Dry extract of *Thymus crebrifolius* has a wide spectrum of antimicrobial action, including against *Helicobacter pylori*. It is non-toxic, and can be used as an antimicrobial agent both individually and in complex therapy [3].

Therefore, the purpose of our work is to study the phenolic compounds of the dry extract of *Thymus crebrifolius* using the HPLC-UV and ESI-MS/MS combined method.

Experimental

For study the aerial part of *Thymus crebrifolius* Klok. was collected in the population of the Karaganda region of the Republic of Kazakhstan, in the vicinity of the city of Zhezkazgan in the Ulytau mountains (N 48°4213′; E 66°5910′) in June 2020 in the full flowering phase. Raw plant materials were dried, crushed and stored in accordance with the requirements of the State Pharmacopoeia of the Republic of Kazakhstan for medicinal plants [1]. Botanical identification was confirmed at the Institute of Botany and Phytointroduction of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (conclusion on the species belonging of plant samples No. 01-04/261).

Dry extract of *Thymus crebrifolius* was obtained by double extraction of air-dry raw materials (leaves, flower baskets and thin stems) with 70% ethanol, without soaking. The ratio of raw material mass and extractant volume was 1:20. This was carried out in an Ultrasonic Cleaner at an ultrasonic frequency of 40 kHz at room temperature (20–22 °C) for 30 minutes. After ultrasonic treatment, the liquid extracts were filtered and the extractant was evaporated on a rotary evaporator to dryness at a temperature of 50 °C [3]. Dry extract of *Thymus crebrifolius* is a dark green mass with a specific odor, which is easily soluble in 70% ethanol, dimethylsulfoxide, partially soluble in purified water, chloroform, ethyl acetate. The yield of dry extract of *Thymus crebrifolius* was 5.76±0.07 %, in terms of air-dry raw materials. The quality indicators of the obtained dry extract of *Thymus crebrifolius* met all the requirements of the analytical regulatory document.

High-performance liquid chromatography (HPLC) combined with an ultraviolet detector (UV) and real-time tandem mass spectrometry (ESI-MS/MS) were used to analyze the polyphenolic compounds of ultrasonic extract. The following reagents were used in the study: acetonitrile (ACN) for HPLC (≥99.9 %, Sigma-Aldrich, France), formic acid (99–100 %, AnalaR NORMAPUR®, VWR Chemicals, France), highly purified water was prepared using a Milli-Q water purification system (Millipore, France). The 17 selected phenolic compounds, standards (gallic acid, caffeic acid, chlorogenic acid, ferulic acid, rosmarinic acid, catechin, epicatechin, naringin, rutin, luteolin-7-O-glucoside, luteolin, quercetin, apigenin, kaempferol, dihydroquercetin, myricetin, naringenin) were purchased from Sigma–Aldrich (USA).

The analysis was performed on an "Agilent 1260 Infinity HPLC system" liquid chromatograph (Agilent Technologies, USA), equipped by G1311C 1260 Pump VL, autosampler G1329B 1260 ALS, thermostatted column compartment G1316A 1260 TCC; variable wavelength detector G1314C 1260 VWD VL+ and *massspectrometer* G6130A Quadrupole LC-MS/MS. Operated by Windows NT based ChemStation software was used.

Chromatographic separations were carried out on a column with a "Zorbax Eclipse Plus C18" reversedphase sorbent (150 mm × 4.6 mm, 3.5 µm, Agilent Technologies, USA). For the separations a gradient of mobile phase A (2.5 % (v/v) formic acid in water) and mobile phase B (2.5 % (v/v) formic acid in acetonitrile) was used. The gradient profile was set as follows: 0.00 min 3 % B eluent, 5.00 min 10 % B eluent, 10.00 min 20 % B eluent, 15.00 min 30 % B eluent, 45.00 min 40 % B eluent, 50.00 min 30 % B eluent, 55.00 min 20 % B eluent and 60.00 min 3 % B eluent. The flow rate was 0.4 mL/min, the column temperature was 30 ºC. The ultrasonic extracts and standards were dissolved in a mixture of solvents acetonitrile : water = 1:1 (v/v). The injection volume was 20 µL for ultrasound extracts and for standards. The column effluent passed through a UV detector before arriving in the MS interface. UV detection wavelengths were 280 nm and 360 nm. The electrospray ionization mass spectrometry detection was performed in negative mode with the following optimized parameters: capillary temperature 350 °C; drying gas N_2 8 L/min; nebulizer pressure 45 psi. Data gaining was performed using multiple reactions monitoring (MRM) method that only monitors specific mass transitions during preset retention times.

The identification of each compound was performed by comparing their retention times with authentic standards and also confirmed by an Agilent G6130A LC-MS/MS spectrometer equipped with an electrospray ionization source. The quantitative content of phenolic compounds in the ultrasonic extract was calculated by the method of an external standard [4].

Results and Discussion

The composition of phenolic compounds of dry extract of *Thymus crebrifolius* was studied for the first time using HPLC-UV and ESI-MS/MS combined method. The composition of the phenolic substances of the dry extract of *Thymus crebrifolius* and the mass spectra for the identified compounds in the negative ionization mode are listed in Table 1. The HPLC-UV and HPLC-ESI-MS/MS chromatograms of the test extract and the identified phenolic compounds are shown in Figure 1.
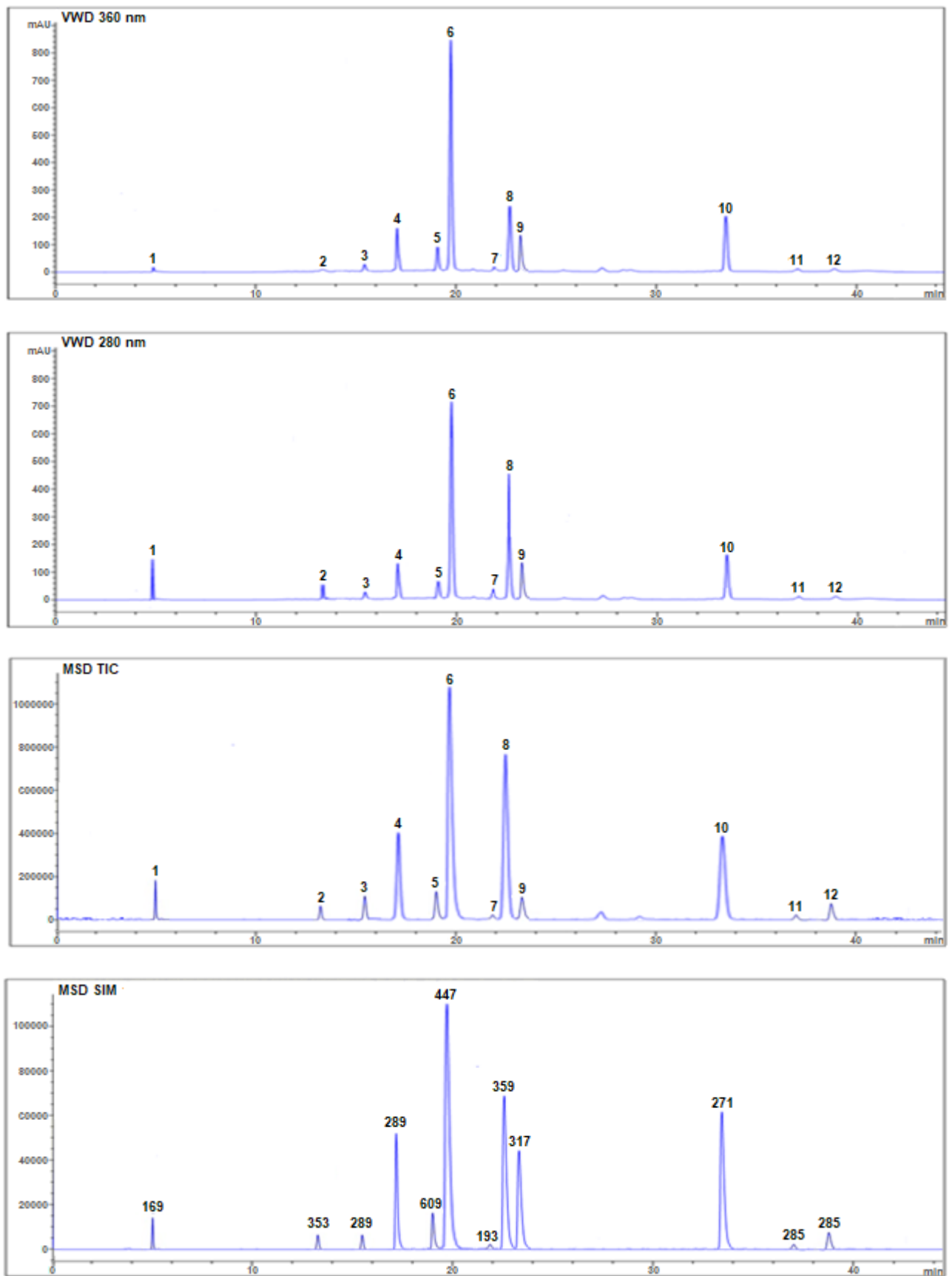
Figure 1. HPLC-UV and HPLC-ESI-MS/MS chromatograms, the total ion chromatogram (TIC)
and of the identified phenolic compounds of dry extract *Thymus crebrifolius* (SIM)

Identification and content of phenolic compounds of dry extract of Thymus crebrifolius

Peak	Retention time (min)	M−H⁻ (m/z)	Compound identity	Quantification (mg g⁻¹ dry extract)
1	4.932	169	Gallic acid	3.41±0.16
2	13.466	353	Chlorogenic acid	0.82±0.08
3	15.588	289	Catechin	1.27±0.09
4	17.187	289	Epicatechin	9.98±0.12
5	19.166	609	Rutin	3.43±0.18
6	19.880	447	Luteolin-7-O-glucoside	109.00±1.18
7	21.926	193	Ferulic acid	0.04±0.01
8	22.699	359	Rosmarinic acid	30.98±0.24
9	23.327	317	Myricetin	6.15±0.37
10	33.723	271	Naringenin	24.84±32
11	37.057	285	Luteolin	0.10±0.01
12	38.924	285	Kaempferol	0.60±0.05

The use of a "Zorbax Eclipse Plus C18" column with a particle size of 3.5 μm and a gradient elution mode made it possible to achieve a satisfactory separation of $\alpha > 1$. Identification and assignment of each compound was performed by comparing their HPLC-UV retention times and HPLC-ESI-MS/MS mass-spectra with data from authentic phenolic standards and by the addition of witness taps. Phenolic compounds were quantified by the integration peaks on HPLC-UV chromatograms using an external standard method.

The dry extract of *Thymus crebrifolius* contains such phenolic acids, as gallic acid, chlorogenic acid, ferulic acid and rosmarinic acid. The flavonoids identified in the studied extract belong to the groups flavanols (catechin, epicatechin), flavones (luteolin-7-O-glucoside, luteolin), flavonols (rutin, myricetin, kaempferol), flavanone (naringenin). The dominant phenolic compounds are luteolin-7-O-glucoside (109.00 mg g⁻¹), rosmarinic acid (30.98 mg g⁻¹), naringenin (24.84 mg g⁻¹), epicatechin (9.98 mg g⁻¹), myricetin (6.15 mg g⁻¹) and gallic acid (3.41 mg g⁻¹).

The literature reports that the qualitative composition and quantitative content of phenolic compounds in plants of the genus *Thymus* L. vary depending on the species, geographical region, climatic conditions, growing environment and growing season. Rosmarinic acid is the most common phenolic acid in extracts of the genus *Thymus* L. It has a wide spectrum of biological activity: anti-inflammatory, antitumor, antiproliferative, antiviral and others. Rosmarinic acid is one of the most effective natural antioxidants. Luteolin-7-O-glucoside is the most common flavonoid in extracts of the genus *Thymus* L. It has a wide spectrum of biological effects, including suppressing oxidative stress [5–7].

Luteolin-7-O-glucoside and rosmarinic acid are identified as the main components not only in dry extract of *Thymus crebrifolius* Klok., but also in dry extracts of two chemotypes *Thymus serpyllum* L. and two endemic species *Thymus rasitatus* Klok., *Thymus eremita* Klok. Therefore, luteolin-7-O-glucoside and rosmarinic acid can be considered as chemical markers of plants of the genus *Thymus* L. growing on the territory of Central Kazakhstan.

Conclusions

As a result of the study, the composition of the phenolic compounds of the dry extract of the endemic plant of the flora of Kazakhstan *Thymus crebrifolius* Klokov was studied for the first time using the HPLC-UV and ESI-MS/MS combined method. In the dry extract of *Thymus crebrifolius* 12 phenolic compounds have been identified and quantified, four of them are phenolic acids, and eight are flavonoids. The dominant phenolic compounds are luteolin-7-O-glucoside, rosmarinic acid, naringenin, epicatechin, myricetin, and gallic acid. The results of chromatographic analysis will be used to standardize drugs based on dry extract of *Thymus crebrifolius*.

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ЖТСХ–УК және ЖТСХ-МС/МС аралас әдісін қолдануымен *Thymus crebrifolius* құрғақ сығындысының фенолдық қосылыстарын зерттеу

Әлемдік тәжірибеде жыл сайын өсімдік тектес дәрілік препараттарға деген қызығушылық айтарлықтай артып келеді. Осы тұрғыдан алғанда, *Lamiaceae* тұқымдасының *Thymus* L. тұқымдас өсімдіктері сөзсіз қызығушылық тудырады. Бұған дейін ультрадыбысты қолдана отырып, өсімдік шикізатын 70 % этанолмен екі рет экстракциялау арқылы *Thymus crebrifolius* Klokov Қазақстанның эндемикалық флорасының жер үсті өсімдігінен құрғақ сығынды алынған болатын. *Thymus crebrifolius* құрғақ сығындысы микробқақарсы әсердің кең спектріне ие, соның ішінде *Helicobacter pylori*-ге қатысты, улы емес және оны микробқақарсы препарат ретінде пайдалануға болады. Мақалада ЖТСХ-УК және ЖТСХ-МС/МС аралас әдісін пайдалана отырып, Қазақстан флорасының эндемикалық өсімдігі *Thymus crebrifolius* Klokov құрғақ сығындысының фенолдық қосылыстарының құрамын зерттеу нәтижелері ұсынылған. *Thymus crebrifolius* құрғақ сығындысында 12 фенолдық қосылыстар сәйкестендірілді және сандық түрде анықталды, олардың төртеуі фенол қышқылдары, сегізі – флавоноидтар. Доминантты фенолдық қосылыстар лютеолин-7-О-глюкозид (109,00 мг/г), розмарин қышқылы (30,98 мг/г), нарингенин (24,84 мг/г), эпикатехин (9,98 мг/г), мирицетин (6,15 мг/г) және галл қышқылы (3,41 мг/г) болып табылады. Хроматографиялық талдау нәтижелері *Thymus crebrifolius* құрғақ сығындысына негізделген дәрі-дәрмектерді стандарттау үшін қолданылады.

Кілт сөздер: Thymus crebrifolius Klokov, құрғақ сығынды, ЖТСХ-УК, ЖТСХ-МС/МС, фенол қышқылдары, флавоноидтар, лютеолин-7-О-глюкозид, розмарин қышқылы.

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Изучение фенольных соединений сухого экстракта *Thymus crebrifolius* с использованием комбинированного метода ВЭЖХ–УФ и ВЭЖХ-МС/МС

В мировой практике с каждым годом заметно возрастает интерес к лекарственным препаратам растительного происхождения. С этой точки зрения особое внимание привлекают растения рода *Thymus* L. семейства *Lamiaceae*. Нами ранее впервые получен сухой экстракт из надземной части эндемичного растения флоры Казахстана *Thymus crebrifolius* Klokov двукратной экстракцией растительного сырья 70 %-ным этанолом с использованием ультразвука. Сухой экстракт *Thymus crebrifolius* обладает широким спектром антимикробного действия, в том числе в отношении *Helicobacter pylori*, при этом он не токсичен и может быть использован в качестве антимикробного средства. Авторами представлены

результаты исследования состава фенольных соединений сухого экстракта *Thymus crebrifolius* с использованием комбинированного метода ВЭЖХ-УФ и ВЭЖХ-МС/МС. В сухом экстракте *Thymus crebrifolius* идентифицировано и количественно определено 12 фенольных соединений, из них 4 — фенольные кислоты, 8 — флавоноиды. Доминирующими фенольными соединениями являются лютеолин-7-О-глюкозид (109,00 мг/г), розмариновая кислота (30,98 мг/г), нарингенин (24,84 мг/г), эпикатехин (9,98 мг/г), мирицетин (6,15 мг/г) и галловая кислота (3,41 мг/г). Результаты хроматографического анализа будут использованы для стандартизации лекарственных средств на основе сухого экстракта *Thymus crebrifolius*.

Ключевые слова: *Thymus crebrifolius* Klokov, сухой экстракт, ВЭЖХ-УФ, ВЭЖХ-МС/МС, фенольные кислоты, флавоноиды, лютеолин-7-О-глюкозид, розмариновая кислота.

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PHYSICAL AND ANALYTICAL CHEMISTRY

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Pd(II) extraction from acid solutions by bis-(2-hidroxyl-5-alkylbenzyl)amine

It is known that a series of organic compounds contained in the molecule SH, NH qroups have the ability to form the intracomplex compounds under certain conditions. These compounds allow to carry out the extraction in acidic medium and therefore prevent the hydrolysis process. They are not dissolved in water but are soluble in various solvents and form colored solutions and so may be used in extraction chemistry. The main purpose of this paper was to study the ability to extract palladium by bis-(2-hidroxyl-5-alkylbenzyl)amine, synthesized in the laboratory on the basis of industrial alkylphenols. Ammonium acetate with various pH was used as a buffer to extract palladium from PdCl$_2$·2H$_2$O 0.1 mkg/ml solution. The main task for the use of inert organic compound in extraction is the selection of a reagent which dissolves it but does not form any compound. For this purpose the influence of different solvents on this reagent was researched. The experiments show that bis-(2-hidroxyl-5-alkylbenzyl)amine is dissolved well in organic solvents. Its solution, for example in kerosene, is light-resistant, does not hydrolyze in water, alkalis and acids. Thus bis-(2-hidroxyl-5-alkylbenzyl)amine may be recomended for palladium extraction.

Keywords: extraction, palladium, alkilbenzilamines, diluent, intracomplex compounds, acidic environment, hydrolysis, industrial alkylphenol.

Introductıon

A consistent and thorough study of the search and synthesis of new extractants and their ability to extract important elements, in particular, platinum group metals, are important. Every work done in this area leads to the development of extraction chemistry of platinum group metals and accelerates the solution of practical issues.

From this point of view, a number of organic compounds have the ability to form inner complex combinations with metal ions under certain conditions. These organic compounds mainly include SH, NH groups in the molecule. Extraction became a modern technique to recover and separate noble metals, including palladium(II). Several reagents were proposed, including hydroxyoximes, alkyl derivatives of 8-hydroxyquinoline, hydrophobic amines and esters of pyridine carboxylic acids [1]. Some of them are used in the industry. However, the extraction occurs very slowly which is caused by the nature of hydrophobic extractant and symmetrical palladium complex.

The amine type extraction reagents are perspective for the separation of palladium from acidic nitrate solutions like waste solutions. Palladium is extracted by quaternary ammonium salts from the nitric acid solutions effectively, tertiary amines offer low distribution ratios. The effectiveness of extraction by these reagents increases considerably in the presence of small amounts of chloride ions [2].

The mechanism of palladium extraction from hydrochloric acid is well studied; the extraction from nitrate medium is less known. At low chloride concentrations, it has been observed that with an increase of palladium concentration the distribution ratio increases, and the mechanism of extraction is complex.

It was shown that palladium(II) is efficiently extracted with (RS)-1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole from 0.2–5.0 M HNO$_3$ solutions and can be selectively separated from Ni(II), Cu(II), Pb(II), Fe(III), Ag(I), as well as from lanthanides(III) in 2–4 M HNO$_3$ solutions [3]. The extraction of Pd(II) from

1 M HNO_3 solution proceeds via coordination mechanism; this is an endothermic process in the 10–30 °C temperature range.

It was shown by extraction methods and IR spectroscopy that thiacalixarenes 2 extract complex species $[Pd_nL_mH_{4-2n}]$ ($m = 1$, $n = 1$ and 2) and $[(PdA_2)_nL_mH_4]$ (A = NO_3^-, $m = 1$, $n = 1–4$) from nitric acid solutions at pH 3 [4]. Extraction constants for these palladium species that describe experimental data were calculated.

A comparison [5] was made between the separate extraction and coextraction of neodymium and palladium from nitric acid solutions with bifunctional phosphorylated thiacalix[4]arene (TCPO) and model monofunctional extractants (phosphorylated calixarene (CPO), thiacalixarene (TCA), and their mixtures) for mutual influence evaluation of S- and PO-donor sites of the extractants. The results of the extraction with TCA–CPO mixtures are of interest for a simplified process (PUREX) and a process being developed (CARBEX) as applied to recovery of neodymium and palladium from nitric acid solutions and their separation from carbonate solutions after neodymium stripping.

The work [6] studied the extraction of chloropalladium complexes with solutions of trioctylmethylammonium di(2,4,4-trimethylpentyl)dithiophosphinate in toluene over a wide range of aqueous acidities. Distribution factors and spectroscopic studies of extraction products showed that $(R_4N)[Pd_2Cl_4A]$ complexes are formed in the organic phase. As the concentration of the dialkyldithiophosphinic acid increases, palladium di(2,4,4-trimethylpentyl)dithiophosphinate is formed in the organic phase.

Thus, various derivatives of organic acids have been studied as extractants for the recovery and separation of palladium from acid solutions [7–10].

Successful solution of the problem of protecting the biosphere, reducing the negative impact of industrialization on the state of the environment is directly related to the development of effective analysis methods. And the above extractants for the selective determination of palladium do not always satisfy the requirements for the lower boundaries of the determined contents. These extractants are often unstable reagents that can be gradually oxidized by air. Therefore, it was interesting to study the distribution of palladium over effective extractant solutions based on bis-(2-hidroxy-5-alkylbenzyl)amine, which is highly soluble in organic solvents. Our task was to effectively determine the composition of the extracted compounds.

Experimental

Ammonium acetate buffer was used to obtain a $PdCl_2·2H_2O$ salt solution with a density of 0.1 mg/ml. The solutions were concentrated using concentrated HCl in a water bath before the experiment. Then the solutions were diluted to achieve the required concentrations (C) of metal and acids. The fixed values of chloride ion concentration and ionic strength in aqueous solutions were adjusted using lithium chloride so that $C_{LiCl} + C_{HCl} = 3$ mol/l.

The bis-(2-hydroxyl-5-alkylbenzyl)amine 0.1 M kerosene solution was synthesized on the basis of the industrial alkylphenols (employing Mannich reaction) in the laboratory. The structure of the obtained bis-(2-hydroxy-5-alkylbenzyl)amine was confirmed by spectroscopic methods (Shimadzu (Japan) SF-2000 SKB Spectr, PromEcoLab PE-5300V, UV-1700 and UV-2450 spectrophotometers) [11–12].

The palladium-containing solutions used for extraction were prepared according to the procedure described in [13–17]. Separate solutions of bis-(2-hydroxyl-5-alkylbenzyl)amine in kerosene were used as extractants, followed by stirring an organic solution with an equal volume of 1 M NaOH, and then with water.

Extraction was carried out in test tubes at equal volumes of aqueous and organic phases at 20 °C (±1 °C). The concentration of palladium in solutions was determined by the photometric method, and in organic phases by the difference between the concentrations of palladium in the initial solution and in the aqueous phase after extraction. The optical density of the solutions was determined by IR spectrometer. To assess the degree of extraction the following quantitative values were used in the organic and aqueous phases:

$$R = \frac{q_{org}}{q_w^o} = \frac{C_{Pd,org} \cdot V_{org}}{C_{Pd,org} \cdot V_{org} + C_{Pd,w} \cdot V_w} . \tag{1}$$

The proportion of the substance remaining in the aqueous phase was determined by the formula:

$$\propto_w = \frac{q_w}{q_w^o} = \frac{C_{Pd,w} \cdot V_w}{C_{Pd,org} \cdot V_{org} + C_{Pd,w} \cdot V_w} . \tag{2}$$

To determine the solubility of the synthesized bis-(2-hydroxyl-5-alkylbenzyl)amine in organic solvents an inert solvent was experimentally chosen, which does not form a compound upon dissolution of the extractant. For this, the effect of different grades of solvents was tested (Table 1).

Selection of organic solvents for palladium — bis-(2-hydroxyl-5-alkylbenzyl)amine system at 20 °C

Organic solvents	The result of reaction	The color of the extract	Optical density, (A)	Notes
Benzene	extracted	weak yellow	0.10–0.41	The water phase is blurred
CCl₄	–″–	weak yellow	0.42–0.47	The phase is blurred
Kerosene	–″–	yellow	0.83–0.84	Transparent to both phases
Octane	–″–	colorless	–″–	–″–
Hexane	–″–	colorless	–″–	–″–
Isobutyl alcohol	–″–	weak yellow	0.50–0.52	Phases are clean
n-Butyl alcohol	–″–	weak yellow	0.55–0.56	The phase are blurred

Measurements of optical density were carried out according to the standard method by SF-2000 SKB "Spectrum" and PromEcoLab PE-5300V spectrophotometers in the visible and ultraviolet regions [18].

The transmission (T) of the sample placed between the light source and the detector was determined at a given UV/visible wavelength. Transmission is the ratio of the intensity of the light transmitted through the sample to the intensity of the incident light, which is determined by the formula:

$$T = I/I_0,$$

where I is the intensity of the transmitted radiation; I_0 is the intensity of the radiation incident on the sample.

Optical density was determined as the decimal logarithm of the reciprocal of the transmission for monochromatic radiation. It is a dimensionless quantity, which is determined by the formula:

$$A = \log(1/T) = \log(I_0/I).$$

Results and discussion

Extraction was performed using bis-(2-hydroxyl-5-alkylbenzyl)amine by studying the distribution of palladium between two immiscible solvents (water and an organic solvent). In this case, the extraction obeys the Gibbs phase rule:

$$N + F = K + 2,$$

where N is the number of phases; F is the number of degrees of freedom; K is the number of components.

Therefore, the studied system was monovariant ($F = 1$) at constant temperature and pressure. In this case, if the concentration of dissolved palladium in one phase is constant, then its concentration in the other phase is also constant.

It was found that the bis-(2-hydroxyl-5-alkylbenzyl)amine synthesized by us, on the one hand, allows extraction in an acidic medium, thereby preventing hydrolysis. On the other hand, the extractant increases the selectivity of the palladium extraction process. The reagent gives soluble colored solutions, which is important for their use, in particular in extraction chemistry.

The third light filter was used during all measurements. As can be seen from the Table 1, the largest optical density was obtained for palladium extraction by bis-(2-hydroxyl-5-alkylbenzyl)amine compound with kerosene. Therefore, kerosene is taken as an organic solvent useful in subsequent experiments. One of the main conditions is to study the dependence on the duration of stirring 5 ml of 1N H_2SO_4, 0.5 ml of reagent (0.1 mol), 5 ml of kerosene. The optical density was measured by separating the organic phase. The results are given in Figure 1.

It is sufficient to intensively stir the mixture for three minutes to form palladium bis-(2-hydroxyl-5-alkylbenzyl)amine and complete its transition to the organic phase. On this basis, in all subsequent experiments the mixture was stirred for three minutes.

The effect of temperature (20–60 °C) on the distribution of Pd(II) was investigated (Fig. 2). The results show that there is a decrease in percent extraction with the increasing temperature. It is indicating the process to be exothermic.

To study the durability of the obtained bis-(2-hydroxyl-5-alkylbenzyl)amine palladium compound, 0.5 ml (0.1 M) of a solution containing palladium and 0.5 ml (0.1 M) kerosene solution were mixed for three minutes. Then the optical density of the solution was measured by separating the organic phase.

It was found that the dependence of the optical density of palladium formed by bis-(2-hydroxyl-5-alkylbenzyl)amine at various concentrations ($[Pd^{2+}] = 2$–$4 \cdot 10^{-4}$ M) on time (1–24 h) remains constant. In other

words, the synthesized reagent does not change its optical density for 24 hours, regardless of the palladium concentration. This indicates that it creates a stable complex with palladium.
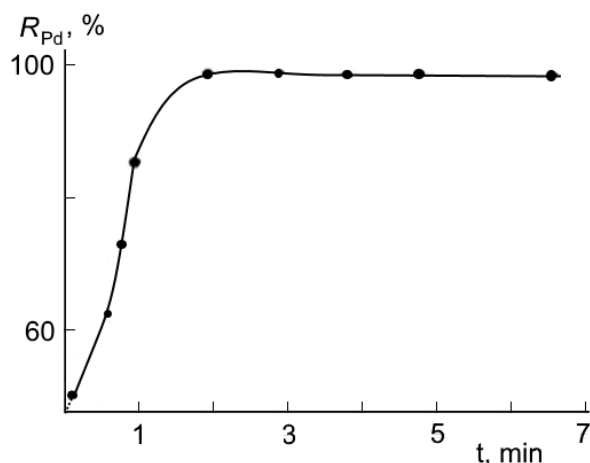
Figure 1. The dependence of palladium extraction degree on stirring time at 20 °C
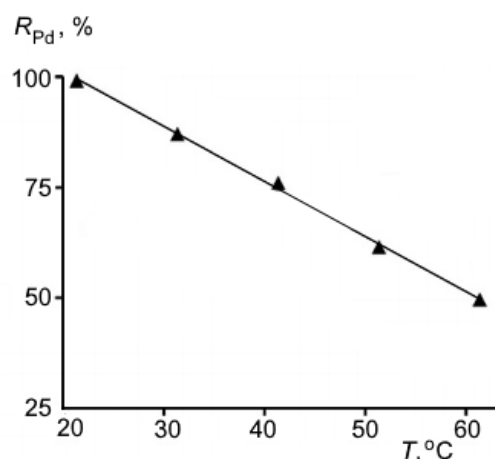
Figure 2. Effect of temperature on the extraction of Pd(II) from H_2SO_4. Conditions: [metal ion] = 5×10^{-4} mol L^{-1}, [bis-(2-hydroxyl-5-alkylbenzyl)amine] = 0.10 mol L^{-1}, [H_2SO_4] = 1.0 mol L^{-1} (for Pd(II))

Ammonium acetate was used as a buffer to create pH medium. To obtain optimal conditions for the formation of a palladium complex with bis-(2-hydroxyl-5-alkylbenzyl)amine, the dependence of the degree of palladium recovery on the pH was studied. With an increase in pH from 1 to 5.0, the main concentration of palladium (100–95 %) is transferred into the organic phase. An increase in the concentration of [OH]$^-$ ions in solution leads to a decrease in the percentage of palladium recovery.

Analysis has revealed that palladium bis-(2-hidroxyl-5-alkylbenzyl)amine is a compound that has an intensive color in the acid medium. Thus, the dependence of the optical density of the resulting compound on various concentrations of chloride, sulfate and phosphate acids has been studied. The results are given in Table 2.

T a b l e 2

Dependence of the optical density of the compound formed by the bis-(2-hydroxyl-5-alkylbenzyl)amine with palladium on mineral concentrations; [Pd^{2+}] = 9.4·10^{-4}M, [HR] = 0.1M, t =3 min, 20 °C

The concentration of acids, N		Optical density, (A)	Pd^{2+}, C_{org}, mg/ml	Pd^{2+}, C_w, mg/ml	Degree of extraction, R_{Pd}, %
HCl	0.01	0.85	0.008	n.f.*	100.0
	0.1	0.84	0.008	n.f.*	100.0
	1.0	0.84	0.008	n.f.*	100.0
	2.0	0.72	0.0076	0.0004	95.0
	3.0	0.72	0.0076	0.0004	95.0
	5.0	0.32	0.0030	0.00150	37.7
H$_2$SO$_4$	0.01	0.87	0.0080	n.f.*	100.0
	6.0	0.87	0.0080	n.f.*	100.0
	7.0	0.74	0.0076	0.0004	95.0
	8.0	0.67	0.0070	0.001	88.0
	9.0	0.60	0.0062	0.0018	70.0
	10.0	0.60	0.0062	0.0018	70.0
H$_3$PO$_4$	0.01	0.85	0.0080	n.f.*	100.0
	1.0	0.86	0.0080	n.f.*	100.0
	7.0	0.71	0.0076	0.0004	95.0
	8.0	0.71	0.0076	0.0004	95.0
	9.0	0.70	0.0076	0.0004	95.0
	10.0	0.70	0.0076	0.0004	95.0

Note. n.f.* – not found.

It was found that palladium(II) passes into the organic phase during the extraction in solutions from 0.01 N to 1 N. The percentage of extracts decreases starting from 2 N. For example, the extraction percentage in 5 N chlorous acid is 37.7%.

In sulfuric acid medium from 0.01 N to 6 N, palladium(II) passes into the organic phase. Starting with a concentration of 7 N sulfuric acid, the percentage recovery is gradually reduced. At 7 N, this indicator was 95 %, and at 10 N ~70%.

Depending on the concentration of phosphoric acid from 0.1 N to 6 N, the degree of palladium(II) extraction with bis-(2-hydroxyl-5-alkylbenzyl)amine remains constant. Palladium passes into the organic phase in this interval. The extraction at 7 N is 95 %, and this indicator remains constant until the concentration of phosphoric acid is up to 10 N.

Conclusion

The present investigation highlights that bis-(2-hydroxyl-5-alkylbenzyl)amine is a useful extractant for Pd(II) as well as for its separation from the most commonly associated metal ions. The separations do not require the addition of any modifier or synergist and can be accomplished at room temperature. The stripping agents used for separations are simple and convenient for further processing of solutions. The developed conditions of separations have been successfully extended to recover Pd(II) from synthetic mixture. The hydrolytic stability and the recycling capacity of the extractant are good and the phase separation is fast.

Thus, it was found that bis-(2-hydroxyl-5-alkylbenzyl)amine has the ability to form complexes with palladium(II) under certain conditions. This reagent allows extraction in acidic medium and, therefore, prevents hydrolysis. Being soluble in various solvents, it forms colored solutions and can be used in extraction chemistry.

Solution of bis-(2-hydroxyl-5-alkylbenzyl)amine in kerosene is light-resistant, is not hydrolyzed in water, alkalis and acids. Palladium extraction by this reagent depends on the aqueous and organic phases. This makes it possible to vary the extraction characteristics in palladium-containing systems. Reagent may be recommended for palladium extraction.

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Қышқыл ерітінділерден бис-(2-гидроксил-5-алкилбензил)аминмен Pd(II) экстракциясы

Молекуласында SH, NH-топтары бар бірқатар органикалық қосылыстар белгілі бір жағдайда ішкікомплексті қосылыстар түзуге қабілетті. Бұл қосылыстар экстракцияны қышқылды ортада жүргізуге мүмкіндік береді, гидролиз процесін болдырмайды. Олар суда ерімейді және әртүрлі еріткіштерде еритін болғандықтан түрлі-түсті ерітінділер түзеді, сондықтан оларды экстракциялық химияда қолдануға болады. Зерттеудің басты мақсаты зертханада өндірістік бис- (2-гидрокси-5-алкилбензил)амин алкилфенолдары негізінде синтезделген реактивтің палладийге қатысты экстракция қабілетін зерттеу. Палладийдің рН ерітінділерінің 0,1 мкг/мл алу үшін PdCl₂·2H₂O бастап буфер ретінде аммоний ацетаты қолданылды. Экстракция кезінде инертті органикалық қосылысты пайдаланудағы басты мақсат — оны ерітетін, бірақ басқа қосылыстар түзбейтін реагентті таңдау. Осы мақсатта әртүрлі еріткіштердің осы реактивке әсері зерттелді. Зерттеулер көрсеткендей, бис-(2-гидрокси-5-алкилбензил)амин органикалық еріткіштерде оңай еріді. Оның ерітіндісі мысалы, керосинде, жарыққа төзімді, суда, сілтілерде және қышқылдарда гидролизденбейді. Осылайша, палладийді экстракциялау үшін бис-(2-гидрокси-5-алкилбензил) аминді ұсынуға болады.

Кілт сөздер: экстракция, палладий, алкилбензиламин, еріткіш, ішкікомплексті қосылыстар, қышқыл орта, гидролиз, өндірістік алкилфенол.

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Экстракция Pd(II) бис-(2-гидроксил-5-алкилбензил)амином из кислых растворов

Ряд органических соединений, содержащих в своей молекуле SH, NH-группы, способны образовывать при определенных условиях внутрикомплексные соединения. Данные соединения позволяют проводить экстракцию в кислой среде, что предотвращает процесс гидролиза. Они не растворяются в воде и, будучи растворимы в различных растворителях, образуют окрашенные растворы, по этой причине могут быть использованы в экстракционной химии. Основная цель данного исследования — изучение экстракционной способности по отношению к палладию реагента бис-(2-гидрокси-5-алкилбензил)амина, синтезированного в лаборатории на основе промышленных алкилфенолов. Ацетат аммония с различными значениями рН был применен в качестве буфера при экстракции палладия из 0,1 мкг/мл раствора PdCl₂·2H₂O. Главным в использовании инертного органического соединения в экстракции является выбор реагента, который растворяет его, но не образует с ним других соединений. С этой целью изучалось влияние различных растворителей на этот реагент. Исследование показало, что бис-(2-гидрокси-5-алкилбензил)амин хорошо растворяется в органических растворителях. Его раствор, например в керосине, устойчив к свету, не гидролизуется в воде, щелочах и кислотах. Таким образом, бис-(2-гидрокси-5-алкилбензил)амин может быть рекомендован для экстракции палладия.

Ключевые слова: экстракция, палладий, алкилбензиламин, растворитель, внутрикомплексные соединения, кислая среда, гидролиз, промышленный алкилфенол.

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Modeling of nonlinear processes of nucleation and growth of GaS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1) solid solutions

The results on the study of modeling and physico-chemical study of the kinetics of nucleation and growth of GaS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1) solid solution. The nucleation heterogeneous process and growth of GaS$_x$Se$_{1-x}$ crystals have been studied and simulated taking into account nonlinear equations considering the kinetic behavior of crystallizing phases. GaS$_x$Se$_{1-x}$ single and nanocrystals were grown from solution, melt, and by chemical transport reaction through steam. GaS$_x$Se$_{1-x}$ crystals were grown by chemical transport reaction in a two-temperature gradient furnace in a sealed quartz ampoule. Iodine was used as a transporting additive. Using the Fokker–Planck equation, the evolution of the distribution function of crystals of solid solutions of the GaS–GaSe system by size at the nucleation time is studied by a numerical method. For the convenience of comparing theory with experimental data, we used the GaS$_{1-x}$Se$_x$ (x = 0.7 molar fraction of GaSe) composition of the solid solution. The Monte Carlo method is used to approximate the time evolution of the nucleation of two types of particles for the GaS$_{0.3}$Se$_{0.7}$ solid solution, simulated by a constant nucleus size. The results of modeling nonlinear crystallization processes are consistent with experimental data.

Keywords: nonlinear modeling, kinetics equation of crystallization, semiconductor GaS$_{1-x}$Se$_x$ solid solutions, numerical solution algorithm, finite-difference equations, Fokker–Planck equation, evolution of the distribution function, Monte Carlo method.

Introduction

The optical properties of the synthesized semiconductor two-dimensional (2D) nanocrystals have prospects for use in devices of quantum electronics (optical elements and switches, transistors, modulators, etc.). The functional capabilities of these devices are determined, in particular, by such parameters of nanocrystals as the average radius, band gap, and component composition.

The processes of nucleation and crystal growth are known to be difficult to predict, describe and control [1]. They are associated with the temporary existence of nanoparticles, making them difficult to quantify. After the formation of nuclei, their growth is observed. In this case, the growth conditions may differ from the initial stages of nucleation. In addition, during experimental crystallization, several technologically interacting processes can operate [2].

This article discusses the processes of nucleation and the subsequent formation and growth of layered crystals of 2D GaS$_x$Se$_{1-x}$ solid solutions [3, 4]. In particular, we consider the GaS–GaSe semiconductor system consisting of a highly volatile inorganic melt, and the process of nonlinear nucleation and crystallization. This situation can arise during crystallization, when trying to obtain small crystals of semiconductor solid solutions and compounds.

Interest in semiconductor materials based on A^{III}B^{VI} compounds, which are characterized by quantum effects, is due to the potential for their use in nanoscale devices. Data on the crystal and electronic structure of GaS and GaSe compounds are given in [5, 6]. GaS and GaSe crystals belong to hexagonal syngony, characterized by a layered structure and space group $D_{3h}^1 - P\bar{6}m2$ [6]. They have several polymorphic modifications.

For example, GaSe has four modifications (β-, ε-, γ- and δ-GaSe). At room temperature β-GaS and ε-GaSe are more thermodynamically stable modifications.

In $A^{III}B^{VI}$ crystals covalent bonds are in the layers, and a weak Van der Waals bond exists between the layers. Due to this anisotropic properties manifest in $A^{III}B^{VI}$. By their optical and electrical properties $A^{III}B^{VI}$ crystals (GaS [7], GaSe [8]) are close to promising nanotechnology materials, such as graphene and topological insulators. GaS and GaSe are wide-gap semiconductors and at room temperature have a band gap of 2.53 and 1.98 eV, respectively. They have several advantages over other $A^{III}B^{VI}$ materials: a large range of operating temperatures, the possibility to create light-emitting devices on their basis in the visible spectrum, high values of the critical field of electrical breakdown, radiation resistance.

GaS and GaSe form a continuous series of GaS_xSe_{1-x} ($0 \leq x \leq 1$) solid solutions between each other [9, 10]. However, the formed poly- and single crystals of GaS_xSe_{1-x} solid solutions often have an inhomogeneous distribution of dislocation density, which leads to mechanical stresses and the formation of intrinsic point defects [11–14]. As a result, such a material has irreproducible electrical, optical, photoelectric, luminescent, and other physical characteristics.

The reasons for the nonuniform distribution of structural defects over the volume of the formed GaS_xSe_{1-x} crystals are determined by several processes. The main ones are crystallization (edge and screw dislocations, grain boundaries, pores can form) and heat treatment of crystals (point defects intrinsic and impurity can be created or eliminated), as a result of which concentration and temperature gradients appear. However, the dimensional and kinetic parameters phases affecting the structure formation and physical properties of GaS_xSe_{1-x} have not yet been considered.

In the present work the crystallization of GaS_xSe_{1-x} solid solutions is considered, taking into account metastable phases, which are formed by fluctuations. The results of studying the crystallization of GaS_xSe_{1-x} in a closed system are presented. Nonlinear crystallization processes of GaS_xSe_{1-x} are considered in the framework of the Fokker–Planck type equation [15] in the size space. The evolution of the two-dimensional distribution of kernels of different types in the GaS_xSe_{1-x} melt is modeled using the Monte Carlo method [16].

Experimental

The elements Ga-5 N gallium, B5 sulfur and OSCh-17-3 selenium with impurity content no higher than 5×10^{-4} mass% were used in the synthesis of GaS and GaSe binary compounds. Syntheses of GaS and GaSe compounds were performed by melting the initial elements taken in stoichiometric ratios in evacuated (10^{-3} Pa) quartz ampoules. The ampoules with the corresponding components were placed in an electric furnace for synthesis. At temperatures above the melting point of GaS and GaSe (melting points of GaS and GaSe are 1288 and 1211 K, respectively), ampoules may be destroyed due to high vapor pressure of chalcogens. The ampoules were held for 6–8 h at a temperature 5–10 K above the melting point of the compounds. Then ampoules with liquid components GaS and GaSe were cooled in the power off mode to room temperature. The GaS_xSe_{1-x} solid solutions were prepared in a similar way. Synthesized GaS (GaSe) compounds and GaS_xSe_{1-x} solid solutions were identified by differential thermal analysis (DTA; a heating/cooling rate of 10 K min⁻¹) and powder X-ray diffraction analysis (XRD). DTA of GaS (GaSe) compounds and GaS_xSe_{1-x} solid solutions was carried out using a NETZSCH 404 F1 Pegasus system. The accuracy of measurements was ±0.5 to 1 K. The XRD phase composition of the obtained samples was performed on a Bruker D8 ADVANCE diffractometer with the Cu K-alpha radiation [10].

When crystallizing a substance from a solution, as it is known, the solute undergoes transition from the liquid phase to the crystalline phase. This process is accompanied by the appearance of many small single crystals (mass crystallization). Mass crystallization was performed by cooling a supersaturated GaS_xSe_{1-x} solution with the subsequent simultaneous formation of many crystallization centers. GaS_xSe_{1-x} single crystals were grown from solution, melt, and by chemical transport reaction through steam [17, 18].

When growing from a melt the ampule was moved in the furnace at a rate of 0.5–1.1 mm·h⁻¹, and the temperature gradient near the crystallization front was 25 ± 3 K. GaS_xSe_{1-x} crystals were grown during chemical transport reaction in a two-temperature gradient furnace in a sealed quartz ampoule. Iodine was used as a transporting additive.

A homogenized solid solution quenched in the concentration region of the $T-x$ phase diagram of the GaS–GaSe system may remain in the metastable state for some time. Ultimately, it reaches thermodynamic equilibrium. At one of the equilibrium concentrations, some micro clusters can form in the matrix GaS_xSe_{1-x} [19, 20].

Fokker–Planck equation. The kinetics of nucleation in the GaS–GaSe system was studied by an equation of the Fokker–Planck type [15]. This equation allows to describe the dynamics of changes in certain crystallization properties, considering the properties to be random walk. The equation allows to consider the evolution of the size distribution function and to describe the walk of nuclei in the size space. In other words, the Fokker–Planck equation characterizes diffusion with the presence of a drifting force field. It describes the evolution in time of the probability density function of the particle's position, which follows the stochastic differential equation. In this case, sample particle trajectories are continuous functions of time. Such a model is used in this work.

Within the framework of this model, we assume that crystallization is described by an equation based on the evolution of the function φ_k of the crystal size distribution (L) in time (t). In the entire volume of the solution, the temperature and concentration are constant. Then the Fokker–Planck kinetic equation for the distribution density is written as

$$\frac{\partial \varphi}{\partial t} = -\frac{\partial(\varphi G)}{\partial L} + \frac{\partial}{\partial L}\left(p \frac{\partial(\varphi G)}{\partial L} \right), \tag{1}$$

where $L \geq L_0$; L_0 is the minimum crystal size; G is the linear growth rate of the crystal face, and p is the fluctuation coefficient of the growth rate.

The supersaturation of a solution is determined as follows: $\gamma(t) = C_k(t) / C_k^\infty$, where $C_k(t)$ is the concentration in time t, C_k^∞ is the concentration of the saturated solution. Here the linear velocity is $G = \beta(\gamma - 1)$, where β is the kinetic coefficient of the growth rate.

The system of nonlinear equations was solved numerically, where a uniform grid was used with a step h in size and t in time. The solution was transferred from the j-th layer to the ($j+1$)-st layer by a purely implicit difference scheme, after this the function G was recalculated. The differencing scheme for equation (1) has the form:

$$\frac{\varphi_i^{j+1} - \varphi_i^j}{\tau} = -\frac{G^j}{2h}\left(\varphi_{i+1}^{j+1} - \varphi_{i-1}^{j+1} \right) + \frac{pG^j}{h^2}\left(\varphi_{i+1}^{j+1} - 2\varphi_i^{j+1} + \varphi_{i-1}^{j+1} \right). \tag{2}$$

Equation (2) has order of approximation $O(\tau + h^2)$. The difference equation for the left boundary condition has the form

$$\varphi_0^{j+1} G^j - pG^j \frac{\varphi_1^{j+1} - \varphi_0^{j+1}}{h} + pG^j \frac{\varphi_0^j 2\varphi_1^j + \varphi_2^j}{h^2} = \eta^j. \tag{3}$$

The equation has order of approximation $O(\tau + \tau h + h^2)$. Difference equations were solved by the sweep method, which is applicable due to diagonal prevalence. The differencing schemes (2) and (3) are stable on the right-hand side. After transferring the solution to the ($j+1$)-st layer, a new value of the concentration C_k was calculated, as well as parameters G and η. The integral was calculated by the trapezoidal rule — its accuracy is of the order of $O(h^2)$, which corresponds to the approximation of the differencing scheme. The obtained concentration value C_k was reused to find the solution on the ($j+1$)-st layer. This procedure was repeated a fixed number of times. Thus, the crystallization of a multicomponent system is considered as a combination of physico-chemical and mathematical models. Such a model allows for the numerical implementation of nonlinear equations by a differencing scheme. Numerical experiments to study the crystallization of GaS$_x$Se$_{1-x}$ were carried out in Delphi software.

Monte Carlo Simulation. Known models of the crystal growth process with their own microphysics allow to describe homogeneous and heterogeneous nucleation and growth with two separate one-dimensional size distributions. With this approach, the model allows to approximate only the average mass of a heterogeneous solution contained in growth units of a certain size. In this case it is impossible to track the spectral distribution of the mass of the heterogeneous solution in growth units.

The evolution of the two-dimensional distribution of phase characteristics during the growth of GaS$_x$Se$_{1-x}$ by transport chemical reactions was simulated by the stochastic algorithm [Gillespie (1976) [21]) for chemical reactions using the Monte Carlo method [22]. Within the framework of this algorithm, the set of a discrete one-component kinetic equation is defined as:

$$\frac{\partial N\left(m,n;t\right)}{\partial t}=\frac{1}{2}\sum_{m'=0}^{m}\sum_{n'=0}^{n}K\left(m-m',n-n';m',n';t\right)N\left(m-m',n-n';t\right)N\left(m',n';t\right)-$$
$$-N\left(m,n;t\right)\sum_{m'=0}^{m}\sum_{n'=0}^{n}K\left(m,n;m',n'\right)N\left(m',n';t\right),$$
(4)

where $N\left(m,n;t\right)$ is the average number of particles consisting of m and n monomers of the first and second kind, respectively.

A continuous version of this equation is known, for example, in the form of Laurenzi et al. [23]:

$$\frac{\partial N\left(n,m,t\right)}{\partial t}=\frac{1}{2}\int_{0}^{m}dm'\int_{0}^{n}dn'K\left(m-m',n-n';m',n'\right)N\left(m-m',n-n';t\right)N\left(m',n';t\right)-$$
$$-N\left(m,n;t\right)\int_{0}^{\infty}dm'\int_{0}^{\infty}dn'K\left(m,n;m',n'\right)N\left(m',n';t\right),$$
(5)

where $K\left(m,n;m',n'\right)$ in (4) and (5) is a constant set of nuclei, which now depends on the composition of coagulating particles.

Discrete equation (4) gives the temporal rate of change in the average number of a polycrystalline monomer with mass m and a single crystal monomer with mass n as the difference of two terms, the first term gives a gain in the number of particles whose polycrystal mass has a size m, and a single crystal mass has a size n.

The equation is calculated as the sum of binary clusters between monomers: one with the mass of a polycrystal from the phase of size m' and the mass of a single crystal from the phase of size n', and the other with the mass of a polycrystal from the phase $m-m'$ and the mass of a single crystal from the phase $n-n'$. The second contribution describes the average rate of depletion (m,n) of particles due to their fusion with particles of other types. To solve equations (4) and (5) the following initial conditions are required:

$$N\left(m,n;0\right)=N_0\left(m,n\right)$$
(6)

For a discrete equation for any t it is also possible to take $N\left(0,0;t\right)=0$. The numerical solution for (4) and (5) is complicated because of the double integral and nonlinear behavior of these equations. The nonlinearity of the equation, in particular during the growth of GaS_xSe_{1-x}, is associated with the nature of the interaction of nuclei and growth cells of a single crystal with different masses in each of them.

Results and Discussion

Figure 1 shows X-ray powder diffraction patterns of GaS_xSe_{1-x} solid solutions and β-GaS and β-GaSe pure compounds, which crystallize in hexagonal syngony with the space group $P6_3/mmc$ and have the following lattice parameters: β-GaS (a = 4.002 ± 0.002 Å and c = 15.447 ± 0.005 Å) and β-GaSe (a = 3.755 ± 0.002 Å and c = 15.475 ± 0.005 Å) at room temperature.
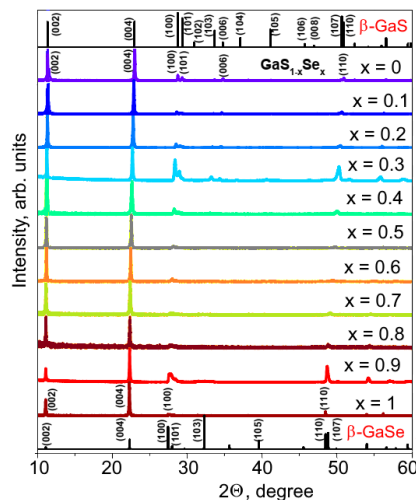
Figure 1. XRD patterns of β-GaS (top), β-GaSe (bottom) and solid solutions $GaS_{1-x}Se_x$ at 298 K

These values of lattice parameters of for polytypes β-GaS and β-GaSe compounds are consistent with the literature data [10, 11] and the JCPDS-ICDD Powder Diffraction File (PDF) card file data: β-GaS (JCPDS No: 30-0576; $a = 3.587$ Å and $c = 15.492$ Å), β-GaSe (JCPDS No: 03-65-3508; $a = 3.7555$ and $c = 15.94$ Å). The values of lattice constants of GaS_xSe_{1-x} solid solutions are also consistent with the data of [10, 11].

The difference between the structural parameters can be explained with the degree of purity of the components used, the experimental procedure and calculation of the lattice parameters, as well as the polytypicity of the GaS and GaSe compounds. The number of formula units in the lattice and the density of the compounds were as follows: $Z = 4$; $\rho_e = 3.87$ g/cm³, $\rho_r = 3.89$ g/cm³ (for GaS) and $Z = 4$; $\rho_e = 5.03$ g/cm³, $\rho_r = 5.07$ g/cm³ (for GaSe).

According to the XRD (Fig. 1) data and DTA (Fig. 2), the components of GaS and GaSe unlimitedly dissolve in each other both in the liquid and in the solid state. Unlimited component solubility in GaS–GaSe occurs because both GaSe and GaS have the same crystal structure, and Se and S have similar radii, electronegativity and valence. In GaSe–GaS system melting occurs over a relatively narrow temperature range between the solidus and liquidus lines. In other words, solid and liquid phases are at equilibrium in a narrow temperature range.
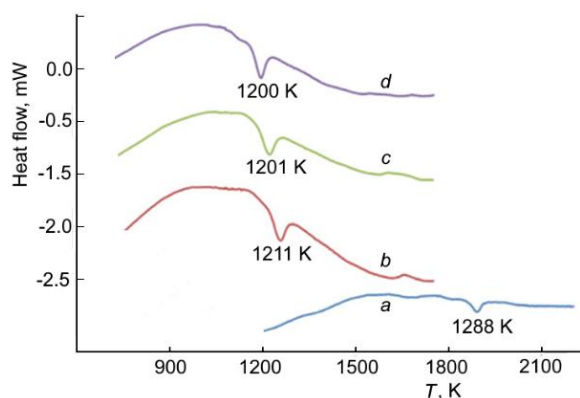
a — GaS; *b* — *x* = 0.8; *c* — *x* = 0.7 mole fraction GaSe; *d* — GaSe

Figure 2. Differential thermal analysis curves of solid solutions $GaS_{1-x}Se_x$ crystals
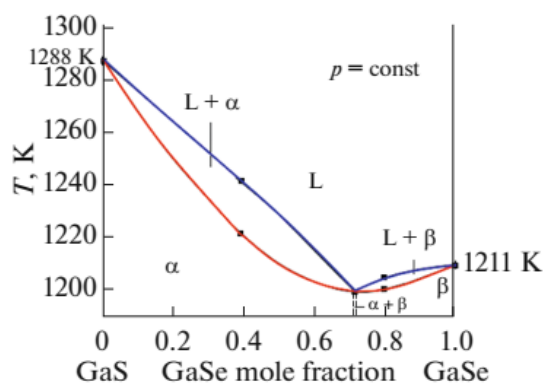
Figure 3. Calculated (curves) and experimental (dots) phase diagram in GaS–GaSe system

According to DTA and DSC data for components GaSe and GaS, the following melting parameters were chosen: ΔH^m (GaSe) = 30300 ± 200 J mol⁻¹, T^m (GaSe) = 1211 ± 3 K, ΔH^m (GaS) = 34800 ± 200 J mol⁻¹, and T^m (GaS) = 1288 ± 3 K. Comparison of these data with experimental data [10] indicates their correspondence.

On the basis of DTA, XRD and thermodynamic calculation, the equilibrium *T–x* phase diagram of the GaS–GaSe quasibinary system with unlimited component solubility is described and modeled (Fig. 3). The phase diagram of the quasi-binary system GaS–GaSe is characterized with unlimited solubility of the components in the liquid and solid states. Crystallization and melting curves have a minimum point at a composition of about 70 mol % GaSe.

Model takes into consideration our experimental thermodynamic data on the initial GaS and GaSe components. The concentration–temperature dependence of the Gibbs free energy of mixing of GaS_xSe_{1-x} solid solutions, calculated taking into account the rule of mixing components, well approximates the *T–x* phase diagram of the GaS–GaSe system. Conductivity smoothly changes with a change in the composition of solid solutions GaS_xSe_{1-x} (*x* = 0–1 mole fraction) single crystals. As the concentration of selenium in solid solutions increases, their conductivity also gradually increases by about two orders of magnitude at 298 K.

Calculated solidus and liquidus temperatures differ slightly from the experimental data (solidus difference was ~5 K and liquidus ~10 K). Phase diagram of the state for GaS–GaSe system is characterized by the minimum (0.7 ± 0.05 mol fraction GaSe and 1200 ± 1 K) and presence of unlimited mutual solubility of the components in the system.

Our calculation and experimental DTA data on the temperatures of liquidus, solidus and the coordinates of the invariant equilibria in the GaS–GaSe system are extremely different from the old data given in [9]. The melting point of GaSe is 1210 K [24], which exactly ±1 K matches our data.

A study of the relief of GaS$_{1-x}$Se$_x$ crystals grown of various compositions indicates the formation of various two-dimensional (2D) nanostructures on the surface [19, 20]. Two main types of heterogeneities can be distinguished: extended structures and local 2D nano-objects.

GaS$_x$Se$_{1-x}$ solid solutions melt without decomposition and have no phase transitions. Depending on the composition of GaS$_x$Se$_{1-x}$, the physical properties of solid solutions differ noticeably.

The mathematical model used by us describes the nucleation in the dispersed region of the melt, deposition in the homogeneous phase region, transfer of monomers between the two regions, formation and subsequent growth of crystals in both regions. The model was composed as a system of coupled nonlinear differential equations. The number of particles of all types present was fixed and stored, which allows to ignore the description of the nucleation rate. Moreover, it is possible to analyze each process step by step.

For convenience of comparison with the experimental data we used the GaS$_{1-x}$Se$_x$ ($x = 0.7$ molar fraction of GaSe) composition of the solid solution in the simulation. GaS$_{0.7}$Se$_{0.3}$ corresponds to the minimum in the GaS–GaSe phase diagram and can be considered as a quasi-one-component.

When deposition occurs in a homogeneous phase region, the concentration of monomers falls below the equilibrium concentration at the surface of the droplets in the dispersed region. This leads to the transfer of monomers from the droplets to the homogeneous region. Then the homogeneous phase is incorporated into crystals and nuclei, i.e., a single crystal is grown. In this case, the presented numerical calculations, taking into account the sizes and/or masses of particles, agree with the experimental data.

Nucleation. The evolution of the dispersed phase in crystallization experiments in a closed system occurs by a complex mechanism. In this case, the formation of metastable intermediate solid phases and the evolution of dispersed particles of the solid phase at the end of the process are possible. The mechanisms of such phase transformations and the crystallization kinetics are described using nonlinear models [25, 26]. Nonlinear properties of the crystallization process are determined taking into account the boundary conditions and coefficients of the kinetic equations, and also depend on the crystallization prehistory. Kinetic coefficients are calculated based on the theory of diffusion growth and dissolution of second-phase precipitates. These coefficients determine the probability of attachment and ejection of one particle per unit time, respectively.

A homogenized solid solution quenched in the concentration region of the *T–x* phase diagram of the GaS–GaSe system [10] can remain in a metastable state for some time. Ultimately, it reaches thermodynamic equilibrium. At one of the equilibrium concentrations, some microclusters can form in the GaS$_x$Se$_{1-x}$ matrix [19, 20].

Taking into account the 2D nucleation mechanism [26], the growth of single crystal can be represented as follows. Crystal faces grow due to the formation of two-dimensional nuclei of critical size in the absence of screw dislocations ending on the surface. 2D nuclei are formed when individual growth units (for example, atoms, molecules, dimers) are adsorbed on the surface of a crystal, diffuse and agglomerate. After a 2D nucleus becomes larger than its critical size, it becomes thermodynamically advantageous for attaching growth units to this nucleus. In a supersaturated solution a 2D nucleus larger than the critical one propagates across the face until it reaches the crystal boundary. These boundaries can be either the edge of the crystal layer, or the front of the layer below it or the growth front from another nucleus.

The nucleation rate $J(t)$ approaches a stable state according to an equation of the form [27]

$$J(t) = J_s \left[1 - exp\left(-t / t_{lag} \right) \right]$$

$$1 / \left(6.3 a (L_c) Z^2 \right) \geq t_{lag} \geq 1 / \left(12 a (L_c) Z^2 \right), \tag{7}$$

where J_s is the stationary nucleation rate; Z is the Zeldovich factor; $a(L_c)$ is the rate at which monomers are absorbed by a cluster with a critical size L_c; t_{lag} is the time lag.

This expression (7) describes the asymptotic behavior of the Fokker–Planck equation and is in qualitative agreement with the numerical calculation for the dependence of the nucleation frequency of GaS$_x$Se$_{1-x}$ on time. Since the gradient (L) in the region $| L - L_c | < 1/2Z$ is small, the cluster will move in this region by random walk with a jump frequency $a(L_c)$. The time required for the cluster to disperse the $1/Z$ distance by random walk is determined by the time lag, which is estimated as $t_{lag} = 1 / 2a(L_c) Z^2$.

Using Fokker–Planck equation. Suppose that crystallization of solid solutions occurs from a uniformly supersaturated solution in a closed system. Solution has a limited volume V at time $t = 0$. If the concentration of the dispersed phase Q exceeds the solubility of the components of the system, then the nucleation and growth of the solid phase occurs. With such crystallization, the formation of various modifications of the solid phase is possible.

Assume that during crystallization a chemical reaction does not occur and a constant temperature of the solution is maintained. Mixing the solution does not lead to cracking and aggregation. Mass crystallization occurs by spontaneous nucleation, i.e., nucleation of crystallization centers, crystal growth and dissolution of particles of the dispersed phase.

Nucleation involves the formation and growth of clusters from molecules of the initial solution. Cluster formation occurs up to the size at which it is possible to distinguish a crystal face as a structural element responsible for growth. The nucleation rate, crystal growth rate and dissolution of the particles of the dispersed phase are determined with the degree of supersaturation of the solution and the size of the crystal face [28, 29].

Since the formed crystals have a limited size, it is necessary to choose the boundary conditions for the equation of distribution density. After that, the kinetic equation is supplemented by the initial condition and the balance equation. Thus, we obtain a system of nonlinear equations that are solved by the difference method [30].

The Fokker–Planck equation approximates distribution density of GaS_xSe_{1-x} crystals by size (Fig. 4a). It was assumed that the temperature dependence on nanocrystals (particle) size is described by the relation

$$T = T_0 \exp\left(\frac{R^2}{R_0^2}\right), \tag{8}$$

where R is the particle radius; R_0 is the initial particle radius.
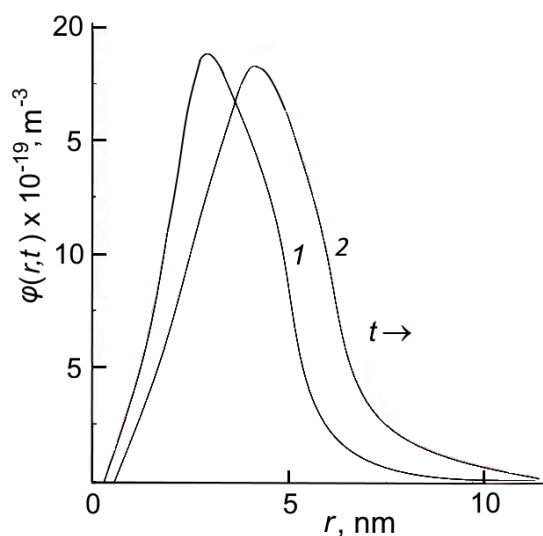
1 — 0.005 and *2* — 0.001. Curve — approximation by dependence (1) at $\gamma = 5$ and $\beta = 1$ (Equation (1))

Figure *4a*. Evolution of distribution function of $GaS_{0.3}Se_{0.7}$ solid solution by size in nucleation time (t, s)
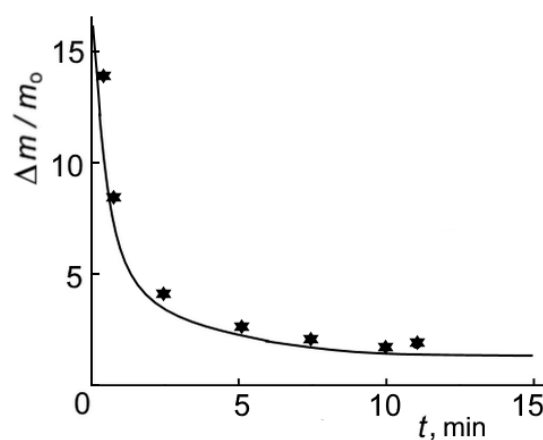
Figure *4b*. Relative mass dependence of $GaS_{0.3}Se_{0.7}$ nanocrystal on time; m is particle mass with diameter $d \approx 30$ nm, m_0 is arithmetic mean mass of particles

Comparison results of the calculation (curve) and experiment (points) of the dynamics of the mass change (Δm) of GaS_xSe_{1-x} nanocrystals with respect to the initial arithmetic mean mass of particles m_0 diameter ~30 nm are shown in Figure 4b. Numerical experiments indicate that the concentration of crystals of a given composition varies from the initial supersaturation to equilibrium concentration in a very short time. From the concentration dependence of the formed GaS_xSe_{1-x} crystals on the formation time, it follows that the bulk of the crystals is formed within 2×10^{-3} s from the moment of crystallization initiation.

At the same time, the crystal concentration of a given composition decreases from the initial supersaturation to the equilibrium concentration. This process is accompanied by a decrease in the oversaturation of the solution. The supersaturation ends with a constant number of nuclei and then the crystals grow with a further

increase in crystal size. Thus, when using the Fokker–Planck equation, the concentration of the crystallizing phase was taken into account, as well as data on the supersaturation and crystal size.

Using the stochastic model by the Monte Carlo method. Within the framework of the stochastic model [21–23] we consider a spatially homogeneous volume V, in which there are particles belonging to N_s different types of particles. Each type is characterized by both its liquid mass and the mass of its nucleus, $\bar{u}_\mu = (u_m, u_n)$. Let us assume that the forming particle with the composition $\bar{u}_\mu$ is a member of the μ-type. After time $t = 0$ the types can be randomly combined according to the reaction $A_{m,n} + B_{m',n'} = C_{m+m',n+n'}$, where $A_{m,n}$ and $B_{m',n'}$ are particles of composition $\bar{u}_\mu = (u_m, u_n)$ and $\bar{u}_\nu = (u_{m'}, u_{n'})$, respectively.

According to this model, the transition probabilities for particle merging events are:

$$a(i,j) = V^{-1}K(i,j)n_i n_j dt \equiv P(i,j;t)dt, \tag{9}$$

where $K(i,j)$ is the set of nuclei; V is the volume of the solution.

$P(i,j;t)dt$ – Pr is the probability that two particles of i and j (for ij) types with n_i and n_j number of particles will collide in the nearest time interval. Then the probability of collision of two particles of the same type i with the number of particles n_i during the inevitable time interval can be represented in the form

$$a(i,i) = V^{-1}K(i,i)\frac{n_i(n_i-1)}{2}dt \equiv P(i,i;t)dt. \tag{10}$$

Within this structure the μ index is possible for each pair of nuclei i, j that can collide. For a system with N types $(S_1, S_2, ..., S_N)$ $\nu \in N\frac{(N+1)}{2}$. The set $\{\nu\}$ defines the total collision space and is equal to the total number of possible interactions. Then the probabilities of $\alpha(i,j)$ and $\alpha(i,i)$ transitions can be represented by one index (α_ν).

This stochastic model for GaS_xSe_{1-x} crystallization was solved using an algorithm introduced by Gillespie [21] for chemical kinetics and modified by Laurenzi et al. [23].

Comparison of Monte Carlo simulations with experimental data. The evolution of the two-dimensional distribution of nuclei (crystal nucleus) during crystal growth was simulated using the Monte Carlo method. A stochastic algorithm for chemical reactions was used to simulate the kinetic behavior of the nuclear distribution. A set of two-component kinetic equations was used.

The performance of stochastic Monte Carlo simulation (MCS) was tested by studying the growth of crystals with a constant nucleus size in solution, and the results were compared with our experimental data on the kinetics of nucleation. The influence of a two-component set of nuclei on the dynamics of mass fluctuations of nuclei of the process was studied.

To simulate random processes associated with the deviation of the types of nuclei from the critical size, the Monte Carlo method was used. Time evolution of particle species was approximated based on the distribution of the output value $N(y)$, where N is the number of particle types, y is the type of particle nuclei. For random $f(m,t)$ and $f(n,t)$, the equations for N are stochastic differential equations. Therefore the statistical description of the growth process was carried out using kinetic collection equations for two corresponding probability distributions.

In MCS the number of particles of a certain critical size grown from a solution in their original form, i.e., the initial number of particles was taken as ≤60, and the average value was calculated for 1000 realizations taking into account the dynamic distribution of particles.

For simulation of a two-component constant of a discrete set of nuclei, the following value was used: $K(m,n;m',n') = 1.1 \times 10^{-4}\,cm^3 s^{-1}$. The monomer particle had a radius of 10 μm (particle mass $m_0 = 3.77 \times 10^{-9}$ g), and the dispersed monomer was a solid-liquid (SL) GaS_xSe_{1-x} with a radius of 0.1 μm (mass of the SL phase $n_0 = 7.11 \times 10^{-15}$ g). The mass grid of the SL-solution was selected in accordance with the mass of the particle $(i) = i \times m_0$, $(i = 1, .., N_p)$ and the mass of the SL phase $(j) = j \times n_0$, $(j = 1, .., N_{s-1})$.

The volume of the studied system in all calculations was taken to be 1 cm^3. 30 intervals for the particle mass grid and 30 intervals for the SL phase mass grid were determined. We also took into account the

possibility of the existence of pure monomeric particles containing pure GaS and/or GaSe particles, as well as pure structural units of SL GaS and SL GaSe. Then the total number of types in our numerical experiment can be calculated as: $N_{\text{total}} = N_p \times N_{s-1} + N_p + N_{s-1}$.

The maximum number of types of structural units that can be generated during simulation, in the selected case, is 960. Solutions obtained as a result of Monte Carlo calculations for $N(1, 1; t)$, $N(1, 0; t)$ and $N(0, 1; t)$ types are shown in Figure 5a–c. Our experimental data are also shown in Figure 5.
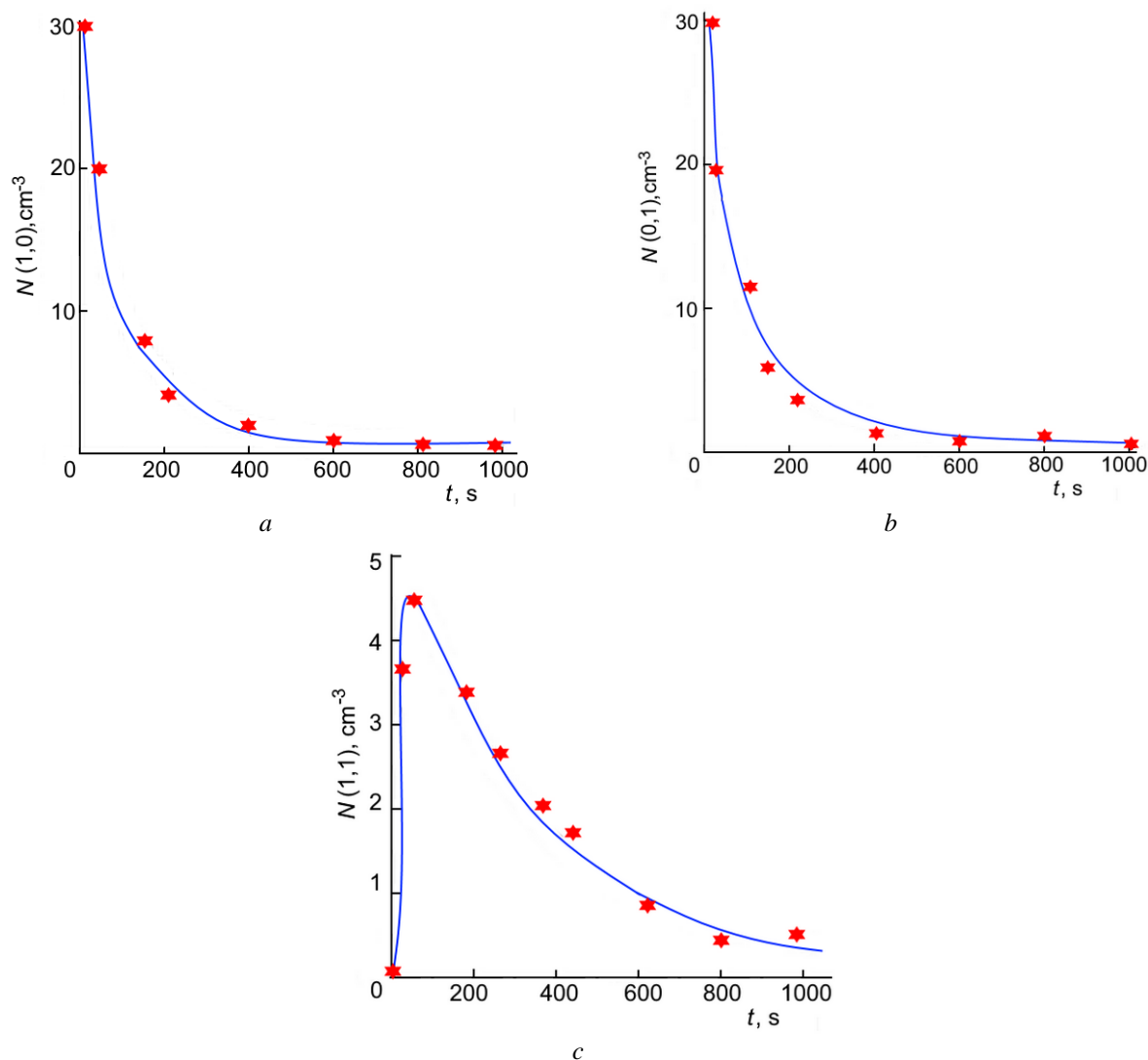
Figure. 5. Modeling of time evolution of the types of nanocrystals (*a*) $N(1, 0)$, (*b*) $N(0, 1)$, and (*c*) $N(1, 1)$ for a GaS$_{0.3}$Se$_{0.7}$ solid solution modeled by a constant nucleus size (a solid phase nucleus in a melt) $K(m, n; m', n') = 1.1 \times 10^{-4} \text{cm}^3\text{s}^{-1}$. Approximation curve are the result of Monte Carlo simulation of the two-component kinetic equation (5). Approximation curve of the averaging result over 1000 realizations

The differences between the mean values of Monte Carlo simulations and experimental data are negligible and they can be substantiated by statistical criteria. Description of the two-dimensional discrete size distribution after 100 s also indicates agreement between the mean values of the Monte Carlo simulation and the experimental data.

Conclusions

We used a model close to the ideal solid solution GaS$_x$Se$_{1-x}$, which resembles the structure of the liquid phase. A set of self-consistent thermodynamic parameters was obtained. The calculated phase diagram and thermodynamic property data were in good agreement with the experimental information. In the GaS–GaSe

system, the existence of continuous GaS$_x$Se$_{1-x}$ solid solutions and the formation of a phase diagram with a minimum at 70 mol% GaSe were confirmed.

Model of kinetics of GaS$_x$Se$_{1-x}$ nucleation using the Fokker–Planck equation takes into account compositional fluctuations due to the initial state of solid solutions. It was established that taking into account random walks into the size space during crystallization allows to describe the dynamics of changes in the S$_x$Se$_{1-x}$ properties.

By numerically solving the equation, the evolution of the size distribution function of the GaS$_x$Se$_{1-x}$ crystal nuclei in nucleation time is approximated. For calculations a purely implicit differencing scheme is used, which involves splitting the extended volume of the solution into independent fragments. It follows from the time dependence of the concentration of GaS$_x$Se$_{1-x}$ crystals ($x = 0.7$) that the bulk of the crystals was formed within 2×10^{-3} s from the moment of crystallization initiation.

The multicomponent Monte Carlo algorithm based on a stochastic approach to chemical reactions, using the example of GaS$_x$Se$_{1-x}$ allowed to calculate statistical fluctuations for two-component aggregation of particles taking into account their radius and composition. Taking into account the transition probability in microphysical processes allows to determine how a specific pair of particles (nuclei, crystals, solid-liquid) with a set of properties will be aggregated in the next time interval.

The solution of the continuous set of the kinetic equation shows that if an individual particle acquires a mass much greater than the rest of the system, then it is necessary to take into account statistical fluctuations in the region of large particle masses. Agreement between the numerical solutions of Monte Carlo simulations and experimental data on crystal growth in the GaS–GaSe system was observed.

The variety of stationary distributions for time evolution of the types of structural units indicates the possibility of controlling the process of two-component aggregation of nuclei by varying the properties of the nuclei of a pair of particles during the formation of crystals of given sizes.

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GaS_xSe_{1-x} $(0 \le x \le 1)$ қатты ерітіндісінің ядролануы мен өсуінің сызықтық емес процестерін модельдеу

GaS_xSe_{1-x} $(0 \le x \le 1)$ қатты ерітіндісінің ядролануы мен өсу кинетикасын модельдеу және физика-химиялық зерттеулердің нәтижелері келтірілген. GaS_xSe_{1-x} кристалдарының ядролануы мен өсуінің гетерогенді процесі зерттеліп, кристалдану фазаларының кинетикалық әрекетін ескеретін сызықтық емес теңдеулерді ескере отырып, модельденді. GaS_xSe_{1-x} монокристалдары мен нанокристалдары ерітіндіден, балқымадан және химиялық бу беру реакциясы арқылы өсірілді. GaS_xSe_{1-x} кристалдары химиялық тасымалдау реакциясы әдісімен герметикалық кварц ампуласында екі температуралы градиент пешінде алынды. Йод тасымалдаушы қоспа ретінде пайдаланылған. Фоккер-Планк теңдеуін қолдана отырып, GaS–GaSe жүйесінің қатты ерітінділерінің кристалдарының үлестіру функциясының эволюциясы сандық әдіспен зерттелді. Теорияны тәжірибелік мәліметтермен салыстыруға ыңғайлы болу үшін $GaS_{1-x}Se_x$ қатты ерітіндісінің құрамы қолданылды $(x = 0{,}7$ молярлық фракция GaSe). Монте-Карло әдісі $GaS_{0,3}Se_{0,7}$ қатты ерітіндісі үшін бөлшектердің екі түрінің ядролануының уақыт эволюциясын жақындату үшін пайдаланылған, тұрақты ядро өлшемімен модельденген. Сызықтық емес кристалдану процестерін модельдеу нәтижелері тәжірибелік мәліметтермен сәйкес келеді.

Кілт сөздер: сызықтық емес модельдеу, кристалдану кинетикасының теңдеуі, $GaS_{1-x}Se_x$ қатты жартылай өткізгіштері, сандық шешімдердің алгоритмі, ақырлы айырымдық теңдеулер, Фоккер-Планк теңдеуі, үлестіру функциясының эволюциясы, Монте-Карло әдісі.

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Моделирование нелинейных процессов зарождения и роста твердых растворов GaS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1)

Приведены результаты исследования моделирования и физико-химического исследования кинетики зарождения и роста твердого раствора GaS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1). Гетерогенный процесс зародышеобразования и роста кристаллов GaS$_x$Se$_{1-x}$ изучен и смоделирован с учетом нелинейных уравнений, учитывающих кинетическое поведение кристаллизующихся фаз. Монокристаллы и нанокристаллы GaS$_x$Se$_{1-x}$ были выращены из раствора, расплава и путем химической реакции переноса через пар. Кристаллы GaS$_x$Se$_{1-x}$ получены методом химической транспортной реакции в двухтемпературной градиентной печи в запаянной кварцевой ампуле. Йод использовался в качестве транспортной добавки. С помощью уравнения Фоккера-Планка численным методом изучена эволюция функции распределения кристаллов твердых растворов системы GaS–GaSe по размерам в момент зарождения. Для удобства сравнения теории с экспериментальными данными применялся состав твердого раствора GaS$_{1-x}$Se$_x$ ($x = 0{,}7$ мольная доля GaSe). Метод Монте-Карло использовался для аппроксимации временной эволюции зарождения двух типов частиц для твердого раствора GaS$_{0,3}$Se$_{0,7}$, моделируемого постоянным размером зародыша. Результаты моделирования нелинейных процессов кристаллизации согласуются с экспериментальными данными.

Ключевые слова: нелинейное моделирование, уравнение кинетики кристаллизации, полупроводниковые твердые растворы GaS$_x$Se$_{1-x}$, алгоритм численного решения, конечно-разностные уравнения, уравнение Фоккера–Планка, эволюция функции распределения, метод Монте-Карло.

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Thermodynamic study of the thallium-thulium tellurides by EMF method

In this study the phase equilibria in the Tl_2Te–Tl_2Te_3–$TlTmTe_2$ compositions area of the Tl–Tm–Te ternary system were studied by powder X-ray diffraction (PXRD) analysis. Based on PXRD data, the solid-phase equilibria diagram was plotted. The thermodynamic functions of the Tl_9TmTe_6 and $TlTmTe_2$ ternary compounds were calculated by the electromotive forces method. The electrochemical cells of the following type (−) TmTe (s.) | glycerol + KCl + $TmCl_3$ | (Tm in alloys of Tl–Tm–Te system) (s.) (+) were assembled and their EMF were measured in the 300-450 K temperature range. Based on obtained EMF data for the Tl_2Te_3–$TlTe$–$TlTmTe_2$ and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 three-phase regions, the relative partial thermodynamic functions of TmTe in alloys were calculated. The combination of these functions with the partial molar functions of thulium in TmTe allowed calculating the corresponding partial functions of thulium in the above phase regions. The potential-forming reactions responsible for the indicated partial molar values were obtained based on constructed solid-phase equilibria diagram. Using indicated potential-forming reactions, for the first time, the standard thermodynamic functions of formation and standard entropies of the Tl_9TmTe_6 and $TlTmTe_2$ compounds were calculated.

Keywords: Tl–Tm–Te system, Tl_9TmTe_6, $TlTmTe_2$, powder X-ray diffraction analysis, solid-phase equilibria diagram, method of electromotive forces, concentration cells, thermodynamic functions.

Introduction

The presence of a wide range of functional properties (thermoelectric, optical, electronic) in chalcogenides of heavy elements makes them promising functional materials in numerous fields of modern technology, such as electronics, optoelectronics industry, photovoltaic and photo-detection applications, fiber-optical communication, etc. [1–6]. Moreover, the discovery of a topological insulators (TI) shown that these compounds also exhibit the properties of TI and can be used in spintronics and quantum computers, medicine, security systems [7, 8].

The introduction of heavy metal atoms as well as d- and f-elements into the crystal lattice of these compounds can lead to an improvement in their thermoelectric properties [9], and also give them additional functionality, for example, magnetic properties, as well as the properties of TI [10–13].

It is known that telluride Tl_5Te_3 exhibits thermoelectric properties [14]. Due to the peculiarities of the crystal lattice it has many ternary analogs of the types Tl_9AX_6 and Tl_4BX_3 (A-Sb, Bi, In, Au, rare-earth elements; B-Sn, Pb, Mo, Cu, rare-earth elements; X-Se, Te) [15–22], also possessing several functional properties, namely optical [23, 24], thermoelectric [25–27], magnetic [28, 29], as well as topological insulators properties [30, 31]. In recent years in order to improve thermoelectric performance intensive work has been carried out to study solid solutions and doped phases based on these compounds [32–34].

Another class of thallium chalcogenides with the common formula $TlCX_2$ (C – Sb, Bi, In, Ag, rare-earth elements) also possess many functional properties [10, 35–40].

For design and optimization of the synthesis and the growth of the single crystal conditions besides the phase diagram, accurate data of the thermodynamic functions are required [43–46]. Usually, the method of differential scanning calorimetry is used to determine the thermal effects of phase transformations and the heat capacity [47, 48]. At the same time, the method of electromotive forces (EMF) has found wide application in practice due to the simplicity of measurements and their high accuracy. EMF measurements are often used to investigate the partial and integral thermodynamic functions of formation. In practice, the several modifications of the EMF method are used. In this case, liquid electrolytes [49–51], solid electrolytes [52, 53], as well as ionic liquids can serve as an electrolyte [54, 55].

However, despite potential interest we did not find in the literature data on the thermodynamic properties of Tl_9LnTe_6 and $TlLnX_2$ compounds. Considering the above, we have undertaken a comprehensive study of solid-phase equilibria and thermodynamic properties of the Tl–Gd–Te and Tl–Er–Te systems [41, 42].

In this experimental study, we present the results of the investigation of the solid-phase relations in the Tl_2Te-Tl_2Te_3-$TlTmTe_2$ system and the thermodynamic properties of the Tl_9TmTe_6 и $TlTmTe_2$ ternary compounds by EMF method.

Experimental

Synthesis

The initial compounds and intermediate samples from the Tl_2Te_3–$TlTe$–$TlTmTe_2$ and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 three-phase regions were synthesized from high-purity thallium (granules, 99.999 %), thulium (ingots, 99.9%), tellurium (ingots 99.999 %), and telluride Tl_2Te in evacuated quartz ampoules. After alloying at 1000 K, non-homogenized intermediate samples were powdered, mixed, compressed into a tablet, and annealed further at 700 K for 1000 h.

The congruently melting Tl_2Te was synthesized by fusing thallium and tellurium in vacuumed ($\sim 10^{-2}$ Pa) quartz ampoule at 750 K followed by slow cooling.

The refractory compound TmTe was synthesized by ceramic method at 1000 K followed by annealing at 900 K for 1000 h.

Methodology

Studies were carried out by powder X-ray phase diffraction analysis (Bruker D8 diffractometer with $CuK\alpha_1$ radiation) and electromotive forces (EMF) method.

For the rational planning of thermodynamic experiments, we first studied the solid-phase equilibria of the Tl–Tm–Te system in the Tl_2Te–Tl_2Te_3–$TlTmTe_2$ compositions area (Fig. 1).
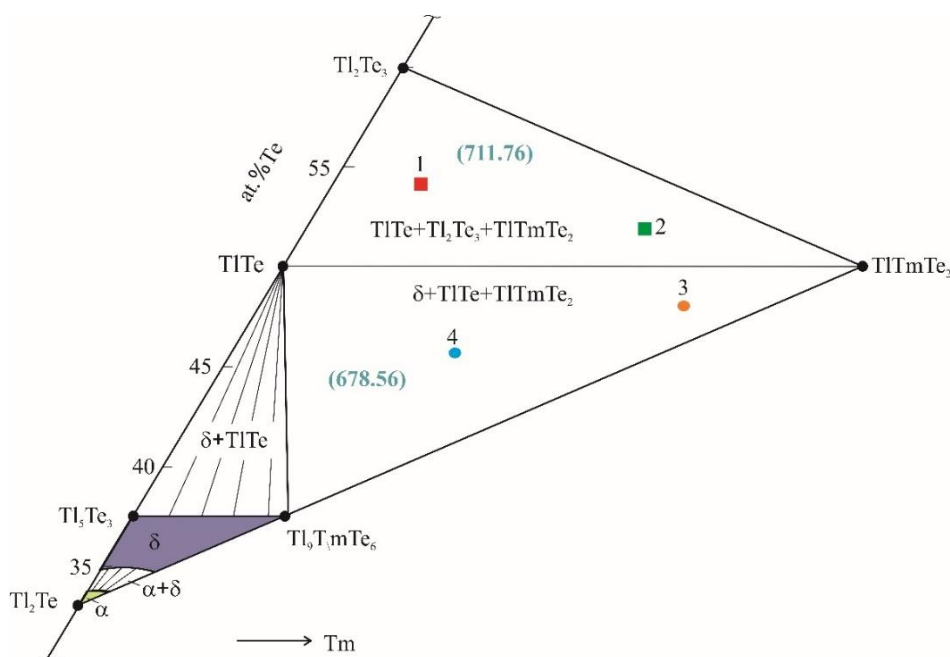
Figure 1. The solid-phase equilibria diagram of the Tl_2Te–Tl_2Te_3–$TlTmTe_2$ subsystem.
1–4 — alloy compositions used for XRD and EMF measurements;
the numbers in brackets are the EMF values (mV) of the cells type (1) in the three-phase regions

The data on phase relations in the Tl_2Te–Tl_5Te_3–Tl_9TmTe_6 composition area were taken from the previous study [56]. The formation of a wide area of solid solutions with the Tl_5Te_3 structure (δ-phase) was found for this system. Also it was established that δ-phase is tie-lined to TlTe (Fig. 1) [57]. As a result, a two-phase region δ+TlTe is formed on the phase diagram. Solid-phase equilibria diagram of the Tl_2Te_3–Tl_2Te–$TlTmTe_2$ system also reflects the presence of three-phase regions Tl_2Te_3–$TlTe$–$TlTmTe_2$ and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 (Fig.1). Their existence is confirmed based on powder diffraction patterns of selected alloys (Fig. 2, samples 1, 4).
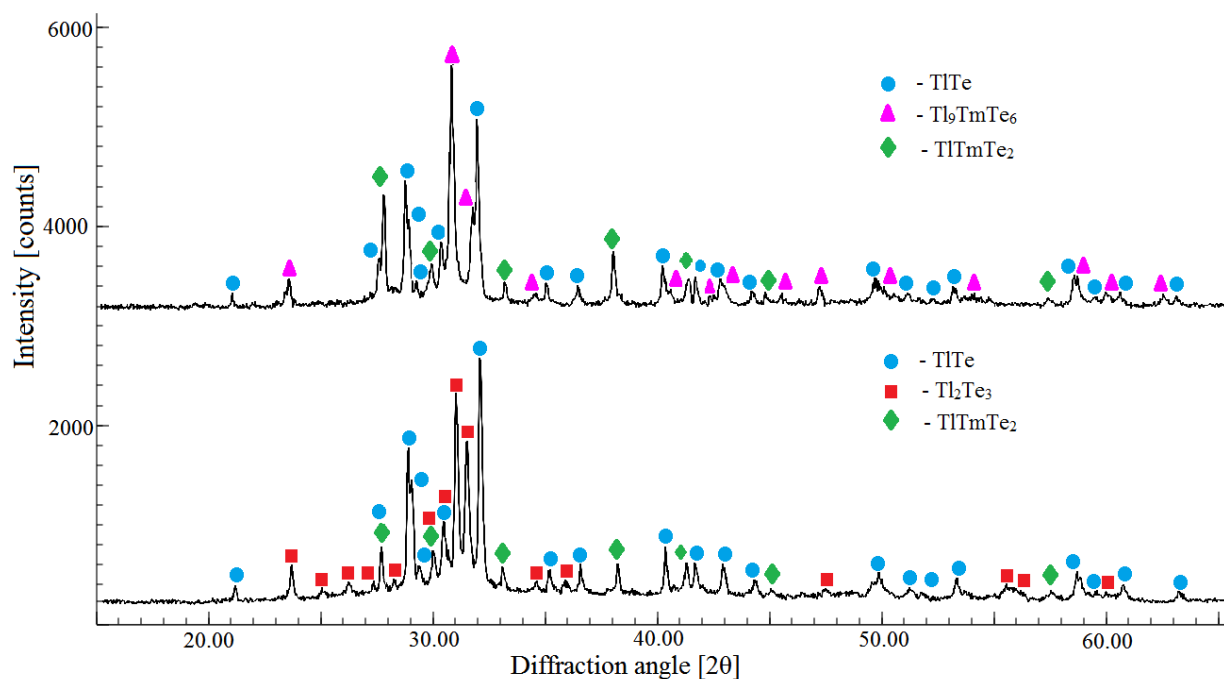
Figure 2. The powder X-ray diffractogramms of the alloys from Tl_2Te_3–$TlTe$–$TlTmTe_2$
and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 compositions areas

Thus, EMF measurements in the indicated three-phase regions can be used for calculations of the thermodynamic functions of the Tl_9TmTe_6 and $TlTmTe_2$ ternary compounds.

The assembled electrochemical cell with a liquid electrolyte can be presented schematically as

$$(-)\ TmTe\ (s.)\ |\ glycerol + KCl + TmCl_3\ |\ (Tm\ in\ alloys)\ (s.)\ (+). \tag{1}$$
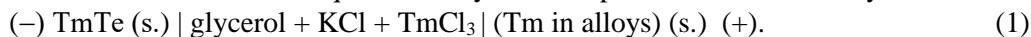
In cells (1) a glycerol solution of KCl with addition of $TmCl_3$ (0.1 %) was used as the electrolyte. It is necessary to pay special attention to the salts (KCl и $TmCl_3$) and glycerol. They must be free from moisture and oxygen. Therefore glycerol was dehydrated and degassed before use by pumping at a temperature of ~450 K. Anhydrous KCl and $TmCl_3$ were used. The electrolyte was stored in a sealed ampoule and used as required. Upon the introduction of the electrolyte in a cell, contact with air was minimal.

TmTe with a negligible (0.1 at.%) tellurium excess was used as the left (negative) electrode. Our previous studies [41, 42] showed that using metallic lanthanide as the left electrode resulted in high EMF values. Right (positive) electrodes in the cells of type (1) were equilibrium alloys from Tl_2Te_3–$TlTe$–$TlTmTe_2$ and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 three-phase regions. The synthesis of the alloys - right electrodes is described above. The methods for preparing electrodes and assembling an electrochemical cell are detailed described in [54, 55]. To control the reproducibility of the EMF results and their compliance with the phase diagram, 2 electrode-alloys with different compositions from each three-phase region were prepared.

The electrochemical cell described [54, 55] was assembled, evacuated, filled with argon, and placed in a cylindrical electric furnace. All contacts and current leads of the cell were kept at the same temperature. The first equilibrium EMF values were obtained after keeping the concentration cell at ~350 K for 60 h, followed by every 3–4 hours after the establishment of a certain temperature. The EMF data were considered equilibrium if they did not differ from each other upon repeated measurements at a given temperature by more than 0.2 mV, regardless of the direction of the temperature change. Within the experiment the EMF of each sample was measured 3 times at two constant temperatures. For example, for an alloy from the Tl_2Te–Tl_5Te_3–Tl_9TmTe_6 phase region at 350.8 K, EMF values were: 683.13, 683.19, 683.224. Table 1 presents the averaged value of 683.18.

Keithley 2100 6 1/2 digital multimeter was used for EMF measurements. Most measurements were carried out when heating and cooling the cell in steps no more than 10°. The chromel-alumel thermocouples and a mercury thermometer (an accuracy of ±0.5 K) were used for measurements of the temperature of the electrochemical cell.

The EMF measurements were conducted in 300–450 K temperature interval. The upper limit of the temperature interval of the EMF measurements was chosen so that the phase composition remained unchanged within the experiment. The mass measurement and X-ray diffraction analysis of electrodes before and after EMF measurements were used to control the reversibility of electrochemical cells and reproducibility of results. The mass and composition of the electrodes remained constant in the time of the experiment.

Results and Discussion

The obtained experimental data, i.e., pairs of temperature and EMF values are listed in Table 1.

T a b l e 1

**Experimentally determined data for temperature and EMF of the Tl_2Te_3–TlTe–$TlTmTe_2$
and TlTe–$TlTmTe_2$–Tl_9TmTe_6 phase regions in the Tl–Tm–Te system**

T, K	E, mV	
	TlTe–$TlTmTe_2$–Tl_9TmTe_6	Tl_2Te_3–TlTe–$TlTmTe_2$
301.2	680.24	712.85
306.7	679.15	711.34
312.7	681.02	712.45
318.3	679.84	714.64
323.3	681.68	715.12
328.2	681.82	713.13
334.2	682.08	715.65
340.1	680.62	713.94
345.5	684.68	714.02
350.8	683.18	718.12
357.7	684.24	714.94
362.2	683.21	719.08
366.4	684.86	719.66
371.5	684.86	716.06
377.9	688.84	720.07
382.9	687.68	717.98
387.4	687.44	716.46
392.3	685.02	719.66
395.3	688.44	719.22
402.1	688.68	722.12
407.5	690.96	718.78
412.3	688.12	719.83
416.7	688.93	722.55
421.3	687.87	721.88
425.7	693.46	722.74
431.1	692.21	722.66
437.2	693.34	722.02
442.7	692.66	724.33
446.2	693.85	724.12
449.2	693.99	725.97

The EMF measurements data of the electrochemical cell of type (1) were in full agreement with the diagram of solid-phase equilibria of the Tl_2Te–Tl_2Te_3–$TlTmTe_2$ system (Fig. 1). At a certain temperature the EMF value in the three-phase regions Tl_2Te_3–TlTe–$TlTmTe_2$ and TlTe–$TlTmTe_2$–Tl_9TmTe_6 were constant and changed during the transition from one phase to another.

The temperature dependences on EMF for all alloys of the Tl-Tm-Te system were linear (Fig.3). Also, the measurements results showed that, in addition to reproducibility, the numerical values of the EMF increase in the radial directions from Tm vertex of the Tl–Tm–Te concentration triangle, which is in agreement with the well-known thermodynamic principle [47, 48].
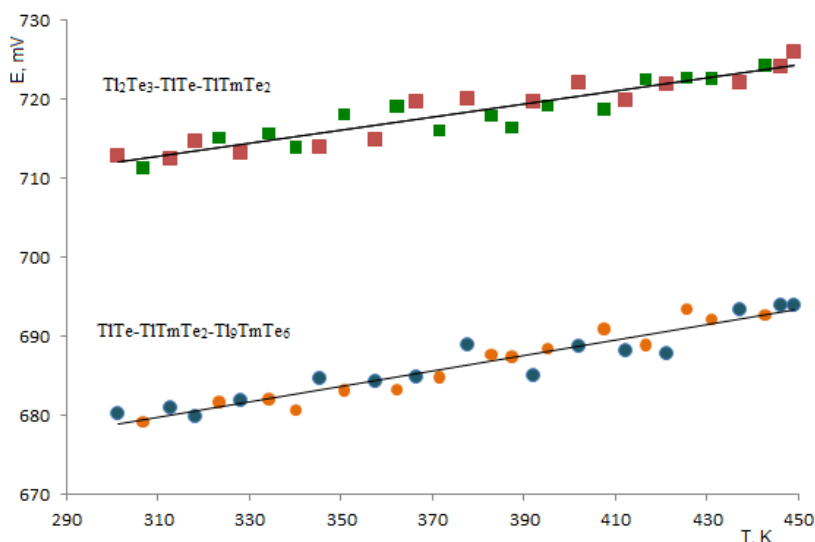
Figure 3. Temperature dependencies of EMF for alloys of the Tl_2Te_3–$TlTe$–$TlTmTe_2$
and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 phase areas of the Tl-Tm-Te system.
Alloys of different composition for each three-phase area are shown in different colors

Alloy designations are the same as in Figure 1.

Therefore, the data obtained were processed by the least-squares method, and temperature dependences of EMF were represented by the linear equation of type

$$E = a + bT \pm t \left[\frac{\delta_E^2}{n} + \delta_b^2 (T - \overline{T})^2 \right]^{1/2}. \tag{2}$$

In equation (2) a and b are coefficients, n is the number of pairs of values E and T; $\overline{T}$ is average temperature in K, t is Student's test, and δ_E^2 and δ_b^2 are the variances of individual EMF values and the constant b. With the number of experimental points $n = 30$, and the confidence level equal to 95 %, the Student's test is $t \leq 2$. Table 2 lists the equations obtained.

The partial molar functions of thulium telluride in the alloys at 298 K (Table 3) were calculated using the following thermodynamic relations:

$$\Delta \overline{G}_{TmTe} = -zFE; \tag{3}$$

$$\Delta \overline{S}_{TmTe} = zF \left(\frac{\partial E}{\partial T} \right)_P = zFb; \tag{4}$$

$$\Delta \overline{H}_{TmTe} = -zF \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right] = -zFa. \tag{5}$$

In the equations (3)–(5), z is the charge of the potential-forming cation Tm^{3+}, F is the Faraday constant, a and b are the constants in relation (2).

Table 2

Temperature dependencies of the EMF for the cells of the type (1) in the 300–450 K temperature interval

№	Phase area	E, mV $= a + bT \pm 2[\delta_E^2 / n + \delta_b^2 (T - \overline{T})]^{1/2}$
1	$Tl_2Te_3 + TlTe + TlTmTe_2$	$687.07 + 0.0828T \pm 2 \left[\dfrac{2.1}{30} + 3.5 \cdot 10^{-5} (T - 378.2) \right]^{1/2}$
2	$TlTe + Tl_9TmTe_6 + TlTmTe_2$	$649.22 + 0.0984T \pm 2 \left[\dfrac{1.9}{30} + 3.1 \cdot 10^{-5} (T - 378.2) \right]^{1/2}$

Relative partial molar functions of thulium monotelluride in the alloys of the Tl-Tm-Te system at T = 298 K

Phase area	$-\overline{\Delta G}_{TmTe}$	$-\overline{\Delta H}_{TmTe}$	$\overline{\Delta S}_{TmTe}$
	kJ·mol^{-1}		J·mol^{-1}·K^{-1}
$Tl_2Te_3 + TlTe + TlTmTe_2$	206.02±0.31	198.88±1.30	23.97±3.40
$TlTe + Tl_9TmTe_6 + TlTmTe_2$	196.42±0.30	187.92±1.23	28.48±3.24

These values represent the difference of the corresponding partial molar functions of thulium for the left and right electrodes of the cells of type (1). For example, for alloys from $Tl_2Te_3 + TlTe + TlTmTe_2$ three-phase area

$$\Delta \overline{G}_{TmTe}(\text{in alloys}) = \Delta \overline{G}_{Tm}\ (\text{in alloy}) - \Delta \overline{G}_{Tm}(\text{in TmTe}),$$

then

$$\Delta \overline{G}_{Tm}\ (\text{in alloy}) = \Delta \overline{G}_{TmTe}\ (\text{in alloy}) + \Delta \overline{G}_{Tm}(\text{in TmTe}). \tag{6}$$

Therefore, the calculation of the partial thermodynamic functions of thulium in the above three-phase regions was carried out by summation of the data in Table 3 with the corresponding partial molar functions Tm in TmTe [58]: $\Delta \overline{G}_{Tm} = -261.31 \pm 0.22$ кJ·mol^{-1}, $\Delta \overline{H}_{Tm} = -267.62 \pm 0.92$ кJ·mol^{-1}, $\Delta \overline{S}_{Tm} = -21.16 \pm 2.42$ J·mol^{-1}·K^{-1}. The obtained results are given in Table 4.

Relative partial molar functions of thulium in the alloys of the Tl–Tm–Te system at T = 298 K

Phase area	$-\overline{\Delta G}_{Tm}$	$-\overline{\Delta H}_{Tm}$	$\overline{\Delta S}_{Tm}$
	kJ·mol^{-1}		J·mol^{-1}·K^{-1}
$Tl_2Te_3 + TlTe + TlTmTe_2$	467.33±0.53	466.50±2.22	2.78±5.82
$TlTe + Tl_9TmTe_6 + TlTmTe_2$	457.73±0.52	455.54±2.15	7.35±5.66

The standard integral thermodynamic functions of the $TlTmTe_2$ and Tl_9TmTe_6 compounds were calculated by the method of potential-forming reactions. According to the solid-phase equilibria diagram (Fig. 1), the values of the partial molar functions of thulium in the Tl_2Te_3–$TlTe$–$TlTmTe_2$ and $TlTe$–$TlTmTe_2$–Tl_9TmTe_6 three-phase areas are thermodynamic functions of the potential formation reactions

$$Tm + Tl_2Te_3 = TlTe + TlTmTe_2 \tag{7}$$
$$Tm + 3TlTe = 0.25Tl_9TmTe_6 + 0.75TlTmTe_2 \tag{8}$$

According to relations (7) and (8), the standard thermodynamic functions of the formation of ternary compounds $TlTmTe_2$ and Tl_9TmTe_6 can be calculated from the relations

$$\Delta_f Z^0(TlTmTe_2) = \overline{\Delta Z}_{Tm} + \Delta_f Z^0(Tl_2Te_3) - \Delta_f Z^0(TlTe), \tag{9}$$

$$\Delta_f Z^0(Tl_9TmTe_6) = 4\overline{\Delta Z}_{Tm} + 12\Delta_f Z^0(TlTe) - 3\Delta_f Z^0(TlTmTe_2), \tag{10}$$

(Z≡G, H), while the standard entropy by using relations

$$S^0(TlTmTe_2) = \overline{\Delta S}_{Tm} + S^0(Tm) + S^0(Tl_2Te_3) - S^0(TlTe), \tag{11}$$

$$S^0(Tl_9TmTe_6) = 4\overline{\Delta S}_{Tm} + 4S^0(Tm) + 12S^0(TlTe) - 3S^0(TlTmTe_2). \tag{12}$$

Using relations (9)–(12) in calculations, beside own experimental data (Table 4), the value of the standard entropy Tm (71.014±0.209 kJ·mol^{-1}) [59] as well as thermodynamic data for TlTe and Tl_2Te_3 (Table 5), determined by using the EMF method [60] and included in the database [59] were used.

When calculating relations (10) and (12), in addition to the partial molar functions of thulium in the three-phase region $TlTe+Tl_9TmTe_6+TlTmTe_2$ we used the standard integral thermodynamic functions of the $TlTmTe_2$ compound determined in this work (Table 5).

Standard integral thermodynamic functions of thallium-thulium tellurides at T= 298 K

Compound	$-\Delta_f G^0 (298K)$	$-\Delta_f H^0 (298K)$	$S^0 (298K)$
	kJ·mol^{-1}		J·mol^{-1}·K^{-1}
TlTe [60]	44.5±0.4	44.9±0.5	115.9±1.5
Tl$_2$Te$_3$ [60]	90.8±0.8	90.0±1.0	279.7±3.3
TlTmTe$_2$	513.6±1.7	511.6±3.7	240.6±10.8
Tl$_9$TmTe$_6$	824.1±12.0	826.2±25.7	965.0±74.0

During the calculations of the partial thermodynamic functions of thulium (Table 4) and integral thermo-dynamic functions of ternary compounds (Table 5), the inaccuracies were determined by the uncertainty prop-agation method. The relatively high errors in the values of the enthalpy of formation and entropy can be ex-plained by the fact that, in contrast to the usual potential-forming reactions with one final product, there are 2 final products in reactions (7) and (8). Therefore, when calculating the thermodynamic functions of TlTmTe$_2$ and Tl$_9$TmTe$_6$ compounds according to relations (9)–(12), the thermodynamic functions of some compounds are subtracted from the general balance, while their errors are summed up.

Conclusion

In this paper we presented a set of experimental data on solid-phase relations in the Tl–Tm–Te ternary system in the Tl$_2$Te–Tl$_2$Te$_3$–TlTmTe$_2$ composition interval and thermodynamic functions of the TlTmTe$_2$ and Tl$_9$TmTe$_6$ compounds obtained by the powder XRD and EMF methods. The relative partial thermodynamic functions of TmTe and Tm in alloys were obtained based on the EMF measurements. The potential-forming reactions responsible for the above partial molar quantities were determined based on constructed solid-phase equilibria diagram, and the standard thermodynamic functions of formation and standard entropies of the TlT-mTe$_2$ and Tl$_9$TmTe$_6$ compounds were calculated for the first time.

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Талий-тулий теллуридтерін ЭҚК әдісімен термодинамикалық зерттеу

Мақалада $Tl_2Te–Tl_2Te_3–TlTmTe_2$ композициялар диапазонындағы фазалық тепе-теңдікті Tl–Tm–Te үштік жүйесінің ұнтақты рентгендік дифракциясы арқылы зерттеу нәтижелері келтірілген. XRD деректері негізінде қатты фазалық тепе-теңдік диаграммасы құрылды. Tl_9TmTe_6 және $TlTmTe_2$ үштік қосылыстарының термодинамикалық қасиеттері электр қозғаушы күштер әдісімен анықталды. (–) TmTe (қатты) типіндегі электрохимиялық ұяшықтар жиналды (қатты.) | глицерин + KCl + $TmCl_3$ | (Tl Tl–Tm–Te жүйесінің қорытпаларында) (қатты) (+) және олардың ЭҚК температурасы 300–450 K температурасында өлшенді. Алынған ЭҚК деректері негізінде үш фазалы аймақтар үшін $Tl_2Te_3–TlTe–TlTmTe_2$ және $TlTe–TlTmTe_2–Tl_9TmTe_6$, қорытпалардағы TmTe салыстырмалы ішінара термодинамикалық функциялары анықталды. Бұл функцияларды тулийдің TmTe ішінара молярлық функцияларымен біріктіре отырып, жоғарыда аталған фазалық аймақтардағы тулийдің сәйкес ішінара функциялары есептеледі. Қатты фазалық тепе-теңдік сызбасын қолдана отырып, көрсетілген ішінара молярлық шамаларға жауап беретін потенциал түзуші реакцияларды пайдаланып, Tl_9TmTe_6 және $TlTmTe_2$ қосылыстарының стандартты термодинамикалық функциялары және стандартты энтропиялары есептелді.

Кілт сөздер: Tl–Tm–Te жүйесі, Tl_9TmTe_6, $TlTmTe_2$, функционалды материалдар, рентгендікфазалық талдау, қаттыфазалық тепе-теңдік диаграммасы, электр қозғаушы күштер әдісі, термодинамикалық функциялар.

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Термодинамическое исследование теллуридов талия-тулия методом ЭДС

В статье представлены результаты исследования фазовых равновесий в области составов $Tl_2Te–Tl_2Te_3–TlTmTe_2$ тройной системы Tl–Tm–Te методом порошковой рентгеновской дифракции. На основании данных РФА построена диаграмма твердофазных равновесий. Термодинамические свойства тройных соединений Tl_9TmTe_6 и $TlTmTe_2$ определены методом электродвижущих сил. Были собраны электрохимические ячейки типа (−) TmTe (тв.) | глицерин + KCl + $TmCl_3$ | (Tm в сплавах системы Tl-Tm-Te) (тв.) (+) и измерены их ЭДС в интервале температур 300–450 К. На основании полученных данных ЭДС для трехфазных областей $Tl_2Te_3–TlTe–TlTmTe_2$ и $TlTe–TlTmTe_2–Tl_9TmTe_6$ определены относительные парциальные термодинамические функции TmTe в сплавах. Комбинируя эти функции с парциальными молярными функциями тулия в TmTe, вычислены соответствующие парциальные функции тулия в указанных выше фазовых областях. Используя диаграмму твердофазных равновесий, составлены потенциалобразующие реакции, отвечающие за указанные парциальные молярные величины. С использованием составленных потенциалобразующих реакций впервые рассчитаны стандартные термодинамические функции образования и стандартные энтропии соединений Tl_9TmTe_6 и $TlTmTe_2$.

Ключевые слова: система Tl–Tm–Te, Tl_9TmTe_6, $TlTmTe_2$, функциональные материалы, рентгенофазовый анализ, диаграмма твердофазных равновесий, метод электродвижущих сил, термодинамические функции.

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CHEMICAL TECHNOLOGY

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Catalytic conversion of isopropyl alcohol on the heteropolic acid – titanium oxide system

A complex of modern physicochemical methods (X-ray phase analysis, low-temperature adsorption of nitrogen, scanning electron microscopy, element analysis) was used to study the phase and texture properties of the phosphomolybdenum heteropoly acid–titanium oxide catalytic system. It was found that the optimal content of phosphomolybdenum heteropoly acid, which leads to an increase in the catalytic activity of titanium dioxide, is 7% wt.: the diisopropyl ether yield is higher, it reaches maximum values in a shorter period of time, and the samples are characterized by greater stability. It is shown that the textural characteristics of the specific surface area and dispersion are not the key factors responsible for the catalytic activity. It has been suggested that the activity of phosphomolybdenum heteropoly acid-containing samples is associated with the emergence of a new type of active centers that exhibit increased electron-donor properties (terminal oxygen atoms of the outer fragments of octahedra M = O heteropolyacids). A drop in the catalytic activity of samples with a phosphomolybdenum heteropoly acid content of more than 7 % wt. associated with the formation of surface metaphosphoric acid and entails a decrease in active centers.

Keywords: isopropyl alcohol, titanium dioxide, phosphomolybdenum heteropoly acid, phase composition, morphology, catalysis, diisopropyl ether, texture analysis, metaphosphoric acid, metatitanic acid.

Introduction

The constant interest in heteropoly acids (HPA) on the part of researchers is due to their unique physico-chemical and catalytic properties [1–4]. In catalysis HPA of the Keggin structure $HnXM_{12}O_{40}$ (X — P^{5+} and Si^{4+}, M — W^{6+} and Mo^{6+}) are most often used. The acidic properties of these HPA were studied quite deeply and in detail, which served as the basis for the creation of several industrial processes with their participation [5–7].

There are three ways to use HPA as catalysts: the use of acid solutions, the use of bulk acids and the use of HPA supported on various carriers. Among the latter, many porous materials are used (silica gel, activated carbon, alumina, etc.) [8–12].

In previously published works [13, 14], the results of catalytic conversions of isopropyl alcohol on the HPA – η-alumina system were discussed. It was found that the modification of HPA leads to an increase in the activity of η-alumina and selectivity for oxygen-containing products. Based on a comparative analysis of the reaction products, it was found that the active centers of unmodified η-alumina are exclusively Lewis centers: strong Lewis acid centers and strong Lewis basic centers, whereas after the modification of HPA they are mainly represented by Bronsted bases. The resulting systems were characterized by X-ray phase analysis, scanning electron microscopy, elemental analysis, and IR spectroscopy. The totality of the results made it possible to establish that during the interaction of the Keggin structure with the basic oxide its destruction occurs and the heteropolyanion is formed, which, having a negative charge, interacts with the electron-acceptor

Lewis acid centers on the surface, forming a surface complex of the surface-ligand type, which has uncompensated negative charge, and then begins to act as the new foundation of Bronsted.

Taking into account these results, as well as studies in which HPA, in particular tungstenosilic acid (HSiW), supported on TiO$_2$ and SiO$_2$ exhibits high activity and selectivity in the process of dimethyl ether formation [8, 14–18], it was of interest to continue this direction. The present work is devoted to the study of the features of the conversion of isopropyl alcohol to diisopropyl ether in the presence of phosphomolybdenum HPA applied to titanium dioxide.

Experimental

A catalyst of a given composition was prepared by impregnating titanium dioxide with a solution of HPA in an aqueous solution of ammonia (based on HPA per carrier) onto a carrier previously calcined for 3 hours to 200 °C. During the process, the following compounds were used:

1) industrial titanium dioxide TiO$_2$ (Evonik Resource Efficiency GmbH);

2) phosphorus-molybdenum heteropoly acid (GPC) H$_7$ [P (Mo$_2$O$_7$)$_6$]·H$_2$O;

3) isopropyl alcohol (GOST 9805-84).

The catalytic properties of the starting and modified TiO$_2$ were studied on a flow through setting in the temperature range of 150–250 °C with a bulk feed rate of 75 h^{-1}.

The analysis of raw materials and liquid reaction products was carried out by a chromatographic method on a CHROM 5 instrument with a flame ionization detector using a column filled with a sorbent — CELIT S-22, with 17 % polyethylene glycol applied to the sorbent. The reaction gas products were analyzed on a CHROM 5 chromatograph with a thermal conductivity detector. Diethylene glycol ether and n-butyric acid deposited on the Inzen brick INZ-600 were used as the sorbent. The quantitative interpretation of the chromatographic peaks included in the composition of the obtained catalysis was determined by the method of absolute calibration and internal normalization.

The phase analysis of the samples was studied by X-ray phase analysis on a RIGAKU SC-70 instrument in the range of angles of 3–60 °C at an angular scanning speed of 10 deg/min in CuK radiation (40 kV, 15 mA). The interpretation of the diffraction patterns was carried out using the ICDD database, PDF-2.

The surface morphology, as well as the elemental composition of the samples, was studied by scanning electron microscopy (SEM) on a JEOL JSM-6610 LV instrument with a 0.14 nm lattice resolution (with an integrated EDX analyzer (EDS, Genesis 4000, using Si(Li) detector) at an accelerating voltage of 100 kV. The SEM sample was mounted on carbon substrates mounted on copper grids. The statistical particle diameter was measured by SEM analysis of the sample.

The specific surface and pore volume were measured by adsorption–desorption of nitrogen on a universal analyzer ASAP 2400 (Micromeritics, USA). In the calculation the surface area of the nitrogen molecule was taken to be 0.162 nm^2, and the density of nitrogen in the normal liquid state was 0.808 g/cm^3. The measurement accuracy was ±3 %. Adsorption isotherms were obtained at –196 °C after degassing of the sample at 500 °C to a residual pressure of 0.013 Pa. The pore volume and their diameter distribution were calculated based on the desorption branch of the isotherm using the standard Barrett-Joyner-Highland procedure (measurement accuracy ±13 %).

Results and Discussion

Catalytic properties

The catalytic activity and selectivity of the formation of isopropyl alcohol conversion products are shown in the Figure 1. It should be noted that the presented results were reproduced upon repeated preparation of samples of each composition. Over the entire temperature range studied the conversion of isopropyl alcohol increased the stronger, the higher the content of HPA was. The minimum conversion value was observed for a sample containing 5 % wt. HPA: it is 16.7 % at 150 °C and increases to 43.8 % at 250 °C (the latter value is almost identical to unmodified titanium dioxide). In the low-temperature region the highest conversion is typical for 13 % wt. of the sample, which reaches 54 %, significantly exceeding the others, but with rising in temperature to 250 °C the conversion of 7, 10, and 13 % of HPA-containing catalysts becomes almost the same (from 71 to 76 %).

The main products of the conversion of isopropyl alcohol under the reaction conditions were diisopropyl ether, propylene and water. In addition, in the presence of a 5 % HPA-containing sample at temperatures of 200 and 250 °C the formation of a small amount of acetone was noted. The highest ether selectivity was observed for 7 % and 10 % of HPA samples.

Table 1 presents the data on the selectivity and yield of ether depending on the composition of the catalyst obtained within 12 hours of the process (here it is necessary to clarify: the process was not carried out continuously, but for 3 intervals, when every 4 hours of "work" were followed by "rest" of the catalyst, after which the process was resumed again). As can be seen from the results presented in the table, the process of conversion of isopropyl alcohol in the presence of titanium dioxide modified with phosphoformolybdenum HPA differed in characteristic features. If the initial titanium dioxide had the highest ether yield every time after three hours of catalyst operation, after which a sharp drop was observed, the trend for the modified samples is different: the yield of ether in HPA-containing samples is higher (with the exception of 5% HPA), in addition, the catalyst went down these parameters after already 1 hour, and they remained stable until the end of the current interval. Here we are not faced with the task of finding an explanation for this fact, we only fixed the trend. In general, the 7 % HPA + TiO$_2$ catalyst is most active: the diisopropyl ether yield from the 2nd to the 4th hour of each operation interval is 20.5–22 % with an ether formation selectivity of 49.2–77.1 %.
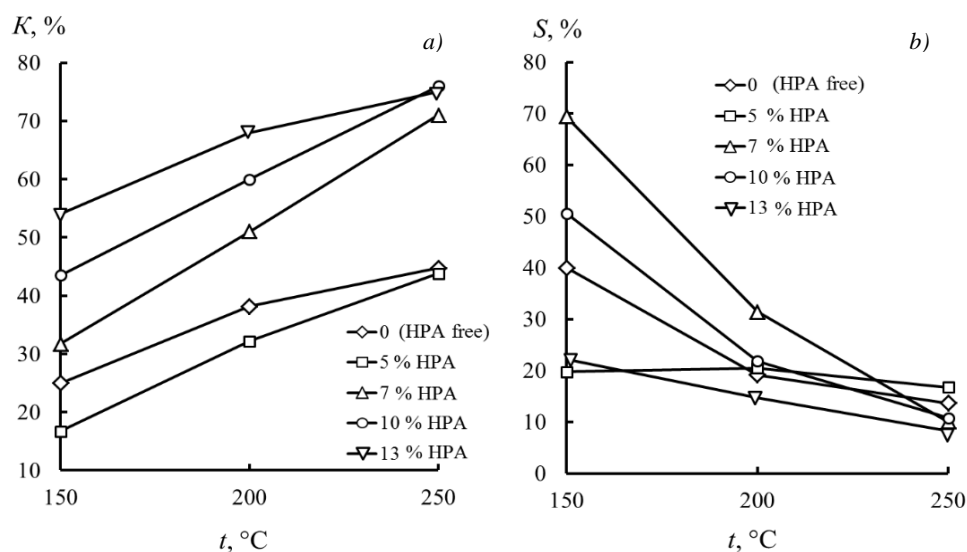
Figure 1. The effect of the composition of the catalyst on the conversion of (*a*) isopropyl alcohol and the selectivity (*b*) of the formation of diisopropyl ether

T a b l e 1

Effect of duration on process indicators

Duration, hours	Composition of the catalyst									
	TiO$_2$		5 % HPA + TiO$_2$		7 % HPA + TiO$_2$		10 % HPA + TiO$_2$		13 % HPA + TiO$_2$	
	S, %	α, %	S, %	α, %	S, %	α, %	S, %	α, %	S, %	α, %
1	46.7	4	9.6	1.6	28.8	6.7	18.3	6.5	30	12
2	30.9	6.7	15.2	3.3	66.2	21	50.6	22	28.9	13
3	40.1	10	16.4	3.4	69.4	22	40.5	21.9	23.9	12.9
4	60.2	8	16.5	3.3	77.1	21.6	37.1	22.1	41.0	13
5	40.2	8	8.5	1.7	52.2	16.7	32.3	16.4	39.5	15
6	37.6	8	12.3	2.7	56.7	21	35.4	18	30	18
7	26	9.2	12.9	2.7	55	20.9	41.4	18.2	30.5	18.3
8	22.9	6	10.5	2.1	55	20.2	45.2	18,1	41.6	18
9	11.6	3	5.2	1.3	42.9	16.3	29.5	15	33.7	14
10	16.6	4.8	7.4	2	50.1	20.9	27.1	16	23.8	15
11	18.6	5.2	7.2	1.2	49.2	20.8	30.0	16.1	23.9	15.1
12	13.9	1.6	6.4	1	56.7	20.8	32	16	44.1	15

Notes. The process temperature is 150 °C. Designations: S — selectivity, α — yield of diisopropyl ether.

Phase composition

Figure 2 shows the diffractograms of titanium dioxide before and after the introduction of HPA.
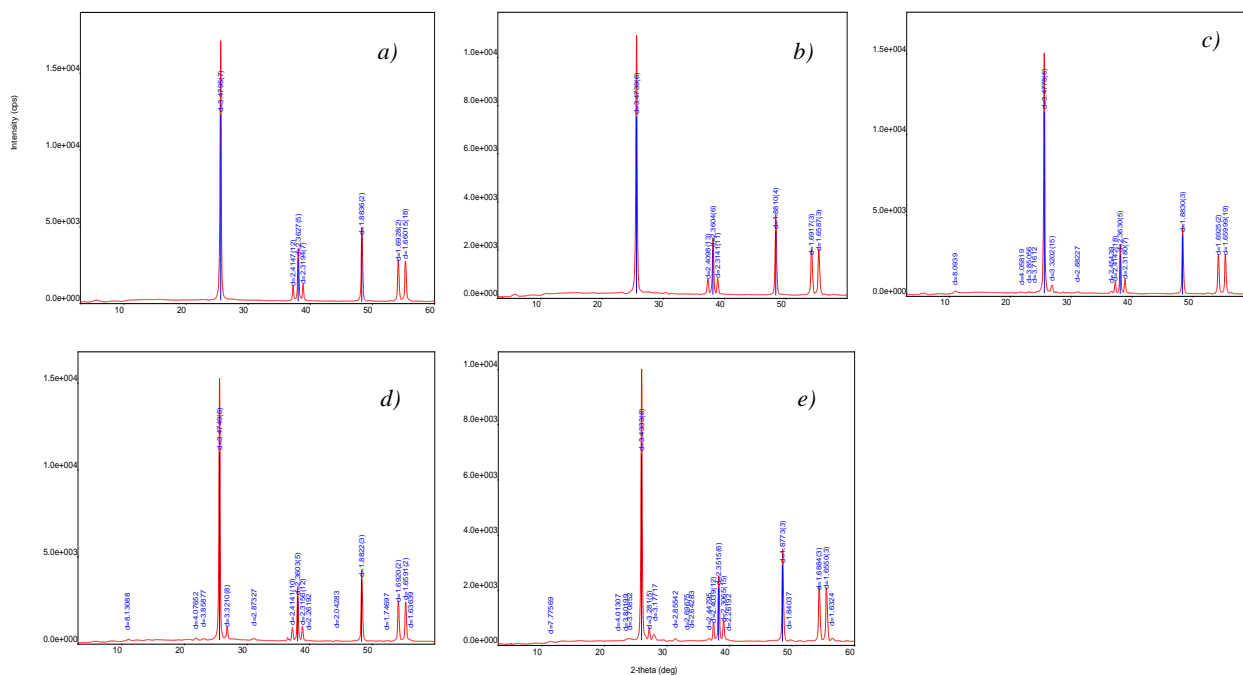
Figure 2. The difractograms of titanium dioxide: the original, not containing HPA (*a*),
containing 5 % wt. HPA (*b*), 7 % wt. (*c*), 10 % wt. (*d*) and 13 % wt. (*e*)

As can be seen from Figure 2*a*, the initial unmodified titanium dioxide is a well crystallized phase, anatase with characteristic narrow and high diffraction reflections at 25.58, 37.20, 38.06, 38.79, 48.28, 54.13 and 55.29 °C 2θ (the interplanar distances of this phase are unchanged for all 5 samples). Type of diffraction pattern when entering 5 % wt. GPC (Fig. 2*b*), with the exception of a decrease in the intensity of all reflexes, does not change; the appearance of the HPA phase is not noted; the crystallinity of anatase is preserved. The decrease in the intensity of reflexes of the anatase phase here and hereafter is probably associated with the appearance of microstresses caused by the introduction of the modifier. With an increase in the content of HPA up to 7 % of the mass (Fig. 2*c*) along with the anatase present on the diffractogram, the appearance of new reflections corresponding to five new phases is noted: 56.32 °C 2θ — $TiMoO_4$; 21.7, 36.56 and 44.39 °C 2θ — $H_2Ti_5O_{11} \cdot H_2O$; 10.89, 15.53 and 31.02 °C 2θ — HPA ($H_3PMo_{12}O_{40} \cdot 21H_2O$); 26.86, and 52.37° 2θ — $H_3P_3O_{10} \cdot 2H_2O$, as well as 32.01 and 47.04 °C 2θ — PO_4, in addition, a decrease in the crystallinity of the sample was noted. The increase in the content of HPA to 10 % wt. (Fig. 2*d*) does not lead to a significant change in the phase composition relative to the previous sample, with the exception of the appearance of another phase of titanium dioxide — brookite (weakly intense reflections at 39.68 and 52.24 °C 2θ). In the last of the studied, 13 % HPA-containing sample (Fig. 2*e*), of the previously marked six phases, there are reflexes related to only three phases, namely TiO_2 (anatase — 25.55, 37.17, 38.02, 38.73, 48.25, 52.24, 54.1, 55.26° 2θ and brookite — 39.75° 2θ), $H_2Ti_5O_{11} \cdot H_2O$ (7.98, 21.49, 36.19° 2θ), $H_3PMo_{12}O_{40} \cdot 21H_2O$ (10.92, 15.33, 18.46 and 31.02° 2θ). In addition, this sample is also characterized by the greatest amorphism. Of undoubted interest is the fact that the PO_4 phase observed in the sample 7 % was not detected in subsequent samples.

Texture analysis

The textural characteristics and the content of elements in the samples are given in Table 2 and in the Fig. 3. The introduction of HPA leads to a decrease in the specific surface and pore volume by 15.8–35 % and 8.3–29.2 %, respectively, relative to unmodified titanium dioxide. The presence of HPA is also accompanied by a decrease in the total pore volume. It can be assumed that with a GPC content of up to 10 % wt. its compounds are located mainly in smaller pores (pores < 5 nm in size decrease up to 10 times compared to the initial titanium dixide; Table 2), which leads to their "overgrowing", while with an increase in the content of HPA over 10 % wt., — on the contrary, in a wide pore space.
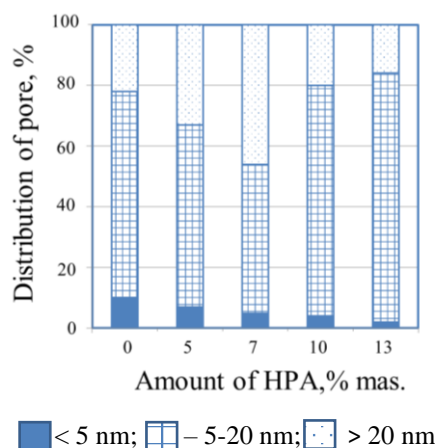
Figure 3. The effect of the amount of HPA on the distribution of pore volume by diameter:

T a b l e 2

Physical-chemical characteristics of the samples

№ of the sample	HPA content, wt. %	S_{BET}, m²/g	V_{pores}, sm³/g	Phase composition (according to the results of X-ray phase analysis)	Elements content, mass. %		
					Ti	Mo	P
1	-	57	0.24	TiO_2 (anatase)	59.04	-	-
2	5	31	0.21	TiO_2 (anatase)	55.1	2.94	0.48
3	7	47	0.22	TiO_2 (anatase), $TiMoO_4$, $H_2O_5P_{11} \cdot H_2O$, $H_3PMo_{12}O_{40} \cdot 21H_2O$, $H_3P_3O_{10} \cdot 2H_2O$, PO_4	54.9	4.89	0.64
4	10	42	0.22	TiO_2 (anatase, brookite), $TiMoO_4$, $H_2O_5P_{11} \cdot H_2O$, $H_3PMo_{12}O_{40} \cdot 21H_2O$, $H_3P_3O_{10} \cdot 2H_2O$, PO_4	53.3	6.93	0.81
5	13	43	0.22	TiO_2 (anatase), $H_3PMo_{12}O_{40} \cdot 21H_2O$, $iMoO_4$	47.3	10.06	0.97

Note. S_{BET} is the specific surface area by BET; was determined by single-point nitrogen adsorption at p = 135 Torr and T = 77K.

According to SEM data (Fig. 4), the surface of the initial titanium dioxide is represented by numerous isolated irregular crystallites, mainly 21–60 μm in size. In addition to isolated particles, a non-significant number of their aggregates with a size of 81–100 microns also can be seen. It should be noted that, without exception, all HPA-containing samples are characterized mainly by the content of crystallites of larger average sizes (41–80 μm) than the initial sample, which indicates a decrease in the dispersion of surface particles in the presence of HPA and is consistent with the above texture data analysis.

By means of an EDX analysis the spectra of the five test samples were obtained, which made it possible to reveal the peculiarities of the localization of phosphorus in a sample containing 13 % HPA. The distribution maps of titanium, molybdenum and phosphorus in this sample also confirmed the presence of a certain heterogeneity in the distribution of phosphorus.

Summarizing the study, we note that based on the nature of the modifier and the data obtained, it can be assumed that the increased selectivity for diisopropyl ether 7 % wt. HPA-containing titanium dioxide in the process of conversion of isopropyl alcohol is associated with the emergence of a new type of active sites, which exhibit enhanced electron-donor properties. Provided that the integrity of the HPA structure is preserved after its introduction into the composition of titanium dioxide (and this fact is confirmed by the data of phase analysis), the oxygen atoms included in the HPA can act as such centers. Taking into account that 12 terminal oxygen atoms of the outer fragments of the M = O octahedra can act as electron donor centers in the structure of phosphomolybdic acid, the quantitative growth of the basic centers with the introduction of HPA is natural. It is likely that the aforementioned low activity of modified titanium dioxide in ether with an HPA content of up to 7 % is associated with an insufficient concentration of a new type of active sites. does not seem possible to it unambiguously explain the noted drop in catalytic activity when the content of HPA is higher than 7 % wt. The authors assume that the reason for these differences is the peculiarity of the distribution of phosphorus, or rather, a sharp increase in the content of metaphosphoric acid ($H_3P_3O_{10} \cdot 2H_2O$) due to the combination of surface tetraders of PO_4 into

rings. An indirect confirmation of the formation of metaphosphoric acid is the appearance of its additional reflex at 22.5 °C 2θ in 13 % of the HPA sample. Whether this is accompanied by an increase in the acidity of the catalyst, as stated in the work [19] is the subject of further research.
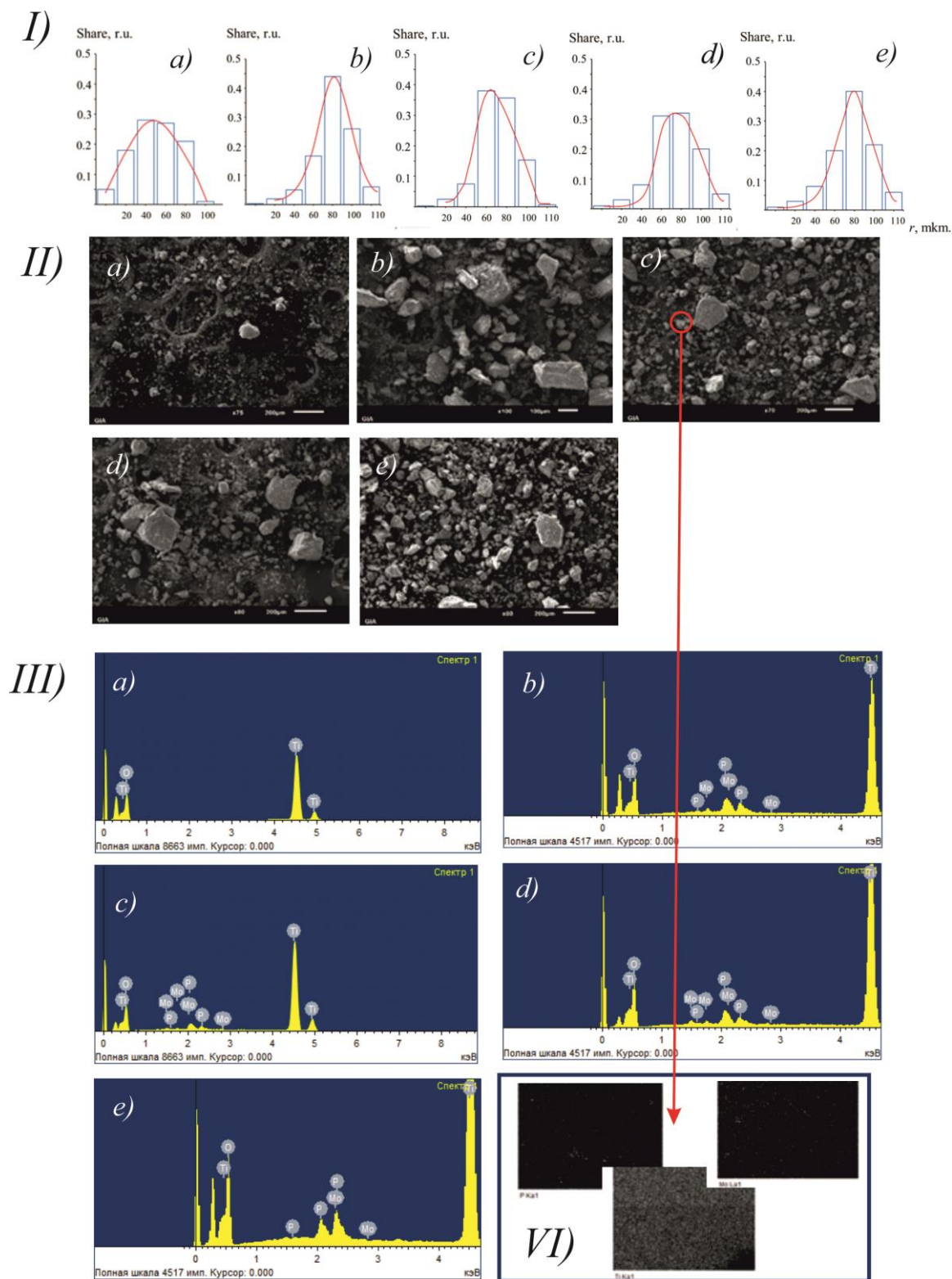
Figure 4. Comparative SEM-characteristic of titanium dioxide samples before (*a*) and after the introduction of HPA (*b* — 5 % by weight of HPA; *c* — 7 % by weight of HPA; *d* — 10 % by weight of HPA; *e* — 13% by weight of HPA): I — size distribution of crystallites; II — micrographs obtained by SEM; III — EDX spectra; IV — Cards of elemental composition of 13 % GPC-sample

The formation of metacids can be explained as follows: it is the interaction of titanium dioxide with HPA can be represented as an acid-acid interaction, which leads to the formation of a surface polymer compound due to the complexation of two acids:

$$\ldots - O - Ti - OH + HPA \longrightarrow \left[n\,(\ldots - Ti - OH)^* \; m(\,- O - Ti - O\,)^* \right.$$
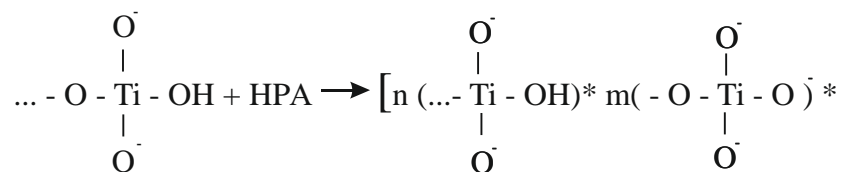
where * HPA, HPAn^{x-} $(m + 4k - y)$ H $+]^{y-*}$ y H, where $(\ldots -O-Ti-O-)-$ and HPAn^x — are heteropolyanoins, which cause the charge of the polymer particle and stabilize its formation on surface.

In this case, according to the literature data [20–22] the acid–acid interaction is carried out due to the formation of hydrogen bonds between the hydrogen atoms of the carrier surface and the oxygen atoms in the HPA structure.

The fact of the discovery of such an interaction at different HPA contents was previously discovered in [22], where it is also indicated that in the acid-acid type of interaction, HPA stability depends on the percentage of HPA deposition on the carrier: at low HPA contents (5–10 wt. %) on the surface of silicon dioxide, HPA of the 12th row is destroyed and HPA of the 6th row is formed, whereas with an increase in the content of HPA on the support (10–25 wt. %), the structure of HPA is retained.

Conclusions

Summarizing the above results, we can make the assumption that specific surface area and dispersion phosphomolybdenum heteropoly acid–titanium oxide catalytic system are not key factors responsible for high catalytic activity in the process of obtaining diisopropyl ether (there is no clear correlation to this effect). It was determined that the catalytic activity of titanium dioxide samples before and after the introduction of heteropoly acid has a different nature (the ether input in the presence of heteropoly acid-containing samples is higher, reaches maximum values in a shorter period of time and is characterized by greater stability). It should be noted that the activity of heteropoly acid-containing titanium oxide catalytic system samples is determined by the ratio of meta-titanic acid hydrate and metaphosphoric acid, when a quantitative increase in the latter entails a decrease in new surface active centers, or their rearrangement. Presumably meta-titanic and metaphosphoric acids are formed when applying more than 7 % wt. phosphomolybdenum heteropoly acid and represent a surface complex polymer compound.

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Гетеропол қышқылы – титан оксиді жүйесінің қатысуымен изопропил спиртінің конверсиясы

Гетерополий қышқылы – титан диоксиді жүйесінің фазалық және текстуралық қасиеттерін зерттеу үшін заманауи физикалық-химиялық әдістер кешені қолданылды (рентгендікфазалық анализ, азоттың аз температуралық адсорбциясы, сканерлеуші электронды микроскопия, элементтік анализ). Титан диоксидінің каталитикалық белсенділігінің жоғарылауына әкелетін фосформолибден гетерополий қышқылының оңтайлы мөлшері 7 %-ды құрайтыны анықталды: диизопропил эфирінің шығымы жоғары, қысқа мерзімде максималды мәндерге жетеді және сынамалар тұрақты. Құрамында фосформолибден гетерополий қышқылы бар үлгілердің белсенділігі электронды-донорлық қасиеттерін көрсететін белсенді орталықтардың жаңа типтерінің пайда болуымен байланысты деп саналады (гетерополий қышқылының М=О октаэдрасының сыртқы фрагменттерінің шеткі оттегі атомдары). Құрамында фосформолибден гетерополий қышқылы бар үлгінің каталитикалық белсенділігінің 7 %-дан көп төмендеуі беткі қабаттағы метафосфор қышқылының түзілуіне байланысты болады және белсенді орталықтардың төмендеуіне әкеледі.

Кілт сөздер: изопропил спирті, титан диоксиді, фосформолибден гетерополий қышқылы, фазалық құрам, морфология, катализ, диизопропил эфирі, текстуралық қасиеттері, метатитан қышқылы, метафосфор қышқылы.

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Превращение изопропилового спирта в присутствии системы гетерополикислота – оксид титана

Комплексом современных физико-химических методов (рентгенофазовый анализ, низкотемпературная адсорбция азота, сканирующая электронная микроскопия, элементный анализ) изучены фазовые и текстурные свойства системы гетерополикислота – диоксид титана. Установлено, что оптимальным содержанием фосформолибденовой гетерополикислоты, которое приводит к повышению каталитической активности диоксида титана, является 7 % масс.: выход диизопропилового эфира выше, достигает максимальных значений за более короткий промежуток времени, а образцы характеризуются большей стабильностью. Выдвинуто предположение, что активность фосформолибденовой гетерополикислото-содержащих образцов связана с появлением активных центров нового типа, которые проявляют повышенные электронно-донорные свойства (концевые атомы кислорода внешних фрагментов октаэдров М=О гетерополикислоты). Падение каталитической активности образцов с содержанием фосформолибденовой гетерополикислоты свыше 7 % масс. связано с образованием поверхностной метафосфорной кислоты и влечет за собой уменьшение активных центров.

Ключевые слова: изопропиловый спирт, диоксид титана, фосформолибденовая гетерополикислота, фазовый состав, морфология, катализ, диизопропиловый эфир, текстурные свойства, метатитановая кислота, метафосфорная кислота.

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Investigation of the process of latex coagulation by cationic surfactants

In the article the estimation of coagulating ability using cationic electrolytes is shown. It was found that in the case of using low molecular weight cationic electrolyte, the completeness of the release of rubber from latex is achieved at their consumption of 20–30 kg/t of rubber. A feature of the behavior of cationic surfactants in the latex coagulation has been established. It is shown that the consumption of cationic surfactants corresponds to the consumption of polymer cationic electrolytes. Also, a hypothesis was put forward that cationic surfactants violate the aggregate stability of latex systems and the mechanism of action, which is based on the interaction of cationic surfactant micelles with latex globules carrying anionic surfactants on the surface is proposed. The use of cationic surfactants can eliminate the use of sodium chloride in the industry of separating emulsion styrene-butadiene rubber from latex, as well as solve some environmental problems. The final stage of the investigation was to determine the parameters of rubber compounds and vulcanizates based on the rubber. These rubbers, rubber compounds and vulcanizates correspond to standard parameters.

Keywords: latex, coagulation, cationic surfactants, rubber, rubber compounds, vulcanizates, parameters, environment.

Introduction

The chemical and petrochemical industry has been actively developing in recent years. The introduction of new technologies, hardware design of processes, catalytic systems and initiators makes it possible to increase the productivity of the process, the quality of the products obtained, reduce environmental pollution and make more complete and rational use of natural resources [1, 2].

Synthetic rubbers obtained by emulsion polymerization have a set of required properties and are widely used in the tire and rubber industry, in composite materials for various purposes, etc. [3, 4]. However, their production is in conflict with the regional ecology. One of the problematic stages in the production of rubbers obtained by emulsion polymerization is the stage of separation from latex. This is due to the fact that in the process of separating rubbers from latex, salt coagulating agents are used, the consumption of which is tens (metal salts of the second group of the periodic system) and hundreds of kg/t of rubber (metal salts of the first group of the periodic system). Therefore, at present, an important and urgent task is aimed at developing new technologies and technical solutions that can reduce the consumption of salts or completely eliminate their use in the technology of production of emulsion rubbers [5]. Quaternary ammonium salts are promising in this regard. The review paper [5] shows the prospects of their application in the technology of rubber isolation from latex. The consumption of low-molecular and high-molecular quaternary ammonium salts is less than that of sodium chloride and other salts. However, the high cost of these salts, as well as the impossibility of their usage in some variants of latex technology largely deters from their integration in the synthetic rubber industry.

In the literature there is no information about the use of cationic surfactants (CPAV) in the technology of rubber isolation from latex [5]. CPAV are available reagents that are widely used in various industrial sectors [6, 7].

The aim of this paper is to study the possibility of using CPAV in the production technology of styrene-butadiene rubbers.

Experimental

The latex coagulation process (Table 1) was researched using cationic surfactants produced on an industrial scale [8].

Characteristics of styrene-butadiene latex produced by emulsion rubbers (SBR)

Parameter	Value
Dry residue, wt%	21.3
Surface tension, mH/m	57.1
pH latex	9.5
Content of bound styrene, wt. %	22.7

The coagulating process was carried out at 21±1 °C. Aqueous solutions of cationic surfactants: do-decylpyridinium chloride with concentrations ~2 wt%, decylpyridinium chloride ~2 %, cetylpyridinium bro-mide ~2 %, cetyltrimethylammonium bromide ~2 %, alkylbenzyldimethylammonium chloride ~2 %, and so-dium chloride — 20 wt%, N,N-dimethyl-N,N-diallylammonium chloride — 5 wt%, poly- N,N-dimethyl-N,N-diallylammoniumchloride — 2 wt% were used as coagulating agents. An aqueous solution of sulfuric acid with a concentration of ~ 2.0 wt% was used as an acidifying agent. The resulting rubber crumb was separated from the aqueous phase (serum), washed with warm water and dehydrated in a drying cabinet at 80–85 °C. The completeness of coagulation was assessed visually by the transparency of the serum and gravimetrically by the mass of the resulting rubber crumb. The following substances were used for the extraction of rubber from latex: dodecylpyridinium chloride (DDPC); decylpyridinium chloride (DPC); cetylpyridinium bromide (CPB); cetyltrimethylammonium bromide (CTMAB); alkylbenzyldimethylammonium chloride (ABDMAH).

Results and Discussion

The conducted studies have established (Table 2) that the amount of rubber crumbs released naturally increases with an increase in the consumption of all the coagulating agents studied. However, a number of interesting features were also noted in the behavior of CPAV during the coagulation of styrene-butadiene latex, which was not previously noted when using other agents used in the isolation of rubber from latex.

Results of the research are presented in Table 2.

Experimental results obtained in the isolation of rubber from emulsion latex using various coagulating agents

TYPE OF COAGULANT	Sodium chloride						
Temperature, ºC	20/60						
Consumption of sodium chloride кg·t^{-1} of rubber	10	30	50	70	100	120	150
Rubber outlet (20°C), mass %	34.5	56.3	74.7	80.5	85.6	90.5	97.1
Rubber outlet (60°C), mass %	22.7	50.9	72.2	80.2	83.6	89.9	95.6
Evaluation of complete coagulation	icc	icc	icc	icc	icc	icc	cc
TYPE OF COAGULANT	N,N-dimethyl-N,N-diallylammonium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	1	3	5	10	15	20	25
Rubber outlet, mass %	34.7	58.9	67.2	78.2	87.6	90.9	96.3
Evaluation of complete coagulation	icc	icc	icc	icc	icc	icc	cc
TYPE OF COAGULANT	Poly- N,N-dimethyl-N,N-diallylammonium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	13.3	25.8	44.7	69.8	86.8	92.9	95.5
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	Cc
TYPE OF COAGULANT	Dodecylpyridinium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.25	1.50	-
Rubber outlet, mass %	12.7	20.9	42.2	80.2	89.1	93.6	-
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	-

TYPE OF COAGULANT	Decylpyridinium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t⁻¹ of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	27.3	37.8	59.9	85.0	91.4	92.1	94.4
Evaluation of complete coagulation	icc	icc	icc	icc	cc	cc	cc
TYPE OF COAGULANT	Cetylpyridinium bromide						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t⁻¹ of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	17.5	50.2	50.8	75.0	90.2	93.2	95.2
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	cc
TYPE OF COAGULANT	Cetyltrimethylammonium bromide						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t⁻¹ of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	28.8	50.2	66.4	75.0	85.6	93.2	94.2
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	cc
TYPE OF COAGULANT	Alkylbenzyldimethylammonium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t⁻¹ of rubber	0.50	1.0	1.5	2.0	2.5	3.0	
Rubber outlet, mass %	40.3	57.7	71.6	83.8	93.9	93.0	
Evaluation of complete coagulation	icc	icc	icc	icc	cc	cc	

Notes. Abbreviations: icc — incomplete coagulation; cc — complete coagulation. The pH of the aqueous phase (serum) — 3,0; consumption of sulfuric acid — 15,0 kg·t⁻¹ rubber.

What is the peculiarity in the behavior of CPAV as agents of coagulation?

The results presented in Table 2 indicate a sharp difference in the efficiency of the coagulating action of low molecular weight cationic reagents, which differ in their colloidal characteristics: the consumption of micelle-forming CPAV (DDPC, CPC, CTAB) is an order of magnitude less than the consumption of similar in chemical structure DMDAAH, which does not have the ability to micelle (2.0–2.5 kgt⁻¹, and 20.0–25.0 kgt⁻¹, respectively). Micelle-forming low molecular weight CPAV are close to (and sometimes exceed) the high molecular weight analog of DMDAAH the VPK-402 reagent in terms of their effectiveness in latex coagulation. The high coagulating capacity of the polymer cationic reagent VPK-402 is due to the fact that in the case of cationic polyelectrolyte, the combined effect of two astabilizing mechanisms acts – neutralization and bridging, the second mechanism enhances the effect of the first one.

The above-mentioned feature in the behavior of CPAV is probably related to their micelle-forming ability. In this case, the coagulation process will be based on the interaction of latex globules carrying adsorption layers of anionic surfactants on the surface not with individual molecules of the cationic electrolyte, but with CPAV micelles (Fig. 1), i.e., a kind of polycondensation reaction will occur with the release of a low-molecular product — an inorganic salt (sodium chlorides) and the formation of an unstable complex latex globule-CPAV micelle.

The disintegration of this complex will be accompanied by the release of the water-insoluble product of the interaction of CPAV with anionic surfactant into the sediment according to the scheme:

Or in general:
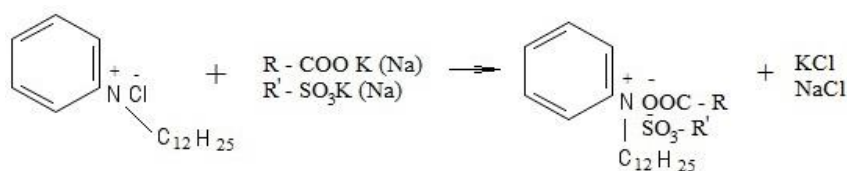
$$nR–COOK + n(\equiv N+ –C_{(10–16)})Cl– \rightarrow ((\equiv N+ –C_{(10–16)})–OOC–R)_n + nKCl$$
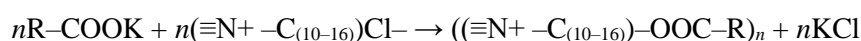
where n is greater than 1.

In an acidic medium, the decomposition of low-stability polymer-complex structures occurs:

$$((\equiv N+ –C_{(10–16)})–OOC–R)_n + H_2SO_4 \rightarrow (\equiv N + –C_{(10-16)})HSO_4– + R–COOH$$
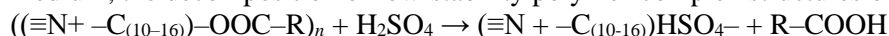
A hypothetical model of the interaction of latex micelles with CPAV allows us to explain the observed (Table 3) the effect of the length of the hydrocarbon radical of CPAV on the process of isolation of rubber from latex. Thus, when the radical contains 10–12 carbon atoms, a bi-beam structure is most likely formed (Fig. 1a), and when the radical contains 16 carbon atoms, the size of the micelle increases and the coagulation process can occur with the formation of 3 and 4 beam structures (Fig. 1b, c). This is also reflected in the consumption of cationic surfactants. These hypothetical considerations are supported by some simple calculations. Namely, we found how many micelles per 1 globule of latex are approximately at the time of the introduction of CPAV in the full coagulation mode (for CTAB, CPC, DPC) (Table 3) [9, 10]. The data in Table 3 show that the number of micelles surrounding the globule at the initial moment of coagulation significantly exceeds the number of latex globules, so there are sufficient grounds for the hypothetical scheme shown in Figure 1.
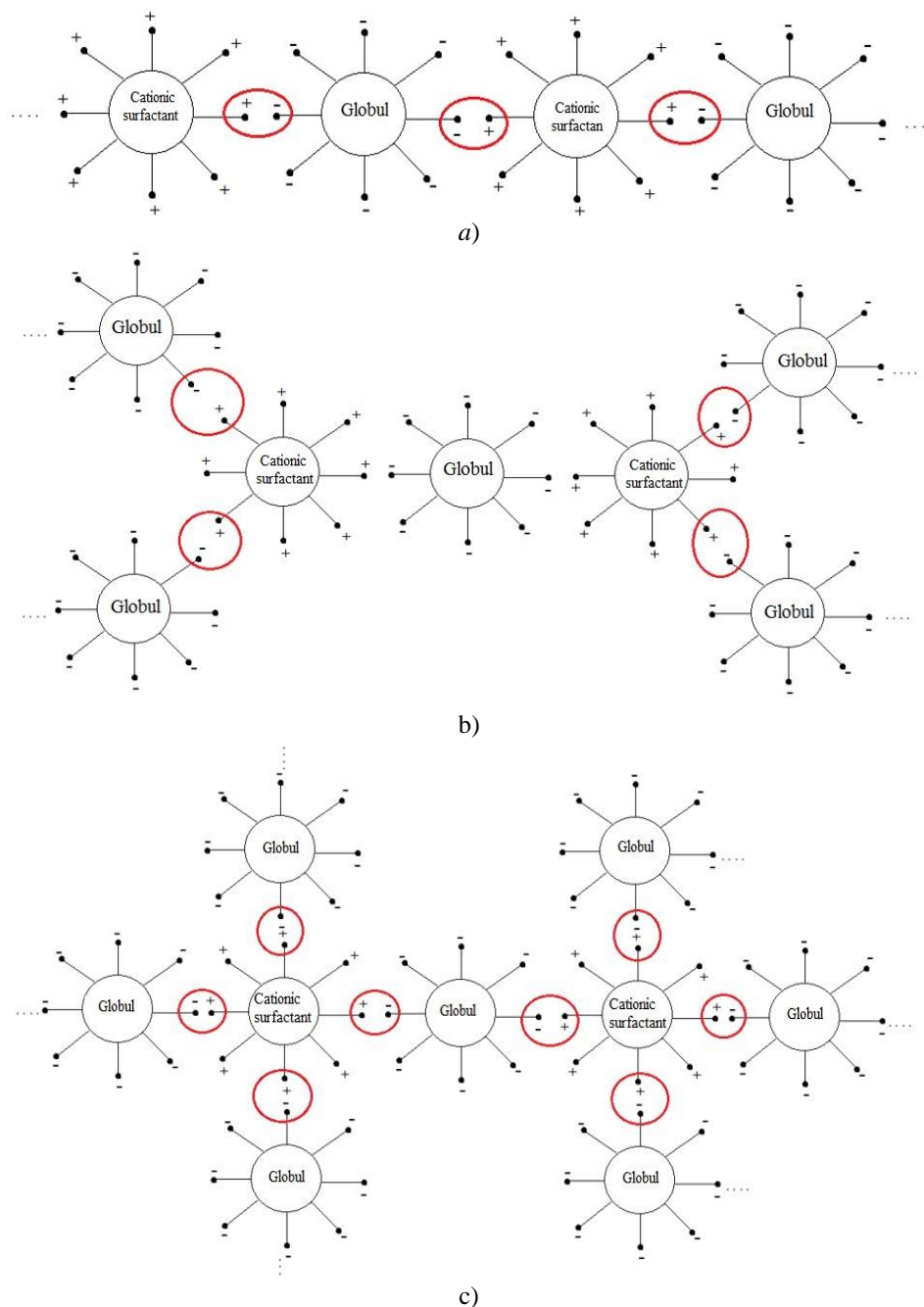
Figure 1.The proposed scheme of interaction of negatively charged latex globules with micelles of cationic surfactants (a) with a relatively short length of the hydrocarbon radical (nC = 10–12) and (b), (c) a long radical length (nC = 16)

Conclusion

Using cationic surfactants in the rubber industry makes it possible to achieve the complete latex coagulation at the expense of the corresponding cationic polyelectrolyte. A hypothesis about the effect of cationic surfactants on the destabilization of the latex aggregate stability is proposed. The process mechanisms occurring during the introduction of a cationic surfactant in a latex system stabilized by anionic surfactants has been introduced.

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Латексті катионды беттік-белсенді заттармен коагуляциялау процесін зерттеу

Мақалада катиондық электролиттердің коагуляциялау қабілеті туралы түсінік кеңейтілген. Төменгі молекулалы катионды электролиттерді қолданған кезде, резеңкеде латекстерді бөліп алудың толықтығына олардың 20-30 кг/т резеңке жұмсау кезінде қол жеткізілетіндігі анықталды. Жүргізілген зерттеулерде стирол-бутадиен каучукты латекстен алу процесінде зерттелген катиондық беттік-белсенді заттармен (ББЗ) әсер етуі барысында ерекшелік байқалды. Катионды ББЗ шығыны полимерлі катионды электролиттің шығынына жақын, ал кейбір жағдайларда одан да аз болатыны көрсетілген. Катиондық беттік-белсенді заттардың латекс жүйелерінің жиынтық тұрақтылығының бұзылуына ықпалы туралы гипотеза алға тартылып, оның әсер ету механизмі ұсынылды, ол катионды ББЗ-дың мицеллаларының бетінде анионды беттік активті заттарды алып жүретін латекс глобулаларымен өзара әрекеттесуіне негізделген. Осылайша, катионды беттік-белсенді заттарды қолдану натрий хлоридінде және қымбат катионды полимерлі электролитті, эмульсиялы стирол-бутадиенді каучук өндірісінде қолдануды болдырмауға мүмкіндік береді. Катионды ББЗ-ды енгізу кейбір экологиялық мәселелерді шешуге мүмкіндік туғызады. Осы зерттеудің соңғы кезеңінде ұсынылған технологияға сәйкес резеңке негізінде резеңке қоспалары мен вулканизаттардың индикаторларын анықтау болды. Барлық негізгі көрсеткіштер бойынша зерттелетін үлгілер талаптарға сай.

Кілт сөздер: латекс, коагуляция, беттік-белсенді заттар, резеңке қосылыстар, вулканизаттар, қасиеттері, қоршаған орта.

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Исследование процесса коагуляции латекса катионными поверхностно-активными веществами

В статье расширены представления о коагулирующей способности катионных электролитов. Установлено, что в случае применения низкомолекулярных катионных электролитов полнота выделения каучука из латексов достигается при их расходе 20–30 кг/т каучука. Проведенными исследованиями была

отмечена особенность в поведении исследуемых катионных поверхностно-активных веществ в процессе выделения бутадиен-стирольного каучука из латекса. Показано, что расход катионных поверхностно-активных веществ близок к расходу (а в некоторых случаях даже меньше) полимерного катионного электролита. Выдвинута гипотеза действия катионных поверхностно-активных веществ на нарушение агрегативной устойчивости латексных систем, предложен механизм его действия, который основан на взаимодействии мицелл КПАВ с латексными глобулами, несущими на поверхности анионные ПАВ. Таким образом, использование катионных поверхностно-активных веществ позволяет исключить применение как хлорида натрия, так и более дорогостоящего катионного полимерного электролита в производстве эмульсионного бутадиен-стирольного каучука. Внедрение КПАВ позволит решить некоторые экологические проблемы. Завершающий этап данного исследования заключался в определении показателей резиновых смесей и вулканизатов на основе каучука, выделенного по предложенной технологии. По всем основным показателям исследуемые образцы соответствовали предъявляемым требованиям.

Ключевые слова: латекс, коагуляция, поверхностно-активные вещества, резиновые смеси, вулканизаты, свойства, окружающая среда.

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Catalytic oxidation of CO in gases
emitted by industrial processes and vehicle exhaust

A new type of catalysts not containing noble metal oxides have been developed and the possibilities of their application both for the complete neutralization of carbon monoxide in exhaust gases and the process of deep oxidation of volatile hydrocarbons are studied. It has been found that the activity of catalysts based on vanadium and phosphorus oxides supported on Al_2O_3, SiO_2, TiO_2 by and their modification with of 1–3 % oxides of Cu, Cr, Co, Zn enhanced the conversion of the deep oxidation process to 95–100 % at the temperatures of 673–693 K and volumetric velocities of 5000–10000 h^{-1}. During the simultaneous oxidation of CO and C_3H_8 at a CO conversion of 90 %, the C_3H_8 conversion was 70 %. It has been established that oxidation of CO and C1–C4 hydrocarbons, and especially propane, with the participation of synthesized catalytic series, occurs by stepwise and associative mechanisms. The oxidation of CO and C_3H_8 required a high oxygen content of 1:20–25 mol. Besides utilizing carbon monoxide in exhaust gases from motor vehicles, these catalytic systems can be successfully used to neutralize industrial gases, especially those emitted from oil refineries and thermal power plants. Preliminary research has shown that these catalytic systems can operate for about 50 000 hours without changing the activity.

Keywords: catalyst, organic compounds, catalytic systems, monoxide, propane, exhaust gases, aluminium oxide, cobalt, chrome, vanadium oxide.

Introduction

It is known that since the second half of the last century the exponential growth of industry, especially oil refining, petrochemicals, metallurgy, energy complexes, organic compounds, automotive industry, spontaneously led to rapid pollution of the environment. It should be noted that most of the toxic gases emitted into the environment fall on the share of metallurgy, thermal power plants (∼50 %), and more recently in the field of rapid development of road transport (∼20 %) in the world [1–6]. Automobiles are the most popular mode of transport used by people. During the operation of these vehicles, air pollution emitted from transportation contributes to emissions of air toxics and poor air quality, which has negative impacts on the health and welfare of mankind [7–9].

The amount of exhaust gases emitted into the environment from industrial plants and vehicles continues to increase from year to year. In particular, 0.3–12 % carbon monoxide, 0.5–1.0 % NO_x gases, 0.2–3 % C_xH_y, 0.1–3 % organic compounds, 3–10 % water vapour, l–15 % soot, and carbon dioxide from internal combustion engines, in addition to SO_2 from the vehicle engines that run on the diesel fuel is also released into the environment. Although many "euro" standards (EURO 4 to EURO 6) are set for the norms and amount of the emitted exhaust gases, they are often not followed, which is associated with many problems [10–14].

Recent research show that catalytic systems based on the most valuable non-ferrous and rare metals are currently used for the conversion and disposal of carbon monoxide, nitrogen gases, and volatile hydrocarbons. Depending on the neutralization process, catalytic methods are the most preferred ones in industrial waste disposal. [15].

Experimental

Initially, a vanadium-phosphorus catalyst was synthesized. Catalyst samples were obtained by known methods, precipitated, and impregnated on aluminium oxide and silicon oxide [16]. The catalysts were then heat-treated by known methods [17]. The catalyst is then cooled, crushed, sieved, and divided into the required 0.2–0.8 mm (or 0.2–0.4; 0.4–0.6; 0.6–0.8 mm) parts. Such catalyst samples are called "newly synthesized" samples. In this case, depending on the initial materials, catalyst samples are taken in ratios such as V:P = 1:10.

It should be noted that the main active mass precipitated or impregnated on the carriers is 8–10 % of the total catalytic system.

The activity and kinetic regularities of the synthesized catalysts in the conversion, oxidation reactions of CO, C_1–C_4 hydrocarbons, and NO_x gases were studied in open-flow and pulse system reactors.

Gas mixtures CO+He, O_2+He, CO_2+He, CO+O_2+He, NO+He, NO_2+He, CH_4+He, C_2H_4+He, C_3H_8+He, C_4H_{10}+He were prepared in certain volume concentrations (volume %) and filled into air balloons. Some of them were prepared by known methods and given to the system directly before the reactions. Gas mixtures are taken at CO (0.5–5.0 %), CO_2 (2–15 %), O_2 (1–20 %), C_xH_y(0.5–2.0 %), H_2O (1–20 %), NO (200–600 ppm), NO_2 (200–1000 ppm), which is close to the emissions of real automobiles, thermal power plants, oil refining, and petrochemical industries. Moreover, the gas mixtures were used separately as a model for kinetic studies. Analysis of CO, CO_2, NO_x, and hydrocarbons was performed on AMX (calorimeter) and SVET-500 chromatographs. The gas carrier was He (helium); separation of the CO, CO_2, and hydrocarbons was carried out in a column filled with "Poropak Q" (length 3.0 m) at a programmed temperature (3°C/min) 30–90 °C. It should be noted that carbon monoxide is obtained by the treatment of concentrated sulphuric acid with formic acid. O_2, N_2, and CO were analyzed in a parallel column using NaX zeolite (1.2 m length), where a rate of helium was 50 ml/min, and N_2O and NO_2 on activated carbon using CKT. Other organic compounds, (acetone, benzene, toluene, chlorobenzene, and others) were taken and analyzed using a carrier adsorbent containing SE-30 on a chromoton in a 3 m column.

Adsorption isotherms, pore distributions, surface area, and pore volumes information has been studied by using the BET method for synthesized and activated (I); promoters added (Cr_2O_3 or Co_2O_3) (II); deactivated samples (III). The results showed that the values of samples I and II do not differ significantly during both adsorption and desorption, but the distribution of the pore volume and surface area of sample III differs from other ones. It should be noted that for samples with added Co and Cr oxides the P/P_o-dependent distribution of the adsorption and desorption isotherms and the P/P_o-dependent distribution occur according to known regularities.

In the laboratory the experiments were carried out with a vertically aligned tubular quartz reactor operating at atmospheric pressure. The schematic of the experiment set up is shown in Figure 1.
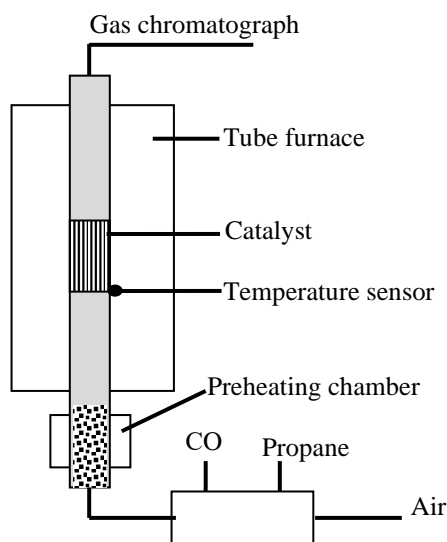
Figure 1. The experimental vertically-aligned reactor

Due to the corrosive reaction products, all materials used in the experimental setup were corrosion-resistant: quartz glass, heated Teflon pipes (T = 180 °C), and Teflon connectors.

Results and Discussion

The activity of the synthesized catalytic systems was initially tested at a temperature of 673–723 K, at a volume rate of 8000–10000 h^{-1}. In all cases, the effect of different promoters on their activity was studied by taking the catalytic systems based on V–P–O/Al_2O_3 and V–P–O/SiO_2 (Table 1).

**The activity of the catalytic systems synthesized for the oxidation reactions of carbon monoxide
and propane depended on the nature of the carriers and added promoters**

Catalysts	Promotor		T, K	V, h^{-1}	Conversion, %	
	P$_1$	P$_2$			CO	C$_3$H$_8$
V–P–O/SiO$_2$	–	–	573	8000	40	50
	–	Zn	573	8000	45	54
	Mg	–	673	8000	45	56
	Co	–	673	8000	50	58
	–	Cu	673	8000	68	62
	Cr	–	673	8000	68	61
	Ni	–	673	8000	52	48
	–	Zn	723	10000	50	55
	Co	–	723	10000	54	62
	–	Cu	723	10000	70	65
	Cr	–	723	10000	74	66
V–P–O/Al$_2$O$_3$	–	–	673	8000	42	52
	Mg	–	723	10000	46	60
	–	Zn	673	8000	48	61
	Ni	–	673	8000	80	54
	–	Cu	723	10000	55	60
	Cr	–	673	8000	70	65
	Cr	–	673	8000	70	66
	–	Cu	723	10000	76	70
			723	10000	72	68
V–P–O/SiO$_2$	Mg	Zn	673	8000	47	54
	Mg	Cu	673	8000	70	64
	Mg	Co	673	8000	52	56
	Mg	Co	723	10000	60	65
	Mg	Cr	673	8000	72	65
	Zn	Cu	673	8000	75	78
	Zn	Co	723	10000	60	60
	Zn	Cr	723	10000	62	60
	Ni	Co	723	10000	73	65
V–P–O/SiO$_2$	Cu	Co	673	8000	80	73
	Co	Cu	723	10000	82	73
	Cu	Cr	673	8000	92	90
	Cu	Cr	723	10000	96	96
	Co	Cr	673	8000	84	90
	Co	Mn	723	10000	78	70
V–P–O/Al$_2$O$_3$	Cu	Cr	673	8000	96	97
	Cu	Cr	723	10000	97	95
	Cu	Co	673	8000	88	83
	Co	Cr	673	8000	90	84
	Cr	Co	723	10000	92	84
	Mg	Cu	673	8000	70	68
	Mg	Co	723	10000	64	70

As can be seen from the results, one or two types of promoters were added to V–P–O/Al$_2$O$_3$ and V–P–O/SiO$_2$, and their activity in the process of CO and propane conversion was studied. The amount of added promoters is 1–3 %. Initially, MgO was added to V–P–O/Al$_2$O$_3$ and V–P–O/SiO$_2$ catalyst after which modified by Zn, Mn, Cu, Co, Cr, Ni oxides, and all catalysts showed 50–70 % catalytic activity. No significant change was observed when MgO was replaced by the NiO, although subsequent additions slightly increased the conversion of CO and C$_3$H$_8$ (70–76%).

As can be seen from the results in the table, catalytic systems obtained with the addition of 1–3 % CuO and then 1–3 % Co$_2$O$_3$ or Cr$_2$O$_3$ showed high (90–95 %) activity in both carbon monoxide conversion and propane conversion.

First we studied the effect of the ratio of CO:O$_2$ on the CO oxidation reaction.

CO conversion on CO:O_2 ratios, T = 713 K, V = 10000 h^{-1}

Catalysts	CO conversion on CO:O_2 ratios				
	0.5:1	1:1	1:5	1:10	1:20
V–P–O/SiO_2	3	13	18	27	46
V–P–O/Al_2O_3	5	15	20	34	48
V–P–O/Al_2O_3 + 2 % Mg	6	15	31	53	61
V–P–O/Al_2O_3 + 2 % Cu	8	20	41	81	87
V–P–O/Al_2O_3 + 1 % Cu	7	18	37	73	86
V–P–O/Al_2O_3 + 2 % Cu + 2 % Cr	10	50	80	98	100
V–P–O/Al_2O_3 +2 % Cu + 1 % Cr	8	46	64	83	93

Some of the catalytic systems that were synthesized and showed high activity were selected, and the oxidation reaction on their surface in the range of CO:O_2 = 0.5–1:20 ratios was studied (Table 2). The results show that the conversion of CO is very low in the presence of V–P–O/SiO_2 and V–P–O/Al_2O_3 catalysts at CO:O_2 = 0.5:l and 1:1.

When a small amount of Mg, Cu is added into the catalyst, the conversion of CO does not increase much. However, CO conversion begins to increase significantly (20–50 %) in the presence of catalyst samples with the addition of Co and Cr. The catalytic oxidation process increases rapidly at a ratio of CO:O_2 = 1:5. In special cases, it reaches 60–80 %. At higher values of this ratio (1:10 and 1:20), the conversion of CO in the presence of all catalyst samples exceeds almost 50 %, and on the V–P–O/Al_2O_3 + 2 % Cu + 1 % Cr catalyst it reaches 90–92 %, and 100 % in the presence of V–P–O/Al_2O_3 + 2 % Cu + 2 % Cr catalyst. The effect of synthesis and preparation methods of catalytic systems on the oxidation of carbon monoxide and propane has also been studied (Table 3).

The effect of catalysts preparation method on oxidation of CO and propane [1]

Synthesis method	Temperature, K	Volume rate, V, h^{-1}	CO conversion, α, %	C_3H_8 conversion, α, %
Co-precipitation	673	8000	100	70
Impregnation	693	8000	95	70
Shifting	673	8000	96	75
Mechanical-chemical	653	10000	95	75
CuO, Al_2O_3, ZnO industrial	573	7000	75	50
CuO, Cr_2O_3 HTK	473	7000	70	50
Perovskite	615	5600	95	100 %, 923 K
Pt (USA)	523	560	95	100 %, 953 K
V/P	$VOPO_4$		V/V = 1/45	

In the presence of catalysts obtained by precipitation and impregnation methods, the conversion of carbon monoxide was 100 % and the conversion of propane was 70 % at a temperature of about 673–693 K and a volume rate of 8000–10000 h^{-1}[17].

Although the conversion of propane varies slightly under approximately the same conditions in the impregnated and mixed samples of catalytic systems, the conversion of carbon monoxide decreases slightly, to 95–96 %. These results can be applied to catalyst samples obtained by mechanochemical methods.

It is known, that the abovementioned methods are easier ways to prepare catalysts. While comparing the activity of the prepared catalysts with the catalyst samples (CuO, ZnO, CaO, Cr_2O_3) used in industry Pt (USA) in motor vehicles, it is observed that the results are nearly the same as (Pt (USA)) or catalysts are during the conversion of carbon monoxide (Table 3). However, the industrial catalyst can provide 100 % conversion of propane at very high temperatures at 933 K. Lowering the temperature by 200–400 K in such processes means saving a lot of energy.

Furthermore, considering the presence of many organic compounds in exhaust gases emitted into the environment from industrial plants and vehicles, including isopropyl alcohol, acetone, benzene, mono- and dichlorobenzene, toluene, the study of their oxidation processes, along with other hydrocarbons, is a very

important problem. The best results were also shown here by the V–P–O/Al$_2$O$_3$ + CuO + Cr$_2$O$_3$ catalytic systems (Fig. 2).

α, %
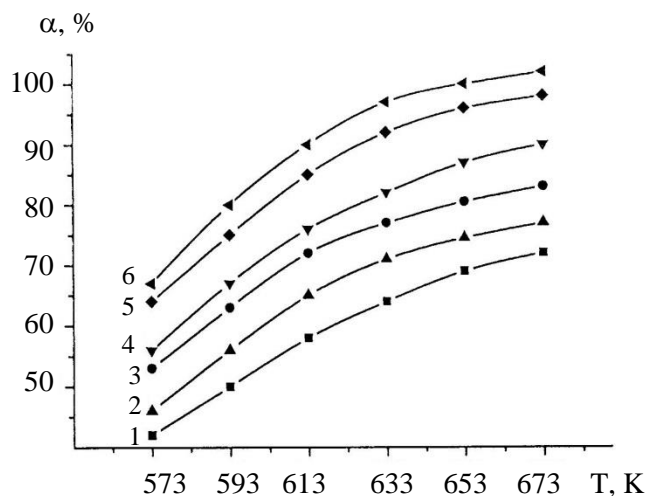
1 — V–P–O/SiO$_2$ + Mg; 2 — V–P–O/Al$_2$O$_3$ + CuO; 3 — V–P–O/Al$_2$O$_3$ + ZnO;
4 — V–P–O/Al$_2$O$_3$ + Cr$_2$O$_3$; 5 —V–P–O/Al$_2$O$_3$ + 1 % Cu + 1 % Cr; 6 — V–P–O/Al$_2$O$_3$ + 2 % Cu + 2 % Cr

Figure 2. The activity of catalytic systems in an oxidation process of different organic compounds
(acetone, isopropyl alcohol, benzenes). CO:O$_2$:H$_2$O:CO$_2$:C$_x$H$_y$ = 1:20:5:10:6

In addition to the hydrocarbons listed on these selected active catalytic systems, we have studied the conversion of other organic compounds. It is also clear that the 100 % conversion of CO at temperatures of 633–673 K and the conversion of organic compounds within the 95–96 % conversion of C$_3$H$_8$–C$_4$H$_{10}$ are also high (97–98 %) (Fig. 3).

α, %
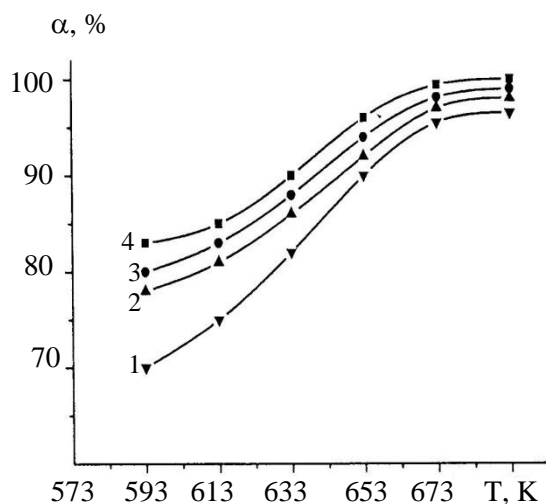
1 — CO; 2 — C$_3$H$_8$; 3 — C$_4$H$_{10}$; 4 — organics (acetone, isopropyl alcohol, benzenes, and toluene)

Figure 3. Temperature effect on the oxidation of hydrocarbon, CO, and organic compounds
in the presence of V–P–O/Al$_2$O$_3$ + 2 % Cu + 2 % Cr

In the ratios of CO:O$_2$ = 1:1 and 1:2, the catalysis proceeds at a very slow rate and is practically stabilized after two pulses. Although the oxidation of CO doubles at a ratio of CO:O = 1:5, a very high rate is still not observed. However, the nature of the kinetic curve does not change at a ratio of CO:O$_2$ = 1:10 and more 1:20, catalysis is observed to proceed at high speed.

Conclusions

Active catalytic systems and optimal conditions for the conversion of 95–98 % CO, 80–85 % C_xH_y have been identified, when the amounts of carbon monoxide, hydrocarbons, water vapor, carbon dioxide were in close proportions to real gas mixtures ($CO:O_2:C_xH_4:CO_2:H_2O–1:15:6:12:6$) in the oxidation. It has been shown that the catalytic systems we obtained and used for the oxidation were more active at temperatures 200–300K less, i.e., at 500–700 K, compared to catalysts containing precious metals such as Pt, Pd, Au.

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Өнеркәсіптік процестерден және автокөлік құралдарынан шығарылатын газдардағы СО-ның каталитикалық тотығуы

Құрамында асыл металл оксидтері жоқ, түрлі қоспалары бар оксидтер негізінде жаңа типті каталитикалық жүйелер әзірленді және оларды пайдаланылған газдардағы көміртегі тотығын толық бейтараптандыру және басқа ұшпа көмірсутектермен терең тотығу процесі үшін қолдану мүмкіндіктері көрсетілді. Al2O3, SiO2, TiO2–ге жағылған ванадий және фосфор оксидтері негізіндегі катализатор-

лардың белсенділігі олардың 1–3 % Cu, Cr, Co, Zn оксидтерімен модификациясы нәтижесінде 673–693 К температурада және 5000–10000 сағ$^{-1}$ көлемдік жылдамдықта терең тотығу процесін 95–100 %-ға дейін жеткізу кезінде жоғары нәтиже көрсететіні анықталды. Бір мезгілде СО және C$_3$H$_8$ тотығуы СО – 90 % конверсиясы кезінде C$_3$H$_8$ конверсиясы 70 % құрады. Сондай-ақ, судың белгілі бір концентрацияға дейін тотығу процесіне оң әсер ететіні анықталды, бірақ осы концентрациядан жоғары болғанда оның әсері, керісінше тежеуші фактор болып саналады. Автокөлік құралдарынан шығатын газдардағы көміртегі тотығын кәдеге жаратудан басқа, бұл каталитикалық жүйелер өнеркәсіптік газдарды, әсіресе мұнай өңдеу кәсіпорындары мен жылу электр станцияларынан шығарылатын газдарды залалсыздандыру үшін сәтті қолданылуы мүмкін екендігі көрсетілген. Алдын- ала зерттеу көрсеткендей, бұл каталитикалық жүйелер ұзақ уақыт аралығында, атап айтқанда, шамамен 50 000 сағат белсенділікті өзгертпестен жұмыс істей алады.

Кілт сөздер: катализатор, органикалық қосылыстар, каталитикалық жүйелер, монооксид, пропан, пайдаланылған газдар, алюминий тотығы, кобальт, хром, ванадий.

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Каталитическое окисление СО в газах, выделяемых промышленностью и автотранспортом

Разработаны каталитические системы нового типа на основе оксидов с различными добавками, не содержащие оксидов благородных металлов, и показаны возможности их применения для полной нейтрализации монооксида углерода в выхлопных газах и процесса глубокого окисления с другими летучими углеводородами. Установлено, что активность катализаторов на основе оксидов ванадия и фосфора, нанесенных на Al$_2$O$_3$, SiO$_2$, TiO$_2$, в результате их модификации 1–3 % оксидами Cu, Cr, Co, Zn показывает высокие результаты при доведении конверсии процесса глубокого окисления до 95–100 % при температуре 673–693 К и объемных скоростях 5000–10000 ч$^{-1}$. Одновременное окисление СО и C$_3$H$_8$ при конверсии СО — 90 %, конверсия C$_3$H$_8$ равна 70 %. Также установлено, что вода до ее определенной концентрации положительно влияет на процесс окисления, но выше этой концентрации оказывает тормозящее действие. Показано, что, кроме утилизации монооксида углерода в выхлопных газах от автотранспортных средств, эти каталитические системы могут успешно применяться для обезвреживания промышленных газов, особенно выбрасываемых нефтеперерабатывающими предприятиями и теплоэлектростанциями. Предварительное исследование показало, что данные каталитические системы могут работать длительное время, а именно около 50 000 ч, без изменения активности.

Ключевые слова: катализатор, органические соединения, каталитические системы, монооксид, пропан, выхлопные газы, окись алюминия, кобальта, хрома и ванадия.

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Research of the process of obtaining potassium fertilizers from carnallite ore

To provide domestic and foreign markets with potash fertilizers Kazakhstan has begun to create own production of these products. But at the moment enterprises engaged in mining potash salts did not reach a practical stage. The Chelkarcarnallite ore deposit is a unique one in solving these urgent problems. The article presents results of the study of processing Chelkar potash ore washed from sodium chloride to obtain a potassium fertilizer containing potassium and magnesium sulfates. The kinetics of nitric acid decomposition of carnallite ore has been investigated. The calculated value of reaction activation energy of potassium sulfate and nitric acid interaction characterizes the kinetic region of the process behavior. Optimal conditions for decomposition of washed calcined ore with 30 % nitric acid solution at 50 °C were determined. It has been found that to ensure better filtration properties and high rate of suspension separation, washed non-calcined ore should be used to exclude gypsum dehydration, which causes its phase conversion into anhydrite. The double salt of potassium-magnesium sulfate was separated by crystallization from nitric acid extract and an ammoniated mother liquor drying allowed to obtain a salt, which is ballast-free chlorine-free complex nitrogen-potassium-magnesium fertilizer.

Keywords: potash ore, mineral fertilizer, potassium sulfate, sodium salts, Chelkar deposit, mother liquor, decomposition, evaporation, crystallization.

Introduction

Application of potash fertilizers along with phosphorus and nitrogen ones is essential for sustainable crop yields, and it is one of main indicators of agricultural development in a country. Among them, sulfate potash fertilizers are most suitable for crops in Southeast Asia, which is the main consumer of potash fertilizers in the world. From an agrochemical point of view, this type of fertilizer is of particular value, since many agricultural crops, such as potatoes, tomatoes, cabbage, peas, flax, soybeans react negatively to the chlorine presence in the soil [1].

Total reserves of potash salts in the world are estimated about 40 billion tons, Canada, Russia, Belarus, and Germany are main potash producers [2]. The Central Asian region of the CIS countries also has significant reserves of potassium-bearing ores. In this regard, to provide domestic and foreign markets with competitive potash fertilizers a number of countries in this region (Kazakhstan, Turkmenistan, Uzbekistan) have intensified efforts to create own production of these compounds in recent years. The interest of the region countries in potash fertilizer production is also determined by the proximity of large markets for products (China, India, etc.) [2].

According to academic data, potash salts are abundant in the Caspian Basin in Kazakhstan. Composition of the salts is predominantly chloride, their beds are found in the arches of many salt domes practically throughout the entire territory of the basin. "Satimola", "Chelkar", "Inder", and "Zhilyanskoe" are the most studied domes [3]. The project of Kazakhstan Potash corporation (China) on creation of an enterprise for mining the potash salts and their processing into fertilizers in Kazakhstan has not yet turned into a practical stage [4]. Among them Chelkar is a rather complex deposit: a layered salt dome containing several minerals: sylvinite, carnallite, bischofite, halite, borate, etc. [5]. Carnallite is a main component of this ore, which consists of two compounds of chlorine with potassium and magnesium. It is a mineral of medium abundance and sedimentary origin. Sylvinite rock is formed as combination of sylvite, halite and other salts. In terms of mineral composition, carnallite ore contains up to 65 % carnallite, 5–15 % of sylvite and 15–25 % of halite. Carnallite ore compares favorably with sylvinite in its composition, it contains a wider range of salts.

Currently there is no technology for processing the Chelkar deposit ore, therefore development of domestic production of potash fertilizers based on this raw material is an urgent problem. To solve these problems it is necessary to carry out a complex studies on processing the natural salts, which are a complex salt system.

Previously we have determined the following average chemical composition of the ore, mass %: Na_2O — 8.47; K_2O — 14.04; CaO — 7.72; MgO — 5.55; SO_4^{2-} — 26.58; Cl^- – 18.77 [6]. Based on the chemical composition and X-ray diffraction patterns, the mineralogical composition of carnallite ore was determined, which showed the heterogeneity of this salt and presence of both water-soluble components in the form of carnallite, glaserite and halite, and insoluble calcium sulfatein its composition [6]. In this regard, the possibility of enriching the Chelkar ore for potassium was studied due to preliminary washing of the impurity mineral halite as a salt with a higher solubility. The results of an experiment on washing ore by incomplete dissolution showed that this is an effective method for removing highly soluble sodium salts from the composition of raw materials (impurity components in potash fertilizers). The obtained data on the degree of ore washing from sodium salts allowed to propose a washing mode for 20 minutes at a mass ratio of water : salt equal to 1:2, which ensures minimal losses of valuable potassium with washing water [7]. Further, the optimal enrichment mode was worked out using a mother liquor, for two-fold washing of the original ore to achieve maximum washing degree from sodium with a potassium saturated solution. As a result of washing, almost all of the sodium chloride was removed from the ore with the keeping potassium and magnesium sulfates, as evidenced by the results of X-ray phase analysis. For further processing of the washed ore into fertilizers the obtained sample was calcined at 550 °C, then subjected to dissolution in water at temperatures of 50 and 90 °C. The results of this study showed that it leads to only a partial transition of potassium and magnesium sulfates to a solution with complete dissolution of residual amounts of sodium salts [8]. Therefore, to obtain chlorine-free water-soluble mineral fertilizer containing potassium and magnesium sulfates it is necessary to search for other chemical methods for processing the concentrated ore.

Experimental

There are known methods of processing polyhalite ores of various deposits on the territory of Russian Federation using nitric acid, which have shown high efficiency of transferring salts into solution with insoluble residue separation [9]. Therefore, the process of dissolution of washed calcined potash ore of above composition with nitric acid solution in the concentration range of 10–50 % at salt : acid ratio 1:1.5 at temperature of 50 °C was studied. The kinetics of ore decomposition with 10% nitric acid was preliminarily studied by composition of liquid and solid phases in the range of 10–40 minutes. The process was carried out in thermostated glass reactor with a stirrer under the exhaust ventilation turned on with sampling from the side neck of the reactor. At the end of the decomposition, the suspension was separated in a vacuum filtration unit with 0.06 MPa, the precipitate was washed with hot water; filtration productivity was determined by a dry washed precipitate. Composition of liquid and solid phases was analyzed for K_2O and Na_2O content using a PFA-378 flame photometer, the content of CaO, MgO, Cl^-, SO_4^{2-} and N was determined by chemical titrimetric method according to standard procedures.

All studies of potassium ore decomposition by nitric acid solution were double-checked for different process conditions. Total standard uncertainty of measurement and standard deviation for analyses of liquid and solid phase composition was calculated of 3 parallel sample measurements taking into account sample weighing, calibration and measurement on the flame photometer. For measurement of K_2O content in the solid phase obtained at nitric-acid decomposition the total standard uncertainty was 0.0067. Relative standard deviation from the averaged value with a confidence level P = 0.95 was 0.0061.

Crystallization of potassium-magnesium salts was carried out by mineral-salt method, taking into account the initial solution composition and crystallization fields on the solubility diagram in K_2SO_4–$MgSO_4$–H_2O system. The solution was evaporated at a constant temperature of 75 °C in UT-4302E laboratory water bath. The precipitated crystals were separated by filtration, washed with ethanol, and examined by X-ray analysis. The mother liquor was ammoniated to pH = 6 and dried in a dryer at 60 °C. Scanning electron microscope JSM-6490l (Jeol, Japan) was used for microscopic spectral analysis of salts. Semi-quantitative X-ray analysis of solid phase samples was carried out on D8 Advance (Bruker) apparatus with Cu-K$_\alpha$ at tube voltage 40 kV and current 40 mA. Processing of the obtained data of diffraction patterns and calculation of interplanar distances were carried out using the EVA software. Sample decoding and phase search were performed using Search/match program with the use of 2020 PDF-2 powder diffractometric data base of the International Center for Diffraction Data (ICDD), USA.

Results and Discussion

The results of studying nitric acid decomposition of washed potash ore are shown in Figure 1 and Table 1. The kinetic dependences (Fig. 1) of potassium and magnesium salts dissolution show that the composition of

liquid and solid phases in terms of potassium and magnesium reaches equilibrium by 30 minutes of decomposition, and the process rate for potassium is higher in the first 10 minutes.
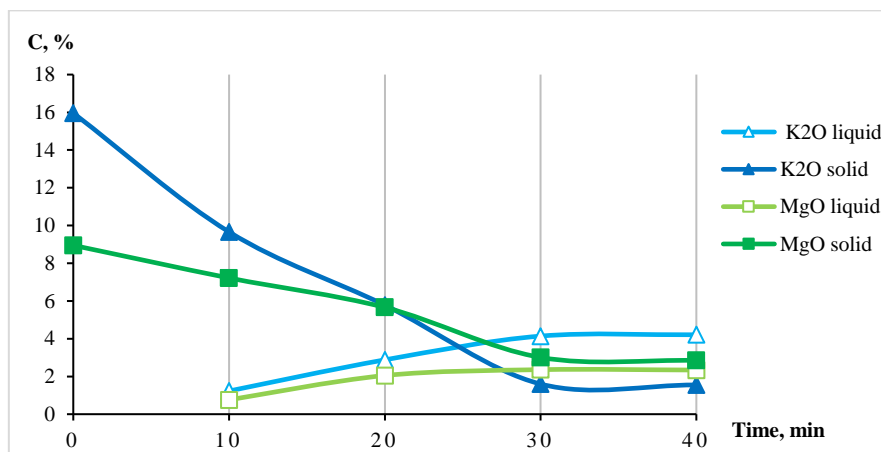

Figure 1. Kinetics of nitric acid decomposition of potash ore

Thus, at 30 minutes the solution contains 4.14 % K_2O and 2.36 % MgO, and further this content is not practically changed. Accordingly, the content of these components in the solid phase decreases by the thirtieth minute to a minimum value of 1.6 % K_2O and 3.01 % MgO, i.e., the equilibrium is reached. Therefore, it is effectually to choose 30 minutes time for the washed ore decomposition.

The process kinetic parameters were calculated; on the basis of experimental data, the order of reactions proceeding in this process was determined:

$$K_2SO_4 + 2HNO_3 \leftrightarrow 2KNO_3 + H_2SO_4 \qquad (1)$$
$$MgSO_4 + 2HNO_3 \leftrightarrow Mg(NO_3)_2 + H_2SO_4 \qquad (2)$$
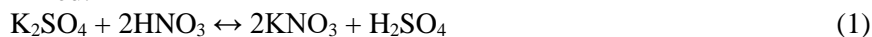
The order of these reactions was determined by Van 't Hoff method [10] in the time interval of 10–40 minutes at 50 °C at the following changing main components concentration in the solution: from 0.13 mol/l to 0.45 mol/l for K_2O, and from 0.19 mol/l to 0.58 mol/l for MgO. Reaction rates were calculated using graphic differentiation method by the tangent to the $C = f(\tau)$ dependence. It was found that 1st and 2nd were of the first order reactions. Therefore the reaction rate is described by the first order equation $V = k \cdot C$ for each of the components. The reaction rate constant calculated for potassium oxide as a main component was 0.09 min^{-1} at a temperature of 50 °C. To determine reaction activation energy in the optimal mode, the process kinetics was calculated in a similar way for a temperature of 40 °C, for which the reaction rate constant was 0.03 min^{-1}. We apply the Arrhenius equation, expressing dependence of the reaction rate on temperature:

$$k = k_0 e^{-\frac{E}{RT}}, \qquad (3)$$

where k — reaction rate constant; k_0 — pre-exponential multiplier (calculates the number of molecule collisions, their special orientation and other factors that do not depend on temperature); R — universal gas constant; E — reaction activation energy.

In the reaction (1) activation energy $E = 92.22$ KJ/mole have been determined by solving the equations for two temperatures. The process rate was determined by the rate of chemical reaction, which increases at temperature growing and does not depend on diffusion stage rate [11]. When potassium ion maximum concentration is reached in the solution, the system comes to a state of equilibrium, and potassium, magnesium, sulfate and nitrate ions are in equilibrium in the formed solution. Therefore, to study the effect of nitric acid solution concentration on the extraction degree of potassium salts into the solution, 50 °C was chosen as the optimum process temperature, which provides the maximum process rate. A higher temperature was not expedient because of acid increased fuming due to accelerating its decomposition with nitrogen oxide release.

Composition of nitric acid extract obtained in the optimal temperature-time mode after separation into liquid and solid phases (Table 1) showed that, upon decomposition with 10 % nitric acid, a part of potassium (1.6 % K_2O), remained in the original salt. The increase of nitric acid concentration to 30 % leads to 100 % extraction degree of potassium salts into a solution is reached; and liquid phase contains 4.51 % of K_2O. At the same time, sulfate ion content increases in the solution from 10.12% to 10.9% and MgO content also grows from 2.36 to 2.54 %.

Influence of nitric acid concentration on phases'composition after calcined ore decomposition

Composition of cal-cined washed ore		Post-decomposition phase	Component content in phases, % at HNO_3 concentration		
Component	%		10 %	30 %	50 %
K_2O	15.96	solid	1.60	0	0
		liquid	4.14	4.51	4.41
CaO	19.30	solid	25.20	29.40	29.21
		liquid	0.22	0.06	0.05
MgO	8.95	solid	3.01	5.00	5.63
		liquid	2.36	2.54	2.70
SO_4^{2-}	62.12	solid	54.80	61,11	64.23
		liquid	10.12	10.90	8.76

Sodium ion absence is associated with preliminary complete ore washing from sodium and chloride ions. At that, calcium oxide is practically absent in the liquid phase and its content is determined by solubility in nitric-acid extract, therefore all calcium is completely bound in the form of insoluble calcium sulfate, represented by anhydrite and gypsum. This fact is confirmed by the X-ray diffraction pattern of the insoluble residue, which consists entirely of the indicated salts (Fig. 2).
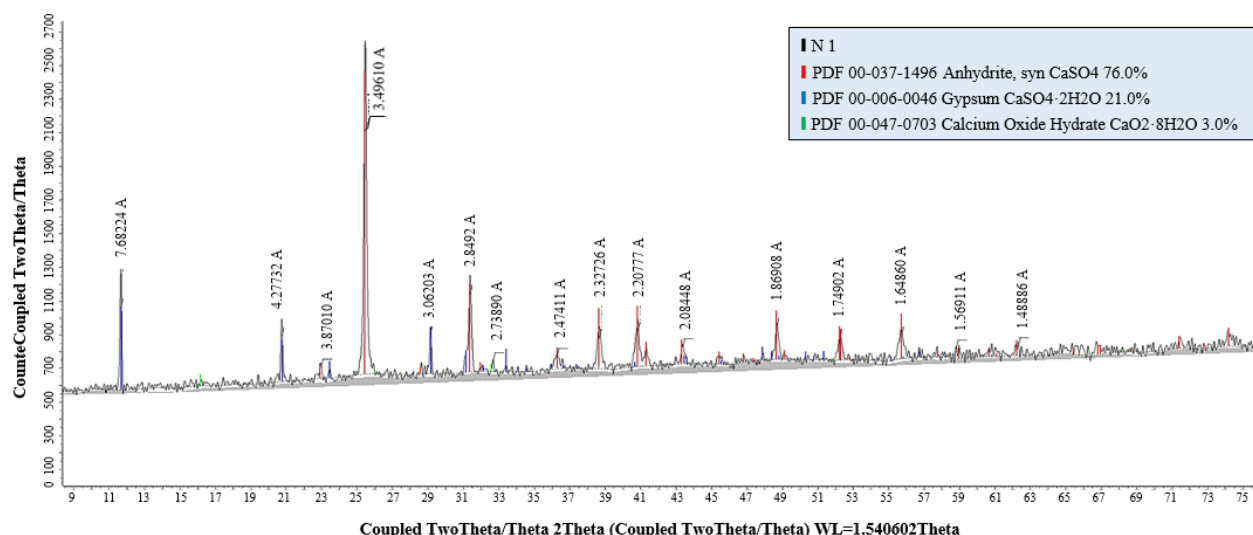
Figure 2. X-ray diffraction pattern of the insoluble residue after nitric acid decomposition of raw materials

Further increase of nitric acid concentration leads to a slight decline of potassium oxide content in the solution; it can be explained by salting out with magnesium salts, of content which increases to 2.7 %. Simultaneously, sulfate ions content in the liquid phase decreases and these ions content increases in the solid phase; it is also caused by salting out of magnesium sulfate. The results obtained allow to conclude that 30 % nitric acid should be used to decompose the washed ore.

Filtration productivity of nitric acid extract is 160 kg/m²·h on dry precipitate; low precipitate filterability is obviously associated with gypsum phase transition into waterless anhydrite during washed ore calcination. This transition is also indicated by the precipitate composition on the X-ray diffraction pattern, which determined $CaSO_4$ content as 76 % and $CaSO_4·2H_2O$ content as 21 %. It is known that anhydrite is formed as small crystals, which determine precipitate filtration properties. Crystals clog filter pores and significantly increase filtration time. Since insoluble residue filtration is a limiting stage [12], conditions should be chosen to increase filtration productivity and accelerate the process. For this, an additional study of washed ore decomposition was carried out, and it was not subjected to preliminary calcination. In this case, gypsum dehydration does not occur and it can improve the precipitate filtration properties. The result of this decomposition and subsequent filtration showed an increase in filtration productivity by 20 times, up to 3200 kg/m²·h on dry washed

precipitate. It confirms an assumption about gypsum content in the precipitate. The water obtained after washing the insoluble residue was used to dilute nitric acid to the required concentration.

The production solution obtained in optimal decomposition mode contains 8.34 % of K_2SO_4, 7.62 % of $MgSO_4$, and 2.03 % of N. Crystals isolated by an isothermal method, i.e., by partial evaporation of the filtrate to half the volume after washing were subjected to X-ray phase analysis. X-ray analysis of the obtained salt (Fig. 3) identified a pure double acidic salt of potassium-magnesium sulfate $KMgH(SO_4)_2 \cdot H_2O$. This indicates that upon evaporation at a temperature of 75 °C a point of the system composition was in the field of joint crystallization of potassium sulfate and this double salt. This composition is confirmed by elemental analysis and a spectrogram of the salt obtained on SEM (Fig. 4). Carbon content in the sample is determined by thorough washing this water-soluble salt from a mother liquor with ethanol.
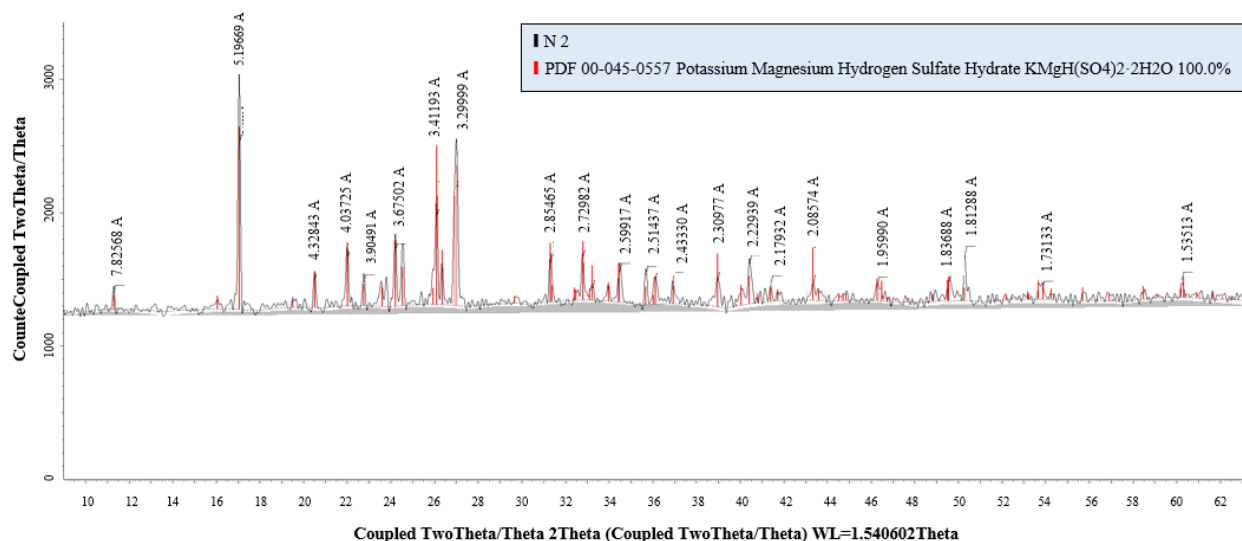
Figure 3. X-ray diffraction pattern of the salt obtained by isothermal crystallization from the filtrate

Element	Mass %
C	5.35
O	53.75
Mg	6.19
S	19.69
K	15.01
Total	100.00
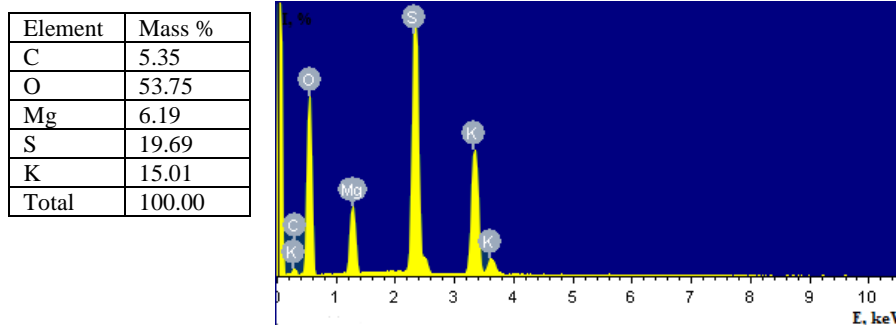
Figure 4. Spectrogram and element composition of the crystallized salt

White crystalline product contains 18.0 % of K_2O and 10.3 % of MgO in the form of sulfates; it does not include chloride ions and insoluble impurities, but contains a small amount of free nitric acid. Acidic mineral fertilizer cannot be used on physiologically acidic and neutral soils, therefore the production solution was ammoniated to pH = 6 to obtain a neutral product. After drying the ammoniated solution, a pale yellow-green close to white solid product was obtained. The product composition was determined by X-ray phase analysis (Fig. 5).

The production salt has pH = 6.0, does not contain insoluble impurities and chlorine; it is completely water-soluble salt consisting of potassium-ammonium nitrate $KNO_3 \cdot NH_4NO_3$ (48.7 %), crystalline hydrate magnesium-ammonium sulfate $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (38.9 %) and ammonium nitrate (12.4 %). This is also indicated by the spectrogram of this product obtained on the SEM (Fig. 6).
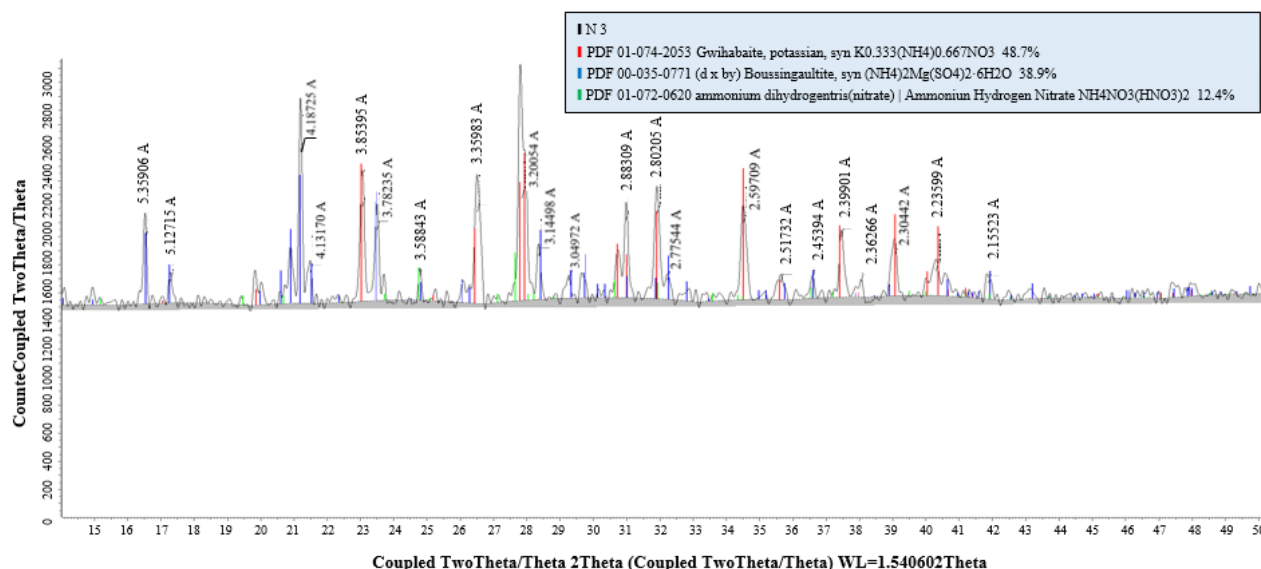
Figure 5. X-ray diffraction pattern of the salt obtained by drying the product solution

Element	Mass %
C	8.85
N	17.03
O	49.96
Na	0.42
Mg	3.01
Al	0.23
P	0.22
S	7.84
Cl	0.25
K	11.49
Ca	0.69
Total	100.00
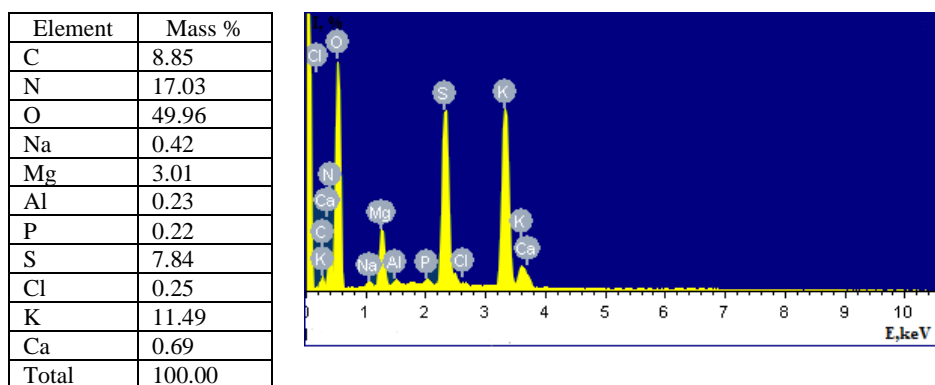
Figure 6. Spectrogram and element compositionof the target salt

The product contains: potassium (11.49 %), magnesium (3.01 %), sulfur (7.84 %) and nitrogen (17.03 %) on average with 9–13 % deviation corresponds to the above salt composition. The presence in the composition of an insignificant fraction of chloride ions (0.25 %), sodium ions (0.42 %) and calcium (0.69 %) is within the solubility of these ions in the product solution from which the salt is obtained. The ratio of main nutrients in the obtained fertilizer N:K was 1.5:1, taking into account the following microelements N:K:S:Mg = 1.5:1:0.7:0.3. The obtained product was a complex potassium-nitrogen-magnesium water-soluble chlorine-free ballastless fertilizer, the main salt components of which were potassium nitrate, magnesium sulfate, nitrate and ammonium sulfate.

Conclusions

The kinetics of nitric acid decomposition of carnallite ore from the Chelkar deposit was studied in order to obtain chlorine-free water-soluble potassium fertilizer. It was found that the equilibrium in potassium and magnesium in liquid and solid phases was reached to 30 minutes of decomposition. The first order of the reactions was determined by calculation. The calculated value of reaction activation energy for interaction of potassium sulfate with nitric acid E_a = 92.22 KJ/mol characterizes kinetic region of the process. The research results allowed to determine the optimal mode of washed potash ore decomposition, which ensures the complete extraction of potassium into the liquid phase: temperature 50 °C, concentration of nitric acid 30 %. The study of nitric acid extract filtration productivity showed that to ensure better filtration properties and high rate of suspension separation, the washed non-calcined ore should be used to exclude gypsum dehydration, which causes its phase transition into anhydrite. Mineral potassium-magnesium sulfate fertilizers were obtained by

crystallization from nitric acid solution by the isothermal method and by drying the ammoniated solution. The composition of obtained products was identified by X-ray analysis.

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Карналлит кенінен калий тыңайтқыштарын алу процесін зерттеу

Ішкі және сыртқы нарықты калий тыңайтқыштарымен қамтамасыз ету мақсатында Қазақстан осы өнімдердің меншікті өндірісін құра бастады. Бірақ қазіргі уақытта калий тұздарын өндіретін кәсіпорындар іс жүзінде ол кезеңге өткен жоқ. Карналлит кенінің Шалқар кен орны осы өзекті мәселелерді шешуде ерекшеленеді. Мақалада калий және магний сульфаттары бар калий тыңайтқышын алу үшін натрий хлоридінен жуылған калий кенін өңдеудегі зерттеу нәтижелері келтірілген. Карналлит кенінің азот қышқылымен ыдырау кинетикасы зерттелді. Калий сульфатының азот қышқылымен әрекеттесу реакциясының активтену энергиясының есептелген мәні процестің кинетикалық аймағын сипаттайды. Жуылған күйдірілген кенді концентрациясы 30 % азот қышқылымен 50 °С-та ыдыратудың оңтайлы шарттары анықталды. Сүзудің жақсы қасиеттерін және суспензияны бөлудің жоғары жылдамдығын қамтамасыз ету үшін гипс дегидратациясын болдырмау үшін жуылған күйдірілмеген кенді пайдалану керек екендігі анықталды, бұл оның ангидритке фазалық өзгеруін тудырады. Кристалдану арқылы азот қышқылы сығындысынан калий-магний сульфатының қос тұзы бөлінген және аммонизацияланған күңгірт сұйықтықты кептіргеннен кейін хлорсыз күрделі азот-калий-магний тыңайтқышы болып табылатын тұз алынады.

Кілт сөздер: калий кені, минералды тыңайтқыштар, калий сульфаты, натрий тұздары, Шалқар кен орны, күңгірт сұйықтық, ыдырау, булану, кристалдану.

Г.М. Сейтмагзимова, А. Асылханкызы, И.А. Петропавловский, Ж.К. Джанмулдаева

Исследование процесса получения калийных удобрений из карналлитовых руд

В целях обеспечения внутреннего и внешнего рынка калийными удобрениями Казахстан приступил к созданию собственного производства данной продукции. Однако в настоящий момент предприятия по

добыче калийных солей не перешли в практическую стадию. Месторождение карналлитовых руд Челкар является уникальным в решении данных актуальных проблем. В статье приведены результаты исследования переработки отмытой от хлорида натрия калийной руды для получения калийного удобрения, содержащего сульфаты калия и магния. Исследована кинетика азотно-кислотного разложения карналлитовой руды. Рассчитанное значение энергии активации реакции взаимодействия сульфата калия с азотной кислотой характеризует кинетическую область протекания процесса. Определены оптимальные условия разложения отмытой прокаленной руды азотной кислотой концентрации 30 % при 50 °C. Установлено, что для обеспечения лучших фильтрующих свойств и высокой скорости разделения суспензии следует использовать отмытую непрокаленную руду для исключения дегидратации гипса, вызывающего фазовое превращение его в ангидрит. Кристаллизацией из азотнокислотной вытяжки выделена двойная соль сульфата калия-магния, и высушивание аммонизированного маточного раствора позволило получить соль, представляющую собой безбалластное бесхлорное сложное азотно-калийно-магниевое удобрение.

Ключевые слова: калийная руда, минеральное удобрение, сульфат калия, соли натрия, месторождение Челкар, маточный раствор, разложение, выпаривание, кристаллизация.

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Thermokinetic parameters of the primary coal tars destruction in the presence of catalysts and polymeric materials

The hydrogen-donor abilities of polymers and the activity of catalysts in the process of thermal destruction of the organic mass of primary coal tar (PCT) are studied by non-isothermal kinetics methods. PCT, magnetic microspheres, nickel-deposited chrysotilechrysotile and Fe_3O_4 nanocatalysts were used as initial raw materials. Polymers such as polyethylene (PE), polystyrene (PS) and polyethylene glycol (PEG) were selected as a hydrogen donor. The phases $Mg_3[OH]_4\{Si_2O_5\}$ and NiO were determined by X-ray phase analysis (XRD) in the obtained catalyst (nickel-deposited chrysotile), and the presence of highly dispersed nickel oxide particles on the surface and inside the nanotubes was shown by the transmission electron microscope (TEM). Nickel oxide particles of 8–11 nm and 30–37 nm were evenly distributed on the surface and inside the chrysotile nanotubes. The kinetic parameters of the thermal destruction of a mixture of PCT, catalyst and polymer material were determined on the basis of thermogravimetric analysis using the integral method and the method for determining the thermokinetic parameters by the inflection point on the thermogravimetric curve (TG). The change in the activation energy, rate constant and pre-exponential factor with an increase in the degree of destruction of the organic mass of the PCT is established. It was shown that the nature of polymers and catalysts significantly affects the value of the rate constant and the activation energy. The calculated activation energies of the thermal destruction of a mixture of coal tar with PS and PE in the presence of a catalyst (nickel-deposited chrysotile) by the first method are 47.6 kJ/mol and 40.4 kJ/mol, and by the second method are 47.3 kJ/mol and 86.5 kJ/mol respectively.

Keywords: primary coal tar, nanocatalyst, chrysotile, magnetic microsphere, polymer, thermal destruction, thermokinetic parameters.

Introduction

At present, due to the high growth of oil and oil products consumption coal, PCT and high-temperature coal tar are considered as an alternative sources of raw materials for secondary processes of the motor fuels production and for petrochemistry industry. Therefore much attention is paid to thermocatalytic and hydrogenation processing of heavy hydrocarbon raw materials (HHR) into light oil products. The method of thermogravimetric analysis allows to determine the weight loss of HHR sample as a function of temperature at a constant heating rate, and thereby establish the parameters of thermal destruction in the presence of various catalysts and hydrogen donors. It is known that polymeric materials are used as a hydrogen donor for thermal destruction of HHR [1]. Various nanosized catalysts and porous materials, such as microspheres isolated from coal ash and mountain mineral chrysotile, can be used as a catalyst for the thermal destruction of HHR.

Recently the natural mineral chrysotile has been of great interest, since this matrix can be of macroscopic size. It consists of nanotubes, the inner diameter of which is about 5 nm and the outer diameter is about 30 nm. These nanotubes can be about 1 cm long, and they are arranged in a close tohexagonal packing [2].

Earlier it was shown that chrysotile mineral is widely used in various fields of science and technology: in electronics, electricity, the production of dielectrics, nanowires, and in the production of nanocatalysts, as well as a carrier for catalysts of destructive hydrogenation of HHR [3–6].

The aim of this work is to study the hydrogen-donor abilities of polymers and the activity of catalysts in the process of thermal destruction of organic mass of PCT using non-isothermal kinetics methods.

Experimental

Primary coal tar of Shubarkol Komir JSC [7] was used as the study object and magnetic microspheres obtained from ash residues of coal [8] (catalyst 1), chrysotile with applied nickel (catalyst 2) and Fe_3O_4 nano-catalyst [9] (catalyst 3) were taken as a catalysts.

Reagent grade polymers such as PE, PS and PEG were chosen as the hydrogen donor. The amount of added catalyst and polymer to the PCT was 1 % on the feedstock.

The chemical formula of chrysotile is $Mg_3Si_2O_5(OH)_4$. Chrysotile fibers are formed from twisted planes of MgO and SiO_2 [6]. Chrysotile was preliminarily leached with 20 % hydrochloric acid solution to remove magnesium, potassium and other alkaline earth metals. The process of filling the channels with chrysotile was carried out using the wet method. Leached chrysotile was dried at 105 ºC for an hour. The chrysotile channels were filled with an aqueous solution of nickel salt ($NiNO_3$). For this, a 5 % solution of nickel nitrate salt was added to the leached chrysotile and heated for 2 hours with periodic stirring. Then the resulting mass was dried at 105 ºC and cooled to room temperature, after which the sample was kept in a muffle oven at 500 ºC for 2 hours.

The structural characteristics of the synthesized catalyst 2 were established by XRD. X-ray diffraction patterns were taken on a *Dron-4-07 X-ray diffractometer*, and the size of nickel particles was estimated by TEM using a *JoelJem-1400Plus*. The presence of nickel metal on the surface of chrysotile was confirmed using the method of X-ray fluorescence analysis, obtained on a *FOCUS-2M spectrometer*.

The kinetic regularities of the thermal destruction of PCT and a mixture of resin with catalyst and polymer were investigated in the temperature range of 33–600 °C using a *LabsysEvoSetaram* device (France) at a heating rate (β) of 20 K/min under non-isothermal conditions, while recording the weight change. Thermal analysis was performed in a nitrogen atmosphere to exclude oxidation reactions [10]. In all experiments 10 mg of the initial samples were used.

To calculate the thermokinetic parameters of the resin decomposition and a mixture of resin with catalyst and polymer, two methods have been used: the first was the integral method proposed in [11], the second was the method for determining the thermokinetic parameters from the inflection point on the TG curve [12].

Results and discussion

Physicochemical properties of catalysts. Using the wet method of incipient wetness impregnation, a solution of nickel nitrate salt was applied to the surface and inside the chrysotile tubes. XRD of the obtained catalyst 2 showed the presence of an intense reflex 7.38; 4.48; 3.66; 2.58; 2.09; 1.53; 1.30; 1.20 Å – Chrysotile $Mg_3[OH]_4\{Si_2O_5\}$ (ASTM 25-645), and reflex: 2.41; 2.09; 1.47; 1.26; 1.20 Å — NiO (ASTM 78-423).

In the synthesized catalyst 2 TEM showed the presence of highly dispersed particles of nickel oxide on the surface and inside the nanotubes. On the basis of statistical processing, a curve of the size distribution of nickel particles was obtained (Fig. 1). The Figure 1 shows that nickel particles 8–11 nm and 30–37 nm are evenly distributed on the surface of chrysotile nanotubes, and the distribution maximum is at 15 nm.
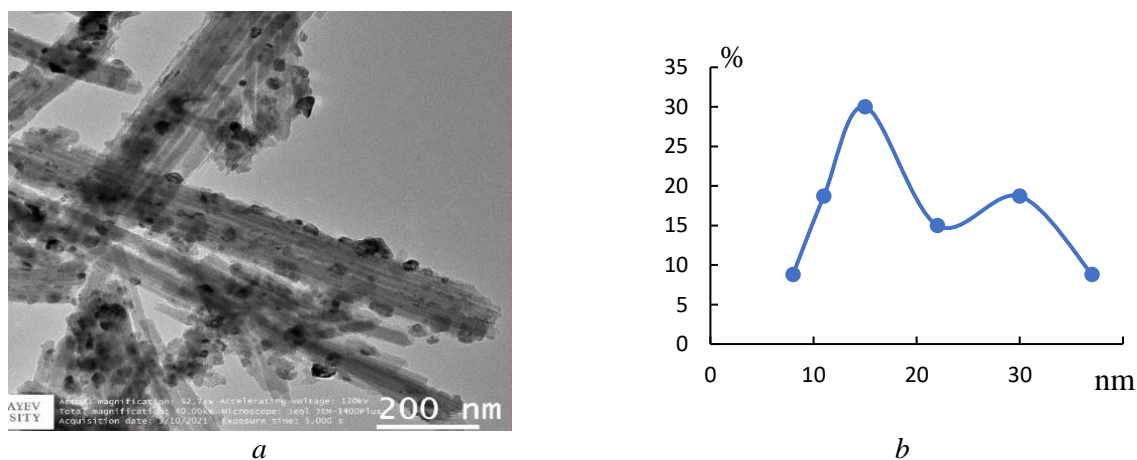

Figure 1. Micrograph of chrysotile, obtained on TEM (*a*)
and the curve of the distribution of nickel particles by size (*b*)

The results of X-ray fluorescence analysis of catalyst 2 showed the presence of nickel Ni (63.68 %), silicon Si (23.1 %), iron Fe (11.57 %), chromium Cr (0.409 %) and manganese Mn (0.03 %).

The kinetics of thermal destruction processes can be studied on the basis of thermogravimetric analysis data [13, 14]. For one-stage process the reaction rate obeys the Arrhenius equation:

$$\frac{dm}{d\tau} = -k_0 e^{-E/RT} \cdot m^n,$$

where m is the mass of the non-volatile substance of the sample at the moment of time τ; E is the activation energy; k_0 is the preexponential factor; R is the universal gas constant; T is the absolute temperature; n is the reaction order.

In the first approach the entire section of the TG curve, which related to one stage, is used to establish the kinetic parameters [11].

The values of the rate in the mass changing of the sample are determined experimentally as the inclination of the tangent to the curve at given points. The parameters a_i and b_i were selected by linearizing the velocity equation:

$$\ln \frac{r_i}{m_{i_{max}} - m_i} = a_i - \frac{b_i}{T_0 + \beta\tau}, \tag{1}$$

where $a_i = \ln k_{0_i}$; $b_i = \dfrac{E_i}{R}$.

The last expression (1) represents the equation of a straight line in coordinates

$$\ln \frac{r_i}{m_{i_{max}} - m_i} = f\left(\frac{1}{T}\right), \tag{2}$$

where a_i — is the cut off segment of the ordinate; b_i — is the slope tangent.

From the slope tangent (2) of the coordinate lines, the activation energy E of the thermal destruction process of the samples were calculated, which depend on the degree of their mass loss.
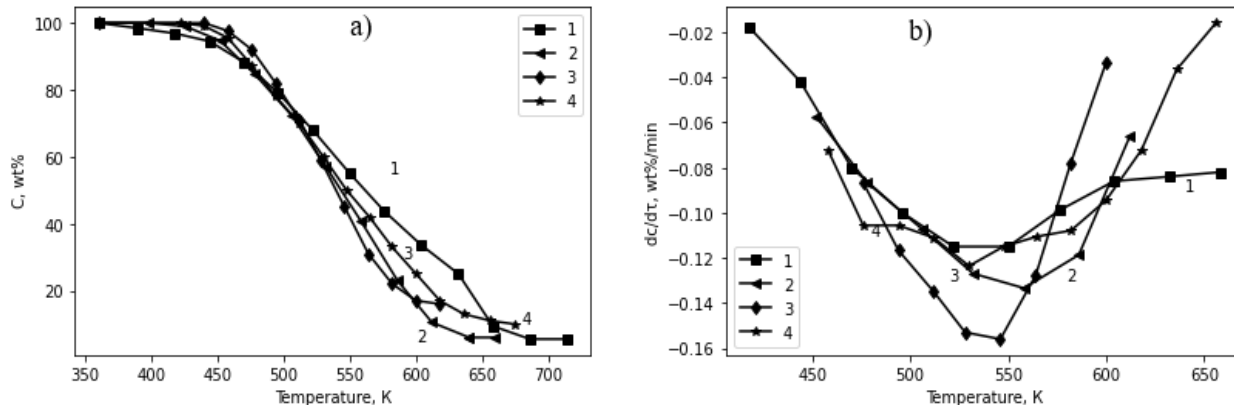
1 — initial PCT; *2* — mixture of PCT with catalyst 1; *3* — mixture of PCT with catalyst 2;
4 — mixture of PCT with catalyst 3

Figure 2. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*) of the initial PCT and a mixture of PCT with various catalysts

TG curves of weight loss versus temperature are depicted in Figure 2*a*. TG curve of thermolysis of the initial resin showed that the main weight loss at a sample heating rate of 20 K/min occurs in the temperature range of 430–650 K. The addition of chrysotile containing nickel to PCT leads to some displacement of weight loss curve towards low temperatures 450–580 K, and the addition of a magnetic microspheres shifts to 450–610 K, nanocatalyst Fe_3O_4 — to 450–610 K. Figure 2*b* shows that the peak characterizing the maximum of decomposition rate of the PCT organic mass mixture in the low-temperature region, corresponds to the peak of organic mass mixture decomposition of the resin with chrysotile containing nickel.
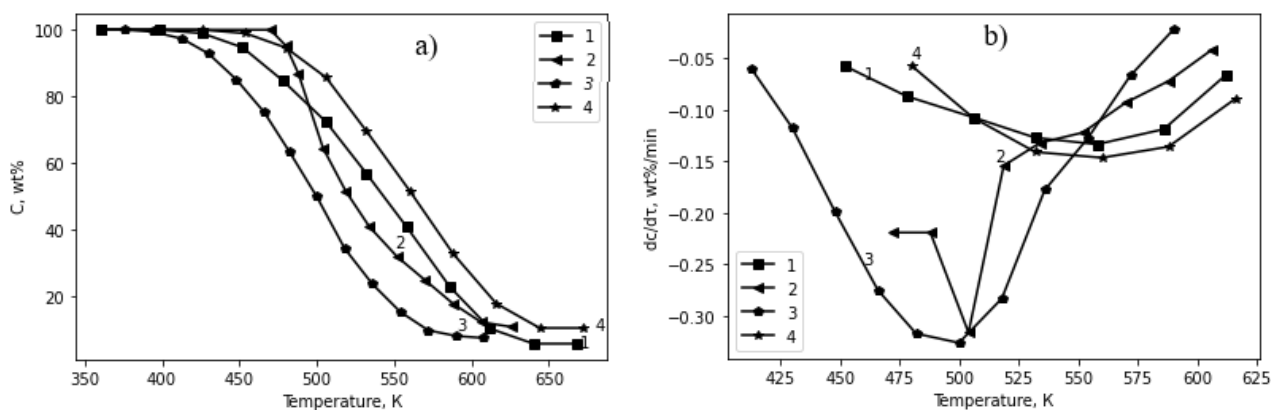
1 — mixture of PCT with catalyst 1; *2* — mixture of PCT with catalyst 1 and PE;
3 — mixture of PCT with catalyst 1 and PS; *4* — mixture of PCT with catalyst 1 and PEG

Figure 3. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*)
of a mixture of PCT with catalyst 1 and various polymers

As shown in Figure 3*a*, when catalyst 1 and polymer additives such as PE, PS, and PEG are added to the PCS, the main weight loss is observed in the temperature range of 440–570 K, 480–580 K, and 470–620 K, respectively. Figure 3*b* illustrates that the addition of catalyst 1, polystyrene, and polyethylene to the initial tar increases the rate of weight loss. When PS is added to the mixture of coal tar and catalyst 1, a high weight loss and rate of weight loss are observed. In addition, a shift of the peak characterizing the maximum decomposition rate (Fig. 3*b*) of a tar mixture and catalyst 1, and PS is observed in the low-temperature region. Based on the TG curve, it was found that the weight loss of the resin increases from 69 (thermal degradation of the initial resin sample) to 93 wt% upon simultaneous destruction of the resin with polystyrene and catalyst 1, and with polyethylene and catalyst 1 to 89 wt%, respectively. These results confirm that polyolefin polymers play the role of a hydrogen donor and promote tar decomposition [1, 15–17]. The use of PEG as a hydrogen donor showed that during the destruction of a mixture of resin and catalyst 1, the polymer reduces the weight loss and the rate of weight loss (Fig. 3*a*, *b*).
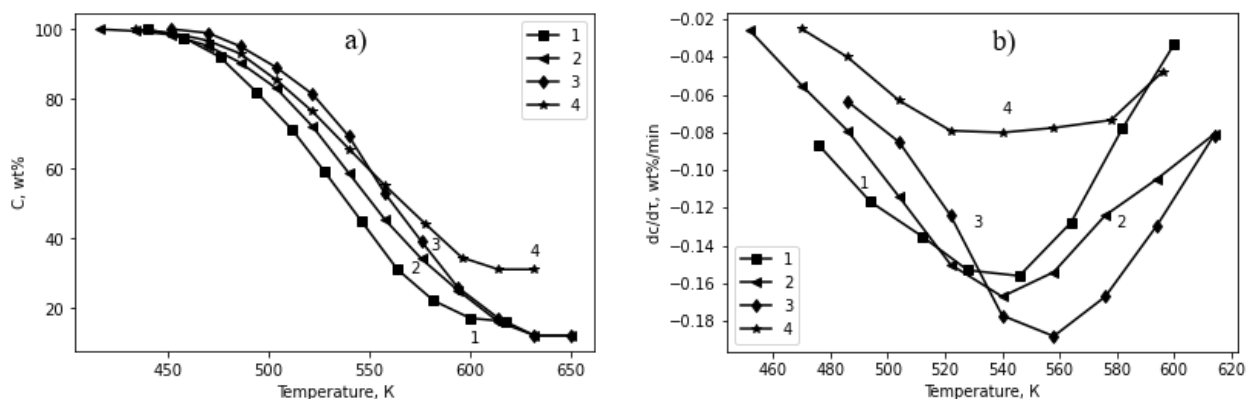
1 — mixture of PCT with catalyst 2; *2* — mixture of PCT with catalyst 2 and PE;
3 — mixture of PCT with catalyst 2 and PS; *4* — mixture of PCT with catalyst 2 and PEG

Figure 4. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*)
of a mixture of PCT with catalyst 2 and various polymers:

Figure 4*a*, *b* illustrates the effect of catalyst 2 and added polymers such as PE, PS and PEG to the resin on the change in weight loss and the rate of weight loss. From the presented TG curve (Fig. 4*a*) it can be seen that the main weight loss of the tar with catalyst 2 and polyethylene occurs in the temperature range 480–570 K, with polystyrene and PEG at 480–580 K. Based on the TG curve, it was found that the weight loss of the tar increases from 69 (thermal destruction of the initial resin sample) to 83 wt% upon simultaneous destruction of the tar with polystyrene and catalyst 1, and with polyethylene and catalyst 1 to 84 wt%,

respectively. When PS is added to a mixture consisting of tar and catalyst 2, a high rate of weight loss and a shift of the peak characterizing the maximum of decomposition rate of the resin mixture to the high-temperature region are observed (Fig. 4b). Figure 4b illustrates that polyethylene and polystyrene promote the coal tar decomposition of the resin, since the rate of weight loss increases, and PEG inhibits of the tar degradation.

From equation (1) the activation energy E and the preexponential factor k_0 of thermal destruction of the tar mixture with catalyst 2 were determined (Fig. 5).
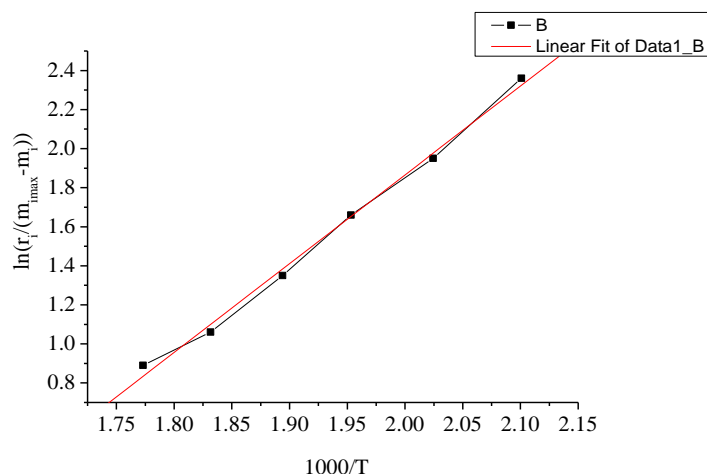
Figure 5. Linearization of the temperature dependence
of the rate of PCT thermal destruction in the presence of catalyst 2

As can be seen from Table 1, for the tar mixture and catalyst 2 the activation energy is 38 kJ/mol, which corresponds to a high rate of weight loss (Fig. 2), and the activation energy of the mixture of resin and catalyst 1 is 34.2 kJ/mol, with catalyst 3, the activation energy is 24 kJ/mol, which corresponds to low rate of weight loss. The values of the pre-exponential factor increase with the growth of the activation energy.

T a b l e   1

**Calculated thermokinetic parameters of thermal destruction of PCT
in the presence of catalysts and polymers [11]**

Investigated composition	E, kJ /mol	k_0
PCT	39.4	$1.86 \cdot 10^3$
PCT + Catalyst1	34.2	$5.1 \cdot 10^2$
PCT + Catalyst 2	38	$1.4 \cdot 10^3$
PCT + Catalyst 3	24	42.3
PCT + Catalyst 3 + PE	35	$7.23 \cdot 10^2$
PCT + Catalyst 1 + PE	32	$2.9 \cdot 10^2$
PCT + Catalyst 1 + PS	35	$1.26 \cdot 10^3$
PCT + Catalyst 1 + PEG	38	$7.9 \cdot 10^2$
PCT + Catalyst 2 + PE	40.4	$1.61 \cdot 10^3$
PCT + Catalyst 2 + PS	47.6	$7.94 \cdot 10^3$
PCT + Catalyst 2 + PEG	38.7	$9.22 \cdot 10^2$
PCT + PE	30.3	$1.69 \cdot 10^2$
PCT + PS	23	18
PCT + PEG	29.6	80

The obtained thermokinetic parameters E and k_0 of the tar thermal destruction (Table 1) in the presence of catalysts and polymers showed that a high activation energy is characteristic of the thermal destruction of the coal tar with PS and catalyst 2, which is 47.6 kJ/mol, and the low value is 32 kJ/mol, which is typical for resins in the presence of PE and catalyst 1. The calculated values of E and k_0 suggest that one of the reasons for the increase in the rate of weight loss under the conditions of thermal destruction of resins with catalyst 2 in the presence of PS and PE is the high donor capacity of these polymers. Another reason is associated with

the developed specific surface area (40 m²/g) of chrysotile with applied nickel and oriented packing of tubes (Fig. 1) with high adsorption properties.

The second approach is to use three equations for the inflection point on the TG curve to determine the thermokinetic parameters [12]. Using the second method, we determined the thermokinetic parameters of the coal tar thermal destruction in the presence of catalysts and polymers.

The thermogravimetric curve of the thermal destruction of the resin with the catalyst 2 is depicted in Figure 6.
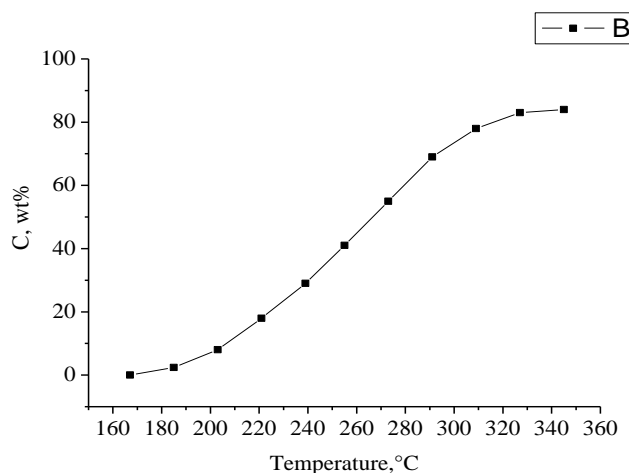
Figure 6. Thermogravimetric curve of the thermal decomposition of PCT with catalyst 2

Based on the TG curve, T_{kink}, β, C_{kink} and $\left(\dfrac{dC}{dT}\right)_{T=T_{kink}}$ have been obtained. Based on the initial data obtained, the process exponent n, the activation energy E, the preexponential factor k_0 and the rate constant k, presented in Table 2, were calculated.

<div align="right">T a b l e 2</div>

**Calculated thermokinetic parameters of thermal destruction of PCT
in the presence of catalysts and polymers [12]**

Investigated composition	E, kJ / mol	n	k_0	k
PCT	28.5	1	1.03	$3.2 \cdot 10^{-3}$
PCT + Catalyst1	66	1	$5.8 \cdot 10^3$	$7.59 \cdot 10^{-3}$
PCT + Catalyst 2	46.4	1	$1.05 \cdot 10^2$	$5.7 \cdot 10^{-3}$
PCT + Catalyst 3	43.4	1	34.5	$4.95 \cdot 10^{-3}$
PCT + Catalyst 3 + PE	30	1	3.96	$4.3 \cdot 10^{-3}$
PCT + Catalyst 1 + PE	43.04	1	$2.56 \cdot 10^1$	$4.71 \cdot 10^{-3}$
PCT + Catalyst 1 + PS	48.25	1	$5.95 \cdot 10^2$	$7.28 \cdot 10^{-3}$
PCT + Catalyst 1 + PEG	17	1	$1.36 \cdot 10^{-1}$	$2.55 \cdot 10^{-3}$
PCT + Catalyst 2 + PE	86.5	3.2	$3.25 \cdot 10^6$	$1.1 \cdot 10^{-2}$
PCT + Catalyst 2 + PS	47.3	1	$1.28 \cdot 10^2$	$5.8 \cdot 10^{-3}$
PCT + Catalyst 2 + PEG	27.4	1	1.19	$3.43 \cdot 10^{-3}$
PCT + PE	105	9.12	$2.16 \cdot 10^9$	$1.12 \cdot 10^{-2}$
PCT + PS	168	71.05	$5.3 \cdot 10^{17}$	$8.4 \cdot 10^{-3}$
PCT + PEG	72.4	45.65	$7.9 \cdot 10^6$	$3.8 \cdot 10^{-3}$

Table 2 shows that the coal tar mixture with the polymer is characterized by the highest index of thermal decomposition (*n*). This is probably due to the fact that there is more thermally unstable C–O, C–N bonds than C–C bonds in coal tar. It is possible that the free radicals formed during the process of thermal decomposition initiate the depolymerization of polymer macromolecules, and thus a synergetic effect is observed. From the literature data it is known that the conversion degree of PE, PS PEG during pyrolysis with coal in the presence of cracking catalysts is less than the corresponding indicators of thermal conversion of individual polymers.

The resulting polymer cleavage products inhibit the activity of catalysts during the thermal decomposition of coal with polymers [15]. This explains the low values of the index of thermal decomposition (n) in the presence of a catalyst in the mixture.

Table 2 shows that the activation energy (E) of the thermal destruction of the resin increases from 17 to 168 kJ/mol. With the addition of polymers without a catalyst high activation energies are observed (72.4 kJ/mol, 105 kJ/mol, 168 kJ/mol), which are explained by the acceleration of the depolymerization reaction of macromolecules, and, possibly, the high-temperature transformations of the resin-polymer mixture with a decrease of volatile products yield.

The different values of the thermal destruction thermokinetic parameters of resin and polymers mixture with and without a catalyst obtained in the first and second methods show the simultaneous occurrence of many parallel reactions with different values of activation energies and rate constants. This is due to the difference in the strength of the dissociating bonds in resin-polymer mixture. It was reported [18] that the high value of the activation energy makes a large contribution to the rate of tar mass loss in the process of pyrolysis. It should be taken into account that the increase and decrease in the activation energy (Table 1, 2) is associated with the complex composition of the primary coal tar.

On the basis of two methods the thermokinetic parameters of the resin thermal destruction in the presence of a polymer and a catalyst were obtained, which allowed to choose a catalytic system consisting of catalyst 2 and PE.

Conclusion

The rate constant, the pre-exponential factor and the activation energy were calculated using two methods of non-isothermal kinetics. The values of the activation energy and the rate of destruction calculated by the first method depend on the nature of the polymer and the activity of the catalyst. The calculated activation energies of 47.6 kJ/mol and 40.4 kJ/mol are characteristic of the thermal destruction of the coal tar with PS and PE in the presence of catalyst 2. The high rate of mass loss under conditions of thermal destruction of the mixture of coal tar, catalyst 2 and polymers (PS and PE) is associated with the high donor abilities of these polymers and the developed specific surface area of nickel-deposited chrysotile.

It was found that the activation energy of the thermal destruction of the tar increases from 17 to 168 kJ/mol when the second method was used to determine the thermokinetic parameters. High activation energies (72.4 kJ/mol, 105 kJ/mol, 168 kJ/mol) were observed when polymers were added without a catalyst. It is explained by the acceleration of the depolymerization reaction of polymer macromolecules, and, possibly, by the high-temperature transformations of the tar-polymer mixture are accelerated with a decrease in the yield of volatile products. PE as the active hydrogen donor and the catalyst 2 were selected for the process of HHR hydrogenation based on the obtained results of determining the thermokinetic parameters of the mixture destruction.

The kinetics of thermal destruction of PCT with various polymer additives and catalysts is necessary for mathematical modeling of the HHR catalytic hydrogenation process.

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Катализаторлар мен полимерлік материалдар қатысындағы біріншілік таскөмір шайыры деструкциясының термокинетикалық параметрлері

Бейизотермиялық кинетика әдістерімен біріншілік таскөмір шайырының (БТШ) органикалық массасының термиялық ыдырау процесіндегі полимерлердің сутегі-донорлық қабілеттері және катализаторлардың белсенділігі зерттелді. Бастапқы шикізат ретінде БТШ, магнитті микросфера, никельмен байытылған хризотил және Fe_3O_4 нанокатализаторы пайдаланылды. Сутегі доноры ретінде полиэтилен (ПЭ), полистирол (ПС) және полиэтиленгликоль (ПЭГ) полимерлері алынды. Синтезделген катализаторда (никельмен байытылған хризотил) рентгендік фазалық талдау (РФТ) әдісінің көмегімен $Mg_3[OH]_4\{Si_2O_5\}$ және NiO фазалары анықталды, трансмиссиялық электронды микроскоп (ТЭМ) нанотүтікшелердің ішкі бөлігінде және беткі қабатында жоғары дисперсті никель оксиді бөлшектерінің бар екенін көрсетті. Никель оксидінің 8–11 нм және 30–37 нм бөлшектері хризотил нанотүтікшелерінің ішкі бөлігінде және беткі қабатында біркелкі таралған. Термогравиметриялық талдау негізінде интегралдық әдіс және термокинетикалық параметрлерді термогравиметриялық қисықтағы (ТГ) иілу нүктесі бойынша анықтау әдісі арқылы БТШ, катализатор және полимерлі материал қоспасының термодеструкциясының кинетикалық параметрлері анықталды. БТШ органикалық массасының деструкция дәрежесінің жоғарылауымен активтендіру энергиясы, жылдамдық константасы және экспоненциалды фактор мәндерінің өзгерісі табылды. Полимерлер мен катализаторлар табиғатының жылдамдық константасы мен активтендіру энергиясы мәндерінің өзгерісіне ықпалды әсері көрсетілді. Катализатор (никельмен қапталған хризотил) қатысындағы шайырдың ПС-мен және ПЭ-мен қоспасы термодеструкциясының активтендіру энергиясы, сәйкесінше, бірінші әдіс бойынша 47,6 кДж/моль және 40,4 кДж/моль, екінші әдіс бойынша 47,3 кДж/моль және 86,5 кДж/моль құрады.

Кілт сөздер: алғашқы көмір шайыры, нанокатализатор, хризотил, магниттік микросфера, полимер, термиялық деструкция, термокинетикалық параметрлер.

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Термокинетические параметры деструкции первичной каменноугольной смолы в присутствии катализаторов и полимерных материалов

Изучены водородно-донорные способности полимеров и активность катализаторов в процессе термической деструкции органической массы — первичной каменноугольной смолы (ПКС) — методами неизотермической кинетики. В качестве исходного сырья были использованы ПКС, магнитная микросфера, хризотил с нанесённым никелем и нанокатализатор Fe_3O_4. В качестве донора водорода были выбраны полимеры, такие как полиэтилен (ПЭ), полистирол (ПС) и полиэтиленгликоль. В полученном катализаторе (хризотил с нанесённым никелем) с помощью рентгенофазового анализа были установлены следующие фазы: $Mg_3[OH]_4\{Si_2O_5\}$ и NiO; трансмиссионый электронный микроскоп показал наличие высокодисперсных частиц оксида никеля на поверхности и внутри нанотрубок. Частицы оксида никеля 8–11 нм и 30–37 нм равномерно были распределены на поверхности и внутри нанотрубок хризотила. На основе термогравиметрического анализа определены кинетические параметры термодеструкции смеси ПКС, катализатора и полимерного материала с помощью интегрального метода и метода определения термокинетических параметров по точке перегиба на термогравиметрической кривой. Установлены изменение энергий активации, константы скорости и предэкспоненциального множителя с увеличением степени деструкции органической массы ПКС. Показано, что природа полимеров и катализаторов существенно влияет на величину константы скорости и энергии активации. Рассчитанные значения энергий активации термодеструкции смеси смолы с ПС и ПЭ в присутствии катализатора (хризотил с нанесенным никелем) составляют по первому методу 47,6 кДж/моль и 40,4 кДж/моль, а по второму — 47,3 кДж/моль и 86,5 кДж/моль, соответственно.

Ключевые слова: первичная каменноугольная смола, нанокатализатор, хризотил, магнитная микросфера, полимер, термодеструкция, термокинетические параметры.

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METHODS OF TEACHING CHEMISTRY

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Application of the CLIL method in the classes of Inorganic Chemistry

The article considers the features of applying the CLIL method to integrated teaching of Inorganic Chemistry in English. To develop students' subject and language skills the content and language integrated learning (CLIL) method was studied in the format of online learning. Inorganic chemistry classes for first-year students of B012 Chemistry Teacher Training Program group were conducted in online format for the control group, and for the experimental group using CLIL method. Students were selected not randomly, according to English and subject level for experimental work based on entrance control work. In the pedagogical experiment the method of mathematical statistics was used to confirm the reliability of the obtained results and to prove the representativeness of the sample. The validity of the proposed research hypothesis was proved by Student's *t*-test method. The levels of students' knowledge are summarized in accordance with learning outcomes according to their competencies. During the lesson, work was carried out on the use of CLIL technology with terminology, glossary, and text in English. Students' language competencies were developed when working with texts and questions in English. The effectiveness of working with terminology, glossary, and English text was determined as a result of a survey of students. The article presents comparative indicators of the midterm control results of students in the control and the experimental group during online format teaching. As a result of a comprehensive study an increase in students' interest in the CLIL method was revealed, which had a positive effect on the educational process.

Keywords: CLIL method, Inorganic Chemistry, online format, offline format, content and language integrated learning, glossary, working with English text, competence.

Introduction

Nowadays, education systems are changing the format of teaching in the context of the coronavirus pandemic (COVID-19) and switching to online learning. The new format of education, along with the obvious problems, offers a wide range of opportunities and prospects for change and improvement of education systems. In this regard, the use of traditional methods of teaching English for academic purposes is insufficient in the context of globalization of science and the international exchange of information. Currently, CLIL (Content and Language Integrated Learning) technology is an important form of subject teaching method in English. CLIL is a method of teaching that is widely used at the international level, especially in Europe, as a way to promote language learning. CLIL technology mainly uses English to teach subject content [1].

The use of the CLIL method via integrated learning in English in Higher Education has been studied in several research papers. The authors shared some experience in online teaching of Inorganic Chemistry during COVID-19 outbreak. To help students feel comfortable with online learning they explored different teaching platforms and adjusted online learning methods. During the online class special attention was paid to the topic-oriented learning process. It also encouraged teachers to interact with students and provide timely feedback [2]. In his research U. Reckino studied two pedagogical methods: Content and Language Integrated Learning (CLIL) and Flipped learning. To achieve the main goal the author proposed a guide to the use of Flipped Learning and CLIL to teach the content of lessons for future English teachers at UNAE [3].

A.B. Arynova, D.A. Kassymbekova and Zh.K. Korganbayeva's research works show the integration of all four content and language-integrated elements (content, communication, cognition, and culture) of the

course "Chemistry of the Elements of the Periodic Table". The course of modeling a lecture with the help of CLIL and the results of the assessment questionnaire is given. The survey questions are aimed at studying the motivation of students to study the course using CLIL technologies. The results showed that students are motivated to the learning process and their vocabulary is enriched with chemical terms [4].

The authors made a three-way comparison of full-time, online, and blended forms of study in the undergraduate course to determine whether there were differences in student academic performance and course satisfaction in different forms [5]. The following article provides an overview of the changes made to the first year of Physical Chemistry Unit. The authors analyzed how they can use this experience to make online learning lessons more effective in the future [6]. J. Fernanda developed a strategic plan for integrated content and language learning (CLIL) at the University of Extremadura (UEx) in Spain for the period of 2014–2018. This event was held in the project "Learn in English". This paper describes the features and results of this project at the Faculty of Natural Sciences UEx, where three different degrees involved: Physics, Chemistry, and Chemical Engineering [7].

A several studies have shown that CLIL methods, like other linguistic skills, do not pay much attention to writing activities. However, writing is a skill that needs to be improved, especially in higher education, due to its importance in the educational and professional context. In his research M. Ramiro explored the potential for understanding the text genres using the CLIL method to improve writing skills at the University of Spain for students majoring in Chemistry [8]. The article presents the results of experimental testing of the effectiveness of group learning activities of students at Inorganic Chemistry laboratory classes. The results showed that the use of group learning activities of students contributes to the formation of the order, and course on Inorganic Chemistry laboratory sessions [9]. This study aims to understand how a team of teachers implements content and language integrated learning (CLIL) in an online context (cycle 1) as well as action plans (cycle 2) to address the issues identified in cycle 1 while teaching undergraduate groups [10].

The authors of the work considered the content and language integrated method as a relatively new way of learning the language in terms of its effectiveness in the process of teaching terminology [11]. The CLIL method has been shown to improve students' English language skills and significantly increase their motivation through interactive methods [12]. Some works contain the most important facts about the current state of research in the field of bilingual education in Natural Sciences [13]. The authors of the work [14] investigated changing in undergraduate L2 students' performance historical reasoning and how it affected their reading and writing skills in English. The article examines the relationship between course progress, English proficiency, motivation, and academic language skills in the English medium instruction (EMI) University context [15]. The following study presents the results of a study of CLIL teachers' understanding of the pedagogical use of translanguage and the impact of these concepts on pedagogical practice in various trilingual schools in Kazakhstan. Conclusions show that teachers' attitudes towards translanguaging are ambiguous [16]. In his study, K. Frances showed how emotion affects the memory of information [17]. The article describes the study of a model of teaching based on CLIL at the Pedagogical University, designed specifically for the development of professional and communicative competence of students [18]. General Chemistry instructors have faced challenges due to the COVID-19 pandemic as they search to engage students in a new online learning format. The authors analyzed student questionnaires about the issues encountered during the pandemic, instructor reflections, and grade allocations across several sections of General Chemistry (I, II) taught by different instructors [19].

According to the research, CLIL has become a widely used method of language learning and teaching in recent years. However the CLIL method of teaching in the Natural Sciences field and especially for chemistry students is not much investigated.

The purpose of the proposed research is the theoretical development, scientific substantiation, and experimental study of teaching methods in English in Higher Education based on a subject-language integrated approach. In our previous research, a pedagogical experiment conducted on secondary school students revealed the formation of language skills as a result of working with the terminology, glossary, English-based text, and calculations in subject-language integrated learning (CLIL) [20]. In the given study, the effectiveness of subject-language integrated learning was determined among High School students.

Experimental

The pedagogical experiment was conducted among B012 Chemistry Teacher Training Educational Program group first-year students of the Faculty of Natural Sciences of Khoja Akhmet Yassawi International Kazakh-Turkish University.

In order to determine the conditions for integrated learning of the subject and language, a test paper was obtained through the Google form. As a control work, tasks from the educational and methodological manual of Inorganic Chemistry were given in English [21]. It allowed determining the level of students' learning skills in subject content as well as in the English language. The selection of participants is not accidental, as students were selected among the multilingual groups. To describe the main results of the study 20 students were selected for the control group (CG), 16 students for the experimental group (EG). Both groups were taught with the same syllabus content approved for the educational program 6B01512-Chemistry, but a different methodology was used during training. In the CG instruction was given by using the traditional method while in the EG experimental training was carried out. In the EG Inorganic Chemistry course was implemented by the CLIL method of teaching and aimed at developing students' knowledge of the subject content.

Inorganic Chemistry classes were conducted in the traditional classroom teaching format (offline) in the pre-pandemic and from early March 2020 continued remotely online due to the sudden coronavirus pandemic outbreak. Online lessons were taught by MOODLE distance learning system. There were some issues in the initial lessons when quickly switching from the traditional learning format to distance learning. But students have adapted to online classes, as we have been organized training seminars on how to use the new format of the learning system. Lecture materials were implemented in all four areas of the CLIL method: the content of the lecture was clearly explained, communication developed by asking each other questions in English, cognition skills increased by writing chemical reactions and solving problem-based task in English. Also, students evaluated each other's activities during the culture lesson.

According to the syllabus of inorganic chemistry, topics "Nomenclature and classification of inorganic compound", "Atomic structure", "Periodic system and the electronic structure of atoms", "Chemical bond" were studied during offline classroom teaching. Due to the pandemic outbreak from the 8th week of the second semester the topics "Chemical thermodynamics", "The science of solutions", "Theory of electrolytic dissociation", "Hydrolysis of salts" continued in the form of remote online teaching.

The effectiveness of terminology, glossary, lecture materials, working with the English text, and tasks in English was studied by implementing the CLIL method via the teaching of Inorganic Chemistry in English in offline and online formats.

During remote online format distance teaching classes (lectures, seminars) were conducted via ZOOM videoconference. Materials of online lessons (lectures, seminars, assignments, glossaries, control work tasks, tests, etc.) are uploaded to tng.ayu.edu.kz (https://tng.ayu.edu.kz/).

To determine effectiveness of the CLIL method, one of the methods of mathematical statistics in processing results was used the Student's *t*-test. The validity of the proposed research hypothesis was proved by Student's *t*-test method.

Results and Discussion

To test the effectiveness of the CLIL method, the results of control work before and after the experiment were obtained, based on the competencies (Table 1) following the learning results.

T a b l e   1

Competencies following the learning outcomes

Education level	Assigned competencies
Lower level:	Understands the chemical tasks given in English
	Selects and uses appropriate mathematical knowledge in solving problems, but makes incorrect assumptions in the answer to many problems, as a result of which faces a contradiction in proving the answer to the problem
	Only individual parts of the task can be completed due to incomplete assimilation of tasks
Average level:	Understands the chemical tasks given in English, can write a short answer
	Knows how to solve this problem, however, because the english dictionary incorrectly writes reagents and reaction products, has difficulty balancing the reaction
	Can give a concise definition of terms and concepts in English, albeit briefly, in theoretical questions
High level:	Understands the chemical tasks given in English, can write a complete answer to the given problems using the acquired knowledge
	Can analyze data to solve a given problem and justify conclusions
	Can give convincing arguments to theoretical questions due to good knowledge of English

For the first statistical processing of the experimental results the numerical characteristics of the sample mean and sample variance of the main set was used. To determine the effectiveness of the lessons used in the CLIL method, the values of the selected medium obtained as a result of the control work were compared and analyzed.

The sample variance describes the extent to which the given mean values deviate from the individual values.

The results of sample and average sample variance values in the course of control work of the studied groups of students are shown in Table 2.

T a b l e 2

Results of control work performed in the CG and EG groups

Groups		Mastering the CLIL method	
		$\bar{x}$	$\overline{s^2}$
CG	Before the experiment	6.8	2.05
	After the experiment	8.9	2.24
EG	Before the experiment	7.37	2.92
	After the experiment	9.5	2.13

The results obtained before the experiment at the first stage of the sample mean and variance showed that the difference between the results in the CT and ET groups of students was small. And the results of the second assessment after experimental training show that there was a significant change between them. These data show that the CLIL method applied to the experimental group affected the dynamics of student learning outcomes.

The results of the control work obtained at the formation stage of the experiment are shown in Figure 1. The figure below compares the $\bar{x}$ — average values of the control work performed.

	Control group	Experimental group
■ Before the experiment	6,8	7,37
■ After the experiment	8,9	9,5

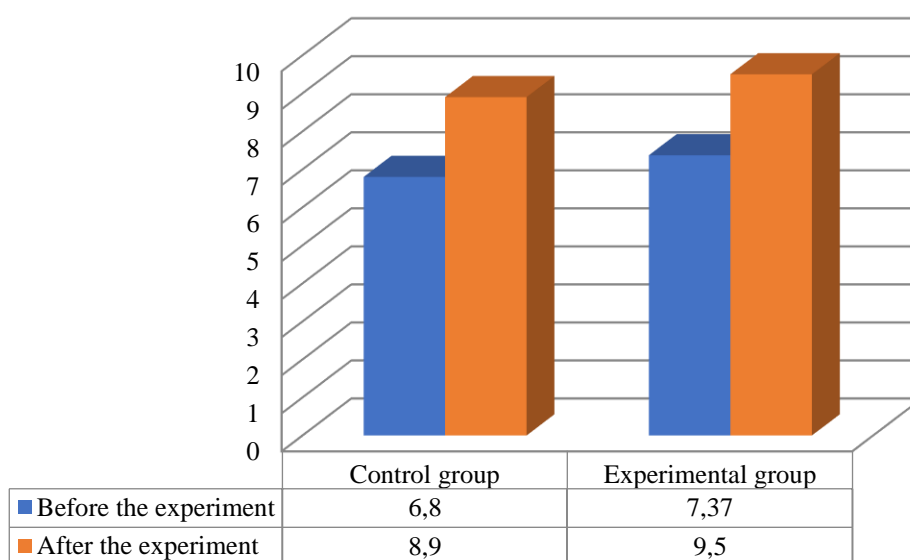Figure 1. Results of control work obtained before and after using the CLIL method

By comparing the sample average values of the experimental data it is possible to see a significant difference between the beginning and end of the experiment in the EG group.

Table 3 shows that at the initial and final stages of the experiment the level of knowledge of the experimental group increased significantly compared to the control group.

**Results of measuring the level of knowledge of control and experimental groups
before and after the experiment**

Education level	Control group		Experimental group	
	Beginning	End	Beginning	End
Low (5–7)	10	7	7	1
Average (8–10)	9	12	8	11
High (11–15)	1	2	1	4

Using the second method of statistical processing of experimental data, the effectiveness of the CLIL method was tested by determining between average values.

To find the exact difference between the statistical average values from each other, we use the Student's *t*-test. Its basic calculation equation is [22]:

$$t = \frac{\left|\overline{x_1} - \overline{x_2}\right|}{\sqrt{\left|m_1^2 + m_2^2\right|}} ,$$

where, $\overline{x_1}$ is the average value of the variable for the first sample data (at the beginning of the experiment); $\overline{x_2}$ is the average value of the variable for the second sample data (at the end of the experiment); m_1^2 and m_2^2 are integrated indicators of the deviations of the partial values of the two compared sample from their corresponding average values, which are calculated by formula:

$$m_1^2 = \frac{S_1^2}{n_1}; \quad m_2^2 = \frac{S_2^2}{n_2} ,$$

where, S_1^2 is the sample variance of the first variable; S_2^2 is the sample variance of the second variable; n_1 is the number of students in the first choice, and n_2 is the number of students in the second choice. In our study the number of students at the beginning and end of the experiment was the same.

Based on the data, we calculate the value of t_{cw}, the data obtained below describe the control work:

$$t_{cw} = \frac{\left|7.37 - 9.5\right|}{\sqrt{\dfrac{2.92}{16} + \dfrac{2.13}{16}}} = 3.78.$$

If we compare the values with the value of the critical distribution of the student, which depends on the number of degrees of freedom, then the probability of error obtained from the error is equal to $f = n_1 + n_2 - 2 = 16 + 16 - 2 = 30$. If $f = 30$, then the critical value, according to a special table, is 3.646. The value of 3.78 is greater than the value of 3.646, so the significance level is less than 0.001. These indicators were higher than the critical value of Student's distribution. The fact that the probability of errors made is equal to or less than 0.01 is sufficient to draw scientifically reliable conclusions, that is, the correctness of the proposed research forecast is proved.

To determine the effectiveness of working with the glossary and the text in English when teaching inorganic chemistry classes in the online format a survey was conducted. The effectiveness of working with a text in the English language in the workshop classes of Inorganic Chemistry during online training was studied in a group work together with the CLIL method. During the seminar sessions a glossary was worked out to improve students' assimilation of English text. Working with the glossary allowed students to better remember definitions related to the topic.

The results of the survey on the effectiveness of working with English text are shown in Figure 2.
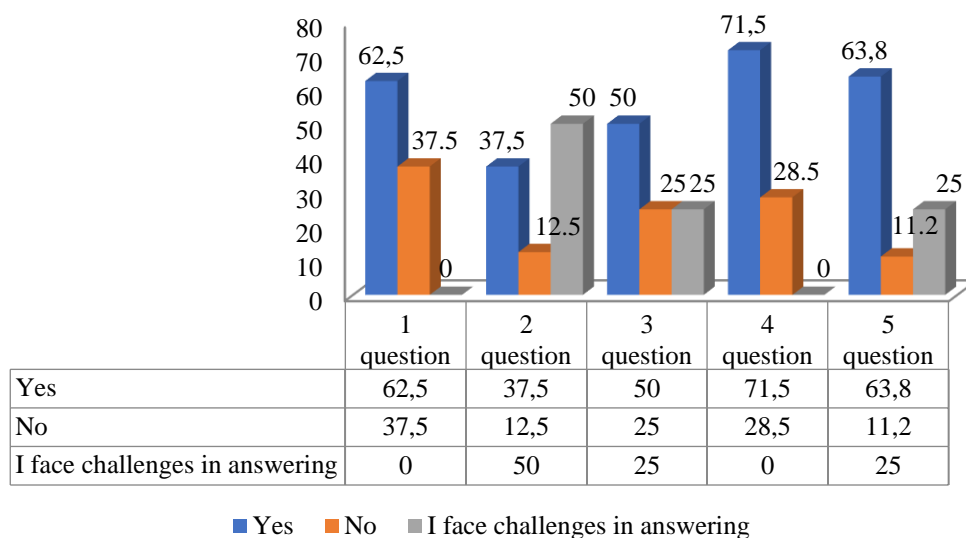
Figure 2. The results of a survey taken during an online lesson
to determine the effectiveness of working with the English text

During the experiment the average result of the second midterm control grades of students of the control group during online training was 86.71, and the average result of the second midterm control grades of students of the experimental group was 90.17 (Fig. 3). This difference means that learning using the CLIL method has shown positive results. Since they are students of the 1st year, they are not trained in direct communication with the teacher and students of the group, it was difficult to immediately get used to the new format. However, in the online format explanatory seminars and consultations were held in ZOOM, and students adapted to the new learning format. As a result, the effective methods used in the lesson and the learning results were positive.
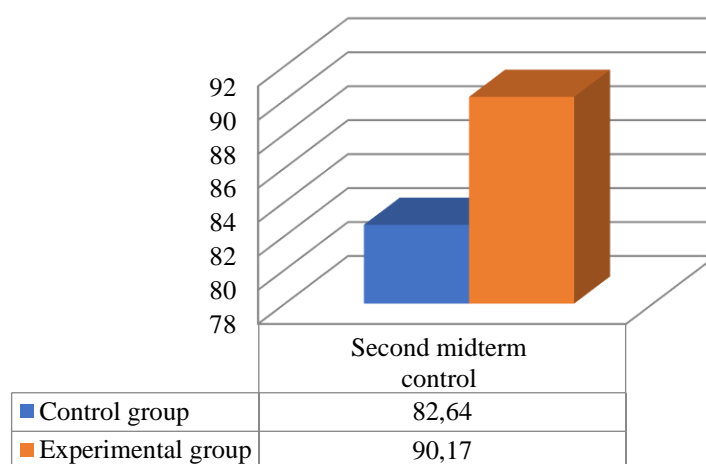
Figure 3. Results of the second midterm control grades of students
of the control and experimental groups

Conclusion

The conducted pedagogical experimental work showed the effectiveness of teaching Inorganic Chemistry classes in English based on the subject-language integrated method. As a result of the proposed research, students of the experimental group showed a higher level of language and subject competence in teaching in an online format than in the control group. The positive dynamics of the development of these competencies was characterized by the fact that the teaching of subject knowledge in English is carried out through the use of

certain teaching methods, in particular, the use of terminology and glossary, working with English text, that is, the use of the CLIL method.

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Р.Н. Нұрділлаева, Г.Ө. Жуман

Бейорганикалық химия пәні сабақтарында CLIL әдісін қолдану

Мақалада бейорганикалық химия пәні сабақтарын ағылшын тілінде кіріктіре оқытуда CLIL әдісін қолдану ерекшелігі қарастырылған. Студенттердің пәндік және тілдік дағдыларын қалыптастыру мақсатында пән мен тілді кіріктіре оқытуда – CLIL әдісі онлайн оқыту форматында зерттелді. В012 Химия мұғалімдерін даярлау білім беру бағдарламасы тобының бірінші курс студенттеріне бейорганикалық химия пәні сабақтары онлайн форматта бақылау тобына дәстүрлі, ал эксперименттік топқа CLIL әдісін қолдану арқылы өткізілген. Эксперимент үшін студенттер кездейсоқ әдіспен емес, кіріс бақылауы негізінде ағылшын тілі мен пәнді білу деңгейі бойынша таңдалды. Педагогикалық эксперименттте алынған нәтижелердің сенімділігін растау және іріктеменің репрезентативтілігін дәлелдеу үшін математикалық статистика әдісі қолданылды. Стьюдент *t*-критерий әдісі арқылы ұсынылған зерттеу болжамының дұрыстығы дәлелденді. Студенттердің білім деңгейлері оқытудың нәтижелеріне сәйкес құзыреттіліктерге сай қорытындыланды. Сабақ барысында CLIL технологиясын қолдануда терминология, глоссарий, ағылшын тілінде негізделген мәтінмен жұмыстар жасалды. Ағылшын тілінде берілген мәтін мен сауалдармен жұмыс жасауда студенттердің тілдік құзыреттіліктері дамыды. Терминология, глоссарий, ағылшын тілінде дайындалған мәтінмен жұмыстардың тиімділігі студенттерден алынған сауалнама нәтижесінде анықталды. Сонымен қатар, мақалада бақылау тобы және эксперименттік топ студенттерінің онлайн форматта оқыту кезінде аралық бақылау нәтижелерінің салыстырмалы көрсеткіштері де келтірілді. Жан жақты зерттеу жұмысының нәтижесінде студенттердің CLIL әдісіне деген қызығушылықтары артқаны, білім алу процесіне жағымды әсер еткені айқындалды.

Кілт сөздер: CLIL әдісі, бейорганикалық химия пәні, онлайн формат, оффлайн формат, пән мен тілді кіріктіре оқыту, глоссарий, ағылшын тіліндегі мәтінмен жұмыс, құзыреттілік.

Р.Н. Нурдиллаева, Г.О. Жуман

Применение метода CLIL на занятиях по неорганической химии

В статье рассмотрены особенности применения метода CLIL при интегрированном преподавании занятий неорганической химии на английском языке. С целью формирования предметных и языковых навыков студентов был изучен метод интегрированного преподавания предмета и языка – метода CLIL в формате онлайн обучения. Занятия по неорганической химии для студентов первого курса группы образовательной программы В012 подготовки учителей химии проводились в онлайн формате для контрольной группы традиционно, и для экспериментальной группы методом CLIL. Для эксперимента были отобраны студенты не случайным методом, а по уровню знания английского языка и предмета на основе входного контроля. В педагогическом эксперименте для подтверждения достоверности полученных результатов и доказательства репрезентативности выборки использован метод математической статистики. Доказана правильность гипотезы исследования, предложенного методом *t*-критерия Стьюдента. Уровни знаний студентов обобщены в соответствии с результатами обучения согласно их компетенциям. На занятиях были проведены работы с терминологией, глоссарием, подготовленным текстом на английском языке при использовании технологии CLIL. Языковые компетенции студентов развивались при работе с текстами и вопросами на английском языке. Эффективность работы с терминологией, глоссарием и текстами на английском языке определяли анкетированием студентов. Кроме того, в статье приведены сравнительные показатели результатов промежуточного контроля при обучении студентов контрольной и экспериментальной групп в онлайн формате. В результате всестороннего исследования выявлено повышение интереса студентов к методу CLIL, что положительно сказалось на образовательном процессе.

Ключевые слова: метод CLIL, неорганическая химия, онлайн формат, оффлайн формат, интегрированное обучение предмету и языку, глоссарий, работа с текстом на английском языке, компетентность.

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Chemistry textbooks as a means of supporting cognitive activity of general secondary education students

The article is devoted to such new direction of research as creating textbooks that provide competency-based approach to teaching Chemistry. A brief description of the results of the analysis of scientific literature on the research topic is presented. Based on them, it was concluded that it is necessary to develop a concept for creating Chemistry textbooks that would allow realizing the competence potential of academic subject. The main provisions of the author's concept are stated. According to them, the textbook should equally present its content and procedural components, which can ensure the formation of students' key and subject competencies. The author's rubrication of the textbooks is presented: "After mastering the material of the unit, you will be able…", "Remember! Pay attention!", "Chemistry is life: a naturalist's page", "Briefly about the main thing", "Erudite page", "Work in groups", "We work with media sources", "We know, we understand", and "We apply". The design of the units is briefly described. The embodiment of the conceptual provisions in school Chemistry textbooks for grades 8–11 created by the author is revealed on specific examples.

Keywords: author's concept, Chemistry textbooks, competence-based approach, key competencies, main provisions of the concept, subject competence, textbook content and procedural components, textbook rubrication, unit design.

Introduction

New goals and content of complete general secondary education in Ukraine require the creation of modern educational books, among which textbooks are of main importance. Even the rapidly developing electronic teaching aids just supplement textbooks, contribute to the implementation of their functions, but in no way replace them. Currently in pedagogy there is a need to develop new approaches to the creation of textbooks, including Chemistry ones.

According to the Law of Ukraine "On Education", achieving the goal of secondary education "is provided by the formation of key competencies needed by every modern person for a successful life" [1]. According to the new paradigm, the content of teaching Chemistry "retains the time-tested basic core necessary for students' education and development; reveals the general cultural, humanistic nature of natural science knowledge; is based on leading worldview ideas of natural science" [2].

The competence-based approach was introduced in Ukrainian schools not long ago, but it has proved to be modern and effective. Therefore in the Chemistry curricula improved in 2017 it is noted that the main task of school chemistry education "is to form key and subject competencies by means of the academic subject. They also ensure developing students' values and worldview, which determine their behavior in real life situations" [1]. One of the characteristic features of these programs in comparison with the previous ones is the expression of learning outcomes in terms of competence. In the program section "Expected results of educational and cognitive activity", the main learning outcomes indicate the components of students' subject chemical competence to be formed: cognitive, activity and value. On the one hand, it is helpful for the authors of textbooks, since the circle of results in which the textbook plays an important role is outlined. But, on the other hand, in view of the fact that "thorough pedagogical research on the definition and justification of the competencies of modern textbooks, the allocation of requirements for the textbook as a comprehensive information model and learning tool in the context of implementing a competency-based educational approach" [3: 37], each author or group of authors have to theoretically substantiate the conceptual provisions of the textbooks they create.

The object of the research is the means of teaching Chemistry, and its subject is the structure, content, and methodological apparatus of a modern Chemistry textbook for students of general secondary education. The purpose of the article is to reveal the author's concept of creating modern Chemistry textbooks for students of Ukrainian schools. The tasks of the article is to substantiate the concept of creating a modern Chemistry

textbook; describe the structure of the author's Chemistry textbooks; confirm implementation of provisions of the concept by examples from Chemistry textbooks for pupils of 8–11 classes.

The article is structured as follows: a brief description of the results of the analysis of scientific literature on the research topic; statement of the main provisions of the author's concept; description of the structure of the textbooks created on its basis; specific examples from the Chemistry textbooks created for students of grades 8–11 [4–7].

Methods and Materials

Taking into account the peculiarities of the research, methods of analysis of literature sources and generalization of the results were used; analysis of documents (curricula, programs, educational standards) was done. Induction and deduction, studying the experience of creating textbooks, conducting a search and pedagogical experiment were applied. The materials used in the study were school Chemistry curricula, Chemistry textbooks by domestic and foreign authors, as well as statistical data of the Ministry of Education and Science of Ukraine on the testing of school textbooks. Quantitative (in %) indicators of students, teachers, and parents' satisfaction with school Chemistry textbooks recommended by the Ministry of Education and Science of Ukraine for use in the educational process were taken into account.

Results and Discussion

In the study state documents regulating secondary education, recent scientific publications by Ukrainian scientists on similar research topics (E. Baranovskaya, Y. Kodlyuk, O. Topuzov, etc.) served as a reference point in the development of the concept of creating textbooks on Chemistry on a competency basis. As the analysis has shown, Y. Kodlyuk has been studying the problem of textbooks for primary school children for a relatively long time. In one of the latest publications by the researcher [8], attention was focused on the informational, developmental, educational and motivational functions of a modern textbook for younger students. A. Polyakova listed the following didactic features of a school textbook: "functional features, the nature of the reflection of the content of education, structural features, and the technology of presentation of the means of guiding the cognitive activity of students" [8: 284]. We share the researcher's views on a school textbook as "a type of educational literature that represents knowledge and activities in a particular subject in accordance with state educational standards and curriculum requirements, taking into account the characteristics of this subject (its dominant function), type of school, age characteristics of students and is based on the dominant concept of learning" [8: 285]. In our opinion, this definition, on the one hand, has accumulated the classical views on the textbook developed in the 70s-80s of the twentieth century (Y. Babansky, I. Lerner, N. Skatkin, V. Kraevsky, etc.). On the other hand, such an interpretation makes it possible to supplement and clarify the definition of a textbook in accordance with the ongoing transformations in education. In view of the above mentioned, application of the competency-based approach in the educational process is considered the dominant concept of modern education. Y. Kodlyuk emphasized that the textbook "is a kind of scenario for the future learning process, as it captures not only the content of the subject, but also the main methodological approaches to its teaching, individual teaching methods (e.g., questions to analyze illustrations; samples of algorithms, instructions; sample records; instructions for doing practical tasks, etc.)" [8: 290].

The development of the main provisions for the creation of textbooks outlined by Y. Kodlyuk can be found in the publications of E. Baranovskaya and O. Topuzov. In particular, E. Baranovskaya pointed out that "the school textbook has to perform cultural, ethical and humanistic, reflective, personal and developmental functions in addition to its basic functions" [9: 10]. In the researcher's opinion, it is important for modern textbooks to focus on "humanitarian content of social sciences and humanities and to strengthen the humanitarian component in the content of the natural and mathematical cycle" [9: 6].

The following opinion of O. Topuzov seems to be constructive: "In order to create conditions for the formation of these components of personality competence in the process of learning the content of education, it is necessary to develop and implement an appropriate apparatus for learning, which creates additional burden on the non-textual component of the textbook" [3: 39]. Equally important is the view of the researcher that "a modern textbook, built on the competence basis should provide for the possibility of using a variety of organizational forms and methods of teaching and enrich their arsenal. In particular, it must create conditions for student self-educational activities" [3: 39].

Stará, M. Chvál, K. Starý pointed out the importance of high-quality school textbooks not only for schoolchildren and teachers, but also for students of higher teacher education institutions [10]. They explained it by the fact that it is sometimes difficult for students in pedagogical practice to fully select educational material,

independently develop a methodology for its presentation, and test the knowledge acquired by schoolchildren. Therefore, student teachers often fully focus on the layout of textbooks and follow it.

It is known that the central link of educational activity is assimilation of knowledge as "complex intellectual activity of a person, including all cognitive processes (sensory perceptual, mnemological), providing reception, semantic processing, preservation and reproduction of the received material" [11].

Therefore, a textbook should perform different functions and at the same time be accessible for perception and understanding.

Based on the study of the researchers' interpretations of the creation and content of textbooks corresponding to the new paradigm of education using a competency-based approach, the following conclusions were made:

• a textbook is a leading and multifunctional teaching tool;

• educational material, teacher activities, and student activities are a kind of equilateral triangle that determines the content of the school textbook.

That is, conceptually, a textbook should equally represent the educational material, students' activities and teacher activities, remaining an important educational book for students.

Based on the above-mentioned, the content of a textbook is made up of educational material that reveals the core knowledge from various branches of Chemistry, selected and adapted for studying at school.

According to V. Beilinson, the basic and guiding function of textbooks is informational. "A textbook embodies the content of the academic subject and provides a minimum of means for its complete assimilation" [12: 34].

As the analysis of the research sources has shown, a school textbook is a multi-functional tool of teaching and learning, which, in addition to the informative functions, provides:

− motivation to study chemistry;

− a holistic model of the educational process;

− a logical and clear presentation, a thorough explanation of the new material based on a sufficient number of facts and illustrations;

− support for the educational process at all its stages: perception, memorization, application, assessment;

− conditions for the optimal use of individual, group and class educational activities of schoolchildren;

− an individual construct of the cognitive activity of each student;

− formation of cognitive skills and the ability to work with educational literature and other information resources;

− a methodological guideline for teachers.

V. Beilinson gave a clear explanation of the methodological purpose of a textbook: "not only students' activity is programmed in a textbook, but also the supposed activity of a teacher. A textbook not only provides material for teaching, but also defines the basic and main features of the method of working with it, guides the course of learning" [12: 39].

We are far from thinking that Chemistry textbooks should replace collections of problems and exercises (there are a number of manuals for that), or be book for reading on the subject under study. It has to correspond to its purpose. The main requirements for textbooks are: a) to correspond to the cognitive capabilities of students, which means to be available for their perception; b) to have a perfect methodological apparatus, which is easy for students to understand and convenient for a teacher to work with; c) to be of developmental nature, that is, provide the material for the performance of mental operations (analysis, synthesis, comparison, generalization, classification and others; d) to foster independent mastering of the educational material by students.

It is also important for textbooks to meet the basic assessment criteria. Concerning the issue, J. Papajani pointed out, "Evaluation checklists should have some criteria pertaining to the physical characteristics of textbooks such as layout, organizational, and logistical characteristics. Other important criteria that should be incorporated are those that assess a textbook's methodology, aims, and approaches and the degree to which a set of materials is not only teachable but also fits the needs of the individual teacher's approach as well as the organization's overall curriculum" [13: 8]. Due to the indicated multi-functionality, textbooks provide the implementation of the competence-based approach.

Let us reveal how the stated conceptual provisions were embodied in the school Chemistry textbooks designed by the author of the article. Initially, the author's heading of units was developed and then implemented, the same for all textbooks, from the eighth to the eleventh grades [4–7]. Figure 1 contains the names and symbols of these headings.
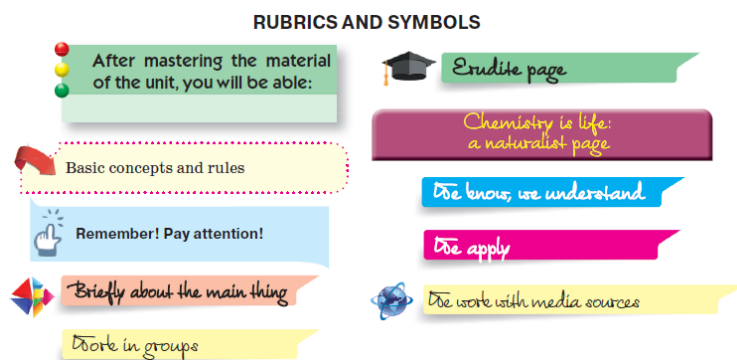
Figure 1. Rubrication of the author's textbooks on Chemistry

The content of the textbooks is compiled in full accordance with the current curriculum in Chemistry. We adhere to the point of view that textbooks are main educational books created primarily for students. Therefore, at the beginning of each topic basic knowledge that students should master in the process of studying the topic as well as skills, values and other qualities that allow the formation and development of subject competence in Chemistry are listed on coloured fly-titles. Methodologically, this is a concise list of expected learning outcomes on a topic. Therefore it serves as a personal educational construct for students, and for teachers it is a methodological guideline for conducting the educational process. It "will orient the teacher on achievement of the purpose of training on each theme of the program, will facilitate planning of the purposes and tasks of lessons, and will give the chance to develop adequate methodical approaches to conducting lessons as well as current and thematic assessment" [2].

Here is an example of the fly-title of topic 2 "Hydrocarbons" (grade 10).

In this theme you will learn about:
− classification of hydrocarbons;
− general formulas, structural isomerism and systematic nomenclature of alkanes, alkenes, alkynes, arenes;
− properties of alkanes, alkenes, alkynes, arenes;
− methods of production, application of hydrocarbons;
− relationships between homologous series of hydrocarbons;
− use of hydrocarbons and their impact on the environment.

After mastering the material on the topic, you will be able to:
− name alkanes, alkenes and alkynes according to the systematic nomenclature;
− give examples of saturated, unsaturated and aromatic hydrocarbons, structural formulas of their isomers;
− explain the essence of the structural isomerism of hydrocarbons; recognize the structural isomers of a substance;
− make molecular and structural formulas of hydrocarbons of a certain homologous series based on the general formula;
− compose reaction equations that describe the chemical properties of hydrocarbons;
− compare the structure and properties of hydrocarbons;
− solve problems on the derivation of the molecular formula of a substance according to the general formula of a homologous series and density or relative density; the mass, volume or quantity of the reagents or reaction products, justifying the chosen method of solution;
− draw conclusions about the properties of substances based on their structure and the structure of substances, taking into account their properties; on this basis to justify the use of hydrocarbons;
− understand the need to preserve the environment during the production and use of hydrocarbons;
− assess the fire hazard of hydrocarbons and the environmental consequences of violations of technologies for production and use of hydrocarbons and their derivatives" [6: 26].

In the textbooks there is no such heading as "Today in Class", which can be found in many other textbooks. It can be explained by the fact that it is more intended for teachers and is not personally oriented for students. Therefore, in order to impart positive motivation (personal colouring) to learning, in addition to fly-titles, we use two more out-of-text components. The first is the announcement located at the beginning of each

unit "After mastering the material of the unit, you will be able…" and the second announcement "Remember! Pay attention!", which are given in the text itself. For example, from the announcement to unit 11 "The degree of electrolytic dissociation. Strong and weak electrolytes. The concept of the pH of a solution", ninth-graders realize that after learning the material they will be able to "find out what is a quantitative indicator of electrolytic dissociation; get to know the classification of substances by the degree of electrolytic dissociation; learn about the factors affecting the degree of electrolytic dissociation; form an idea of the pH value; distinguish between pH alkaline, acidic and neutral; evaluate the pH value of solutions to determine the quality of food, cosmetics and other types of products" [5: 62].

"Remember! Pay Attention!" announcements concern:

– revising something previously learned, e.g., "Remember! Names of symbols of chemical elements, as well as proper names, are written in capital letters, and the names of substances formed by their atoms – in lowercase (H — Hydrogen, O — Oxygen, H_2 — hydrogen, O_2 — oxygen)" [4: 7];

– short-term completion of a specific task in the course of working out educational material, e.g., "Use this pattern to find out: which of the elements of group II of the main subgroup — Magnesium or Calcium — has more pronounced metallic properties; in Oxygen or Sulfur (group VI main subgroup) more pronounced non-metallic properties" [4: 52];

– clarifications to the main text e.g., "Amorphous is one that has no crystalline structure. Amorphous is a substance without a clear three-dimensional arrangement of structural particles" [4: 106];

– precautions when working with chemical substances e.g. "Remember that ethyne (acetylene) with air and oxygen forms explosive mixtures" [6: 55] and others.

The text of each unit is divided into logically complete blocks of educational information. The blocks have titles, from which students find out what the unit is about, and after studying it, they can give feedback. For example, unit 18 of the textbook for 11 grade "Compounds of non-metallic elements with Hydrogen. Features of aqueous solutions of these compounds, their application" is divided into seven blocks. They go under the following titles: physical properties of hydrogen chloride, physical properties of ammonia, features of aqueous hydrogen chloride solution, features of aqueous ammonia solution, ammonium hydroxide NH_4OH, the concept of ammonium salts, and qualitative reaction for the determination of ammonium ions in solutions.

The final informational part of the main text of each unit in the textbooks has the heading "Breifly about the main thing". In it, in a generalized way, with several rules, judgments, conclusions, the main things in the educational material of the unit are conveyed. As practice shows, students willingly work with this rubric, since it focuses on what should be preserved in long-term memory and will be used in the future.

In order for the textbook to be involved in the formation of the key competence of students' communication in the state language (or native one), to form the ability to work in a team and to develop leadership qualities, the column "Work in groups" was created. According to the curriculum, the subject content of the specified competence consists of the following skills: "to use chemical terms, concepts, symbols, modern Ukrainian scientific terminology and nomenclature in speech; give answers to the questions; substantiate the course and conditions of the chemical experiment; discuss the results of the study and draw conclusions; to take part in the discussion of issues of chemical content, to express one's opinion clearly, clearly and figuratively; compose an oral and written report on a chemical topic, and present it" [1]. It is obvious that during the study of Chemistry (as a rule, there are two lessons per week) the skills cannot be formed without the use of group educational activities. Whereas working in small groups, even at the stages of primary perception of new material, students are involved in educational communication, favorable for the formation of that and other competencies. Here an example of the content of the heading "Work in groups" in the above-mentioned unit 18 of the textbook for 11 grade is given.

Task 1. Prove by mathematical calculations that it is necessary to collect ammonia in a test tube located upside down.

Task 2. Ammonia is sold in a dark glass container with a capacity of 150 ml in pharmacies. Assuming that the density of ammonia is 1 g per 1 ml, calculate the amount of ammonia used to prepare the solution for one such vial.

Task 3. Calculate the relative density of hydrogen chloride in the air. How to collect this gas in a test tube properly?

Task 4. From the section, you learned what the solubility of ammonia in water is. Calculate the mass fraction of this substance in a solution made by dissolving 700 liters of ammonia in 1 liter of water, if the density of the solution is considered to be equal to 1 g / ml [7: 96–97].

In addition, short-term group educational activities in the lesson of studying new material help to avoid a teacher monologue and promote the understanding and assimilation of new knowledge directly in the lesson, involving students in active cognitive activity, and intensifying the educational process.

The heading "Erudite Page" has an additional text that allows students to expand and deepen the content of the main material of the unit thanks to the information that is not provided by the program, but corresponds to the topic of the unit. The tasks of the rubric stimulate cognitive interest, motivate learning the history of science, develop thinking, and enhance patriotic education. For example, the main material of the unit on the structure of the atom (grade 8) contains information that, "The scientific assumption about the presence of neutrons in the nucleus was made by a theoretical physicist Dmitry Dmitrievich Ivanenko in 1932" [4]. "Erudite Page" contains some information about D.D. Ivanenko's life and activities in Ukraine, as well as about the period of his work at Lomonosov Moscow State University. It also tells that "the scientific merits of the physicist were highly appreciated by Nobel laureates Paul Dirac, Hideki Yukawa, Niels Bohr, Ilya Prigozhin, and Samuel Ting, who left their famous statements on the walls of Dmitry Dmitrievich Ivanenko's office at Lomonosov Moscow State University" [4: 58]. In the same unit, under the heading "Work with media sources" one of the tasks is formulated as follows "Find out what records were left by Nobel laureates P. Dirac, H. Yukava, N. Bohr, I. Prigozhin and S. Ting on the walls of D.D. Ivanenko's office. Write them down and discuss them in groups" [4: 58].

The attention of schoolchildren to modern sources of information as a means of independent mastering of additional knowledge and skills is attracted by the tasks under the heading "Work with media sources". Often, their implementation involves group work and relates to educational projects. Consider the example from unit 30 "Mineral fertilizers. The concept of acidic and alkaline soils" of the textbook for 11th grade.

1. From various sources learn about the top 10 largest producers of fertilizers in Ukraine (capacity, raw materials, and products).

2. Ask about the professions of employees of modern enterprises for the production of fertilizers, and educational institutions where the necessary qualifications can be obtained.

3. What means of environmental protection from pollution operate in enterprises producing mineral fertilizers? [7: 161].

"Creating a textbook always requires a clear and reasonable answer to the question: what types of problems (exercises) and in what minimum quantity should be in the textbook, and what should be included in an expanded and variable form in the corresponding collection" [12: 38–39]. Adhering to this point of view, we do not overload the textbooks with exercises and tasks; in parallel with them, we created a collection of tasks and exercises, workbooks and notebooks for control and practical work. The assignments and exercises in the Chemistry textbooks are based on competence-based and activity-based approaches. Most of them are located in the final headings of the units entitled "We know and understand" and "We apply". The former contains tasks that require reproduction of knowledge or performing actions according to a model. Here is an example of tasks from paragraph 16 "The nature of chemical bonding and electronegativity of atoms of chemical elements" of the textbook for the 8th grade.

1. Formulate the definition of: a) chemical bond; b) electronegativity; c) completed energy level.

2. Explain how the structural particles of matter can acquire the completeness of the external energy level. What does it depend on?

3. Indicate which of the two elements is more electronegative: a) Nitrogen or Oxygen; b) Nitrogen or Hydrogen; c) Nitrogen or Lithium.

4. Explain why the electronegativity of atoms of inert elements is zero" [4: 96].

To fulfil the assignments under the heading "We apply", students need to apply the knowledge gained in standard or modified conditions. In the above-mentioned unit, the heading consists of the following tasks:

1. In which of the molecules: a) Oxygen; b) water; c) Hydrogen; d) hydrogen bromide — common electrons will be displaced to one of the atoms and why?

2. Specify a pair of symbols of elements whose atoms have the same number of unpaired electrons at the external energy level: a) Li and S; b) Mg and F; c) Li and F. Explain your choice using graphical electronic formulas.

3. Write down the symbols of the following chemical elements in ascending order of their electronegativity: Aluminum, Sulfur, Carbon, and Hydrogen.

4. Prepare questions or tasks on the topic of the unit to suggest them to classmates in class" [4: 96].

As it can be seen from the considered example, the tasks under the heading "We apply" are numbered consecutively in the textbooks, which is very convenient, since the answers are given at the end of the textbook, and students can do self-tests.

Tasks for consolidating and applying the knowledge can also be found under the heading "Work in groups", for example:

1. To ensure that alcohols have more isomers than their corresponding alkanes, formulate all possible isomers of alcohol with the molecular formula $C_5H_{11}OH$ (there should be 6 of them) and pentane.

2. Make one molecular formula of homologues: a) propane; b) methane; c) ethyn [6: 22].

Each topic ends with a page "Assignments of different difficulty levels". The tasks help students to do self-assessment, monitor personal growth, and reflect on educational achievements.

It is well-known that a chemical experiment is an important means and method of teaching Chemistry. Therefore, the sequence of the teacher's performance in the lesson of demonstration experiments, the necessary explanation, as well as illustrations to them are displayed in the main text of the units so that, while working independently with the text of the unit, the students can mentally reproduce the experiment. Traditionally, Chemistry textbooks contain tasks and instructions for performing a school chemistry experiment: laboratory experiments and practical work. In the textbooks, they go under the heading "Chemistry is Life. Naturalist's Page". Description of laboratory experiments contains a list of equipment and substances, instructions for their implementation, which displays the sequence of actions, advice on the presentation of results. Since practical work has a different didactic purpose than laboratory experiments, textbooks contain only the name of the practical work and the texts of assignments for practical implementation. In the content of practical work on solving experimental problems, we strive to include a deliberately larger number of tasks than the students will complete in one lesson. It is aimed at students repeating the material they have covered, getting better prepared for practical work, conducting experiments on all the options of the proposed tasks in their minds. For example, in the Chemistry textbook for the 9th grade for practical work 2 "Solving experimental problems", five experimental problems were selected (three variants of tasks in each). It is illustrated by an example of experimental problem 3: "Carry out ion exchange reactions according to the given schemes.

Variant 1. Sodium hydroxide → sodium sulfate → sodium chloride.

Variant 2. Chloric acid → sodium chloride → sodium nitrate

Variant 3. Cuprum (II) sulfate → Cuprum (II) chloride → Cuprum (II) hydroxide.

Justify the choice of reagents. Make up the corresponding molecular and ionic reaction equations [5: 85]. In practical work students perform only one of those variants that the teacher suggests.

In school textbooks, an important didactic function is performed by illustrative material. "Several factors should be considered, such as the clarity and coherence with which information in graphic visualisations is presented. A textbook layout that guides the learner through the depicted resources and enables the student to easily identify relevant information, includes visual and textual linking between related materials, and the instructional, didactical, technical and aesthetic quality of depicted visuals, to name only a few" [14: 56].

There are many illustrations in the textbooks. The choice of illustrative material is due to its didactic function. All illustrations correspond to the content of the educational material, help its perception, memorization and reproduction, contribute to the development of visual memory, and are used in performing tasks. For example, Figure 2 [4: 194] is an illustration of the experiment to identify the amphoteric properties of zinc hydroxide.
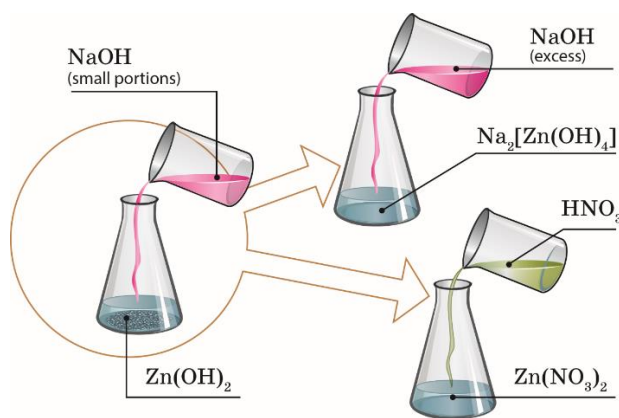
a — extraction of zinc hydroxide; *b*, *c* — dissolution of the precipitate $Zn(OH)_2$

Figure 2. The sequence of the experiment on the detection of amphotericity of zinc hydroxide

Conclusions

The reorientation of teaching Chemistry in modern secondary educational institutions from communicating knowledge to the formation of key and subject competencies determines the relevance of research on the problem of creating textbooks that correspond to this paradigm. As in the course of the study of research papers on the topic there was found lack of concept of creating textbooks that provide teaching Chemistry on a competence basis, and the educational process needed them; the author's concept of textbooks was created that allows to realize the competence potential of this academic subject.

The main provisions of the author's concept are the optimal combination of the content and procedural components of the textbook; taking into account the cognitive capabilities of students; the presence of a perfect methodological apparatus; the suitability of the textbook for use at all stages of the educational process such as perception, memorization, use, assessment; the possibility of conducting group educational activities along with individual and class work; a convenient navigator in the form of headings; modernity and attractiveness of design; and variety of illustrative material.

In accordance with the provisions of the concept, the headings of the author's textbooks of chemistry were substantiated and developed: "Work in groups" (contains tasks for short-term group work in the lesson of studying new material), "Chemistry is life: a naturalist's page" (a student experiment is described. "Briefly about the main" (a generalization of the material of the paragraph is made.) The headings "We know, we understan", "We apply" contain tasks and exercises differentiated by the level of students' cognitive activity. Additional material has been placed in the rubric "Erudite page", tasks involving use of media go under the heading "Work with media sources". In addition, an important motivational function is performed by coloured fly-titles for each educational topic and the following announcements "After mastering the material of the unit, you will be able…"; "Remember! Pay attention!" To use the visual memory of students, the main text of the units is divided into logically completed blocks of the educational information with colored titles; and various illustrative materials are used.

Rubrics of the units and the design of their layout serve as a convenient navigator for students while working with the textbooks. This conclusion is confirmed by the examples considered in the article from the author's Chemistry textbooks for 8–11 grades.

The textbooks of Chemistry that were created on a competence basis do not leave room for authoritarian pedagogy. They provide students with an individual construct of cognitive activity, and give teachers methodological guidelines for planning and implementing the educational process on a competency-based approach. Learning by them involves various activities and communication.

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О.Г. Ярошенко

Химия оқулығы жалпы орта білім беру мекемелері оқушыларының танымдық іс-әрекетін ұйымдастырудың құралы ретінде

Мақала зерттеудің жаңа бағытына, яғни оқушыларды құзыреттілік негізінде оқытуды қамтамасыз ететін оқулықтар жасауға арналған. Зерттеу тақырыбы бойынша ғылыми әдебиеттерді талдау нәтижелері қысқаша сипатталған, химия оқулықтарын құру тұжырымдамасын әзірлеу қажеттілігі айтылған, бұл оқу пәнінің құзыреттілік әлеуетін іске асыруға мүмкіндік береді. Авторлық тұжырымдаманың негізгі ережелері: оқушылардың танымдық мүмкіндіктерін ескеру; мінсіз әдістемелік аппараттың болуы; оқулықтың оқу процесінің барлық кезеңдерінде қолдануға жарамдылығы; топтық оқу қызметін ұйымдастыру мүмкіндігі; тақырыптар түріндегі ыңғайлы мәтін навигаторының болуы; дизайнның қазіргі заманға сай болуы; иллюстративті материалдың әртүрлілігі. Авторлық оқулықтардың рубрикасы ұсынылған. «Топпен жұмыс» айдарында жаңа материалды үйрену сабағында қысқа мерзімді топтық жұмыстарға арналған тапсырмалар берілген. Оқушылардың тәжірибесі «Химия — өмір: табиғатты зерттеушінің парағы» айдарында сипатталған. Материалдың қысқаша мазмұны «Басты нәрсе туралы қысқаша» айдарында келтірілген. Тапсырмалар мен жаттығулар «Біз білеміз, түсінеміз», «Біз қолданамыз» атты айдарларға бөлінген. Қосымша материал «Эрудит беті» және «Медиадереккөздермен жұмыс» айдарында келтірілген. Параграфтардың дизайны қысқаша сипатталған. Параграфтар «Параграфтың материалын пысықтағаннан кейін сіз жасай аласыз» деген хабарландыруымен басталады. Параграфтардың негізгі мәтіні әртүрлі иллюстрациялық материалдармен және «Есіңізде сақтаңыз! Назар аударыңыз!» сияқты түрлі бейнелі материалдармен жабдықталған. Жаңа ұғымдар мен ережелер түрлі-түсті беттерде орналасқан. Автордың 8-11 сыныптарға арналған химия оқулықтарынан алынған нақты мысалдары тұжырымдаманың негізгі ережелерінің орындалуын растайды.

Кілт сөздер: химия оқулығының авторлық тұжырымдамасы, параграфтарды жобалау, құзыреттілікке негізделген тәсіл, негізгі құзыреттер, тұжырымдаманың негізгі ережелері, пәндік құзыреттілік, оқулық тақырыбы, оқулықтың мазмұны және процедуралық компоненттері, химия оқулығы.

О.Г. Ярошенко

Учебник химии как средство организации познавательной деятельности учащихся учреждений общего среднего образования

Статья посвящена новому направлению исследований — созданию учебников, обеспечивающих обучение учащихся на компетентностной основе. Кратко описаны результаты анализа научной литературы по теме исследования, отмечена необходимость разработки концепции создания учебников химии, позволяющей реализовать компетентностный потенциал этого учебного предмета. Основными положениями авторской концепции являются: учет познавательных возможностей учеников; наличие совершенного методического аппарата; пригодность учебника к использованию на всех этапах образовательного процесса; возможность организации групповой учебной деятельности; наличие удобного навигатора текста в виде рубрик; современность дизайна; разнообразие иллюстративного материала. Представлена рубрикация авторских учебников. Рубрика «Поработайте группами» содержит задания для кратковременной групповой работы на уроке при изучении нового материала. Ученический эксперимент описан в рубрике «Химия – это жизнь: страница природоисследователя». Обобщение материала приведено в рубрике «Коротко о главном». Задания и упражнения дифференцированы на рубрики «Знаем, понимаем» и «Применяем». Дополнительный материал вынесен в рубрики «Страница эрудита» и «Работаем с медийными источниками». Кратко описан дизайн параграфов. Параграфы начинаются анонсом «Проработав материал параграфа, вы сможете». Основной текст параграфов скомпонован в логически завершенные блоки учебной информации, сопровождается разнообразным иллюстративным материалом и анонсами «Вспомните! Обратите внимание!». Новые понятия и правила расположены на цветных плашках. Конкретными примерами из созданных автором учебников химии для 8–11 классов подтверждено воплощение основных положений концепции.

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