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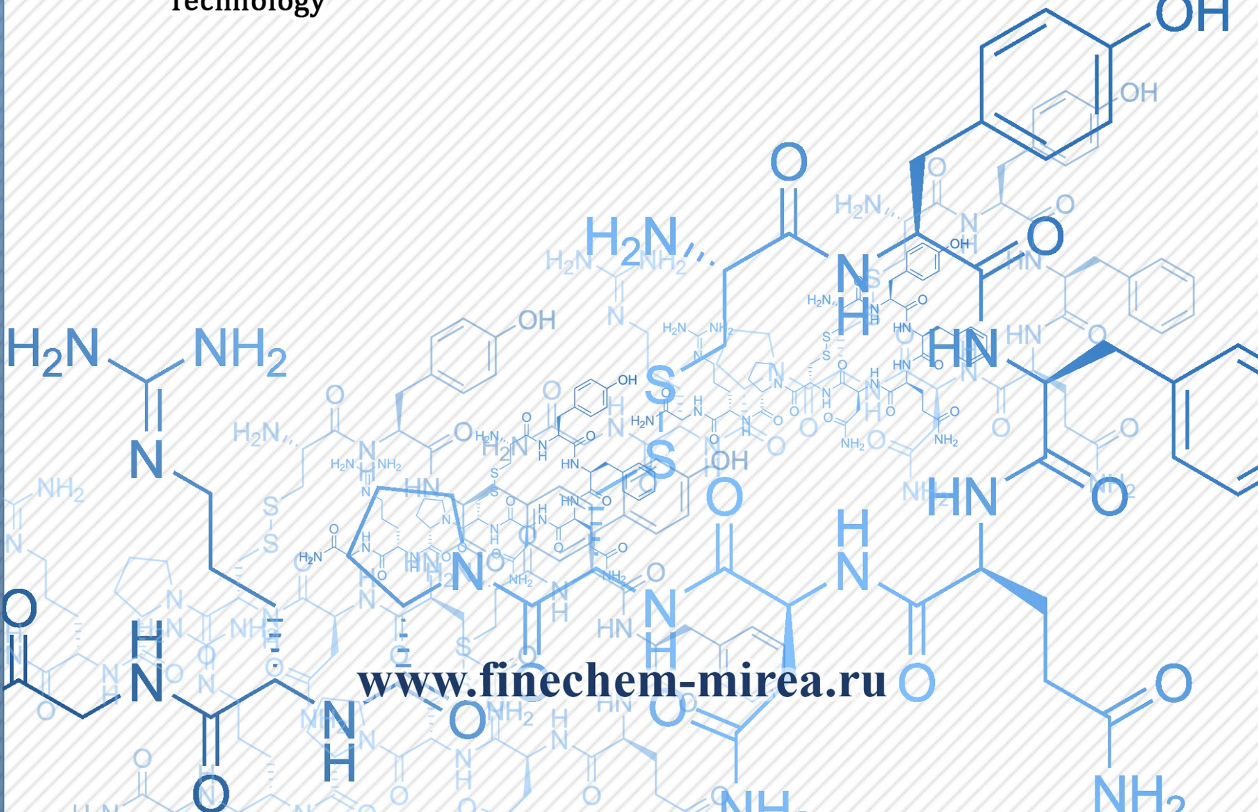
ТОНКИЕ ХИМИЧЕСКИЕ ТЕХНОЛОГИИ
Fine Chemical Technologies

- Theoretical Bases of Chemical Technology
- Chemistry and Technology of Organic Substances
- Chemistry and Technology of Medicinal Compounds and Biologically Active Substances
- Synthesis and Processing of Polymers and Polymeric Composites
- Chemistry and Technology of Inorganic Materials
- Analytical Methods in Chemistry and Chemical Technology
- Mathematical Methods and Information Systems in Chemical Technology



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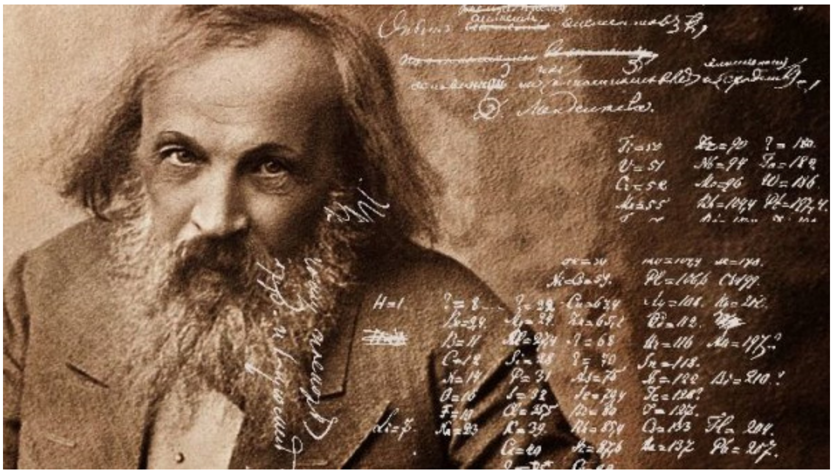
On the 150th anniversary of the D.I. Mendeleev Periodic Table

The year 2019 was a landmark for the world chemistry community, when it was declared by UNESCO the International Year of the Periodic Table of chemical elements[1]. The discovery of the periodicity of changes in the properties of elements, the design of these patterns in a table, the powerful predictive power of the Periodic Law are the brilliant achievements of Dmitry Ivanovich Mendeleev[2]. They reflect such important modern criteria for fundamental knowledge as systematic thinking, the possibility of scientific forecasting, and reprography (compression) of information. Today, mastery of these concepts characterizes the scientific culture and maturity of a researcher. They are actively used in scientific practice, including in the development of high-tech chemical technologies.



With his discovery, Dmitry Ivanovich demonstrated a magnificent example between the logical relationship of content and form. A series of scientific articles in the journal Fine Chemical Technologies, represented by its authors, the editorial board, the entire faculty and research staff of the M.V. Lomonosov Institute of Fine Chemical Technologies RTU MIREA pays tribute to the greatness of this Russian scientist.

A new impulse to modern ideas about the predictive power of the Periodic Law and the possibilities of its application was given by quantum mechanics that originated in the 1930s. Based on fundamental discoveries in the field of atomic structure, its most important section – quantum chemistry – made it possible to explain the nature of chemical bonds, the stability of chemical systems, and to predict the formation mechanisms for organic and inorganic compounds. The generally recognized leader in this field in Russia was Yakov Kivovich Syrkin, whose 125th birthday is being celebrated these days. Academician Ya.K. Syrkin made an outstanding contribution to the development of the fundamental branches of physical chemistry – chemical thermodynamics, kinetics, structural theory, and the nature of the bonding of chemical compounds. His foundational work allowed for the rational application of various research methods – spectral, magnetic, resonance, and x-ray – to establish new types of chemical bonds and fine effects in organic and metalloorganic chemistry.

The true triumph of the Periodic Law is the Soviet atomic project, covering the entire Periodic Table of chemical elements: from the first element in the table (hydrogen) to the last at the time of the project's completion (plutonium). In an article by Professor R.E. Kuzin, based on rare open publications, the main stages and chemical-technological problems of creating the nuclear shield, in other words atomic and thermonuclear weapons, are taken into consideration. New fundamental results are given on the chemistry and technology of isotopes of hydrogen, lithium, beryllium, polonium, uranium and plutonium, which have significantly expanded the Periodic Table. A noteworthy publication is that (Professor T.M. Buslaeva, et al.) dedicated to ruthenium – one of the most interesting elements in the D.I. Mendeleev

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[1] https://iypt2019.org

[2] Photo: www.globallookpress.com

Periodic Table, discovered 175 years ago by the outstanding Russian chemist Karl Karlovich Klaus. The "youngest" stable element of the Periodic System, dvi-manganese, also known as rhenium, predicted by D.I. Mendeleev, the history of its discovery, the many uses of rhenium and its compounds in Russia are described in an article by Professor D.V. Drobot and a co-author.

In general, the history of the discovery and use of chemical elements is closely connected with the history of mankind and is fraught with many mysteries. One of them is associated with element No. 13 in the D.I. Mendeleev Periodic system, aluminum. Professor P.P. Fedorov, et al. presented a possible scenario of the ancient Roman technology for producing aluminum. Based on modern ideas about chemical transformations and known technological parameters, the authors conclude that the main components in the process of producing metal aluminum from an unknown Italian master could be available. However, the likelihood of this creative process, in the opinion of the authors, is quite low.

This year's 29th Mendeleev Competition of chemistry students was also marked by the 150th anniversary of the Periodic System of Elements, which gave solemnity, significance and a sense of youth involvement in great discoveries. The lecture that was delivered by Doctor of Sciences Sergey Nikolaevich Dmitriev, Director of the Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, showed the results of the contemporary work of Russian nuclear physicists, physicists and chemists, and technological equipping of research. As a result of close scientific cooperation between Russian and foreign scientists, four superheavy elements in the Periodic Table were discovered with the atomic numbers 113 (nihonium), 115 (moscovium), 117 (tennessine), and 118 (oganesson). Such achievements fill the hearts and minds of young scientists with pride and are the best motivation for serving science "to the true benefit and glory of the Fatherland" as said by another great Russian scientist Mikhail Lomonosov.

Alla K. Frolkova

Translated by H. Moshkov

ON THE 150TH ANNIVERSARY OF THE D.I. MENDELEEV PERIODIC TABLE OF CHEMICAL ELEMENTS
К 150-ЛЕТИЮ ПЕРИОДИЧЕСКОЙ ТАБЛИЦЫ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ Д.И. МЕНДЕЛЕЕВА

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Periodic Table of chemical elements and Soviet atomic project[1]

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The Soviet atomic project, also known as the nuclear shield, is a true triumph of the Periodic Law. Unlike other global projects, it covers the entire Periodic Table of chemical elements: from the first element of the table (hydrogen) to the last one at the time of the project's completion (plutonium). The article, based on rare open publications, describes the main stages and chemical-technological issues surrounding the creation of atomic and thermonuclear weapons – the main goal of the nuclear shield. New fundamental results of the chemistry and technology of isotopes of hydrogen, lithium, beryllium, polonium, uranium, and plutonium have been obtained that could significantly expand the Periodic Table of chemical elements.

Keywords: *Soviet atomic project, Periodic Table of chemical elements.*

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Периодическая таблица химических элементов и советский атомный проект

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Советский атомный проект или, по-другому, ядерный щит, является подлинным триумфом Периодического закона. В отличие от других глобальных мировых проектов, он единственный охватывает всю Периодическую таблицу химических элементов: от первого элемента таблицы (водорода) до последнего на момент завершения проекта (плутония). В статье на основе редких открытых публикаций рассмотрены основные этапы и химико-технологические проблемы создания атомного и термоядерного оружия – главной цели ядерного щита. При этом получены новые фундаментальные результаты по химии и технологии изотопов водорода, лития, бериллия, полония, урана и плутония, существенно расширившие Периодическую таблицу химических элементов.

Ключевые слова: *советский атомный проект, Периодическая таблица химических элементов.*

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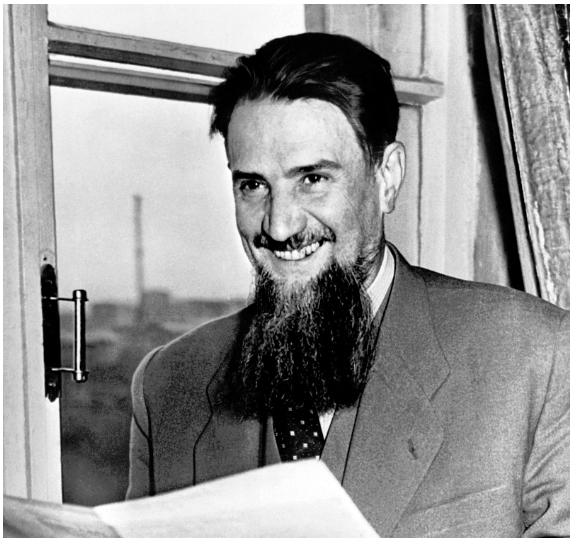
The official start date for the Soviet atomic project (SAP) was September 28, 1942. Today, September 28th is celebrated as the Day of the Nuclear Engineer in Russia. Back then the Chairman of the Council of Defense of the USSR J.V. Stalin (the actual head of state) signed a document "On the resumption of our work on the study of the possibility of obtaining explosives or energy in the fission of uranium nuclei." The basis for such a document was reliable intelligence data that Germany (the Soviet Union's enemy in World War II) and the United States, together with England (the USSR's allies), were secretly developing a new atomic weapon of unprecedented power.

The Soviet Union was shedding blood in the difficult fight against fascism and could not allocate significant resources to the new nuclear project. In addition, at a meeting between J.V. Stalin and luminaries of Soviet science (V.I. Vernadsky, A.F. Ioffe, P.L. Kapitsa, and S.I. Vavilov), the academics all expressed doubt about the creation of the bomb. All this determined the insignificant amount of resources at the project's inception. Special laboratory No. 2 was created to work on the project, headed by Igor Vasil'evich Kurchatov, on the recommendation of A.F. Ioffe. This appointment turned out to be an excellent solution. I.V. Kurchatov was a well-educated physicist-chemist, possessed extraordinary engineering intuition, and before the war he led the uranium group at the Physicotechnical Institute, headed by A.F. Ioffe, and was personally familiar with a very narrow circle of specialists in radiochemistry, chemical physics, and atomic nucleus physics.



Igor Vasil'evich Kurchatov

After the atomic bomb explosions over the Japanese cities of Hiroshima and Nagasaki in August 1945, it became clear that the United States possessed a monopoly on atomic weapons. The response of the Soviet government was instant. On August 20, 1945, the First Main Directorate for the industrial implementation of SAP was created under the USSR Council of Ministers, headed by Minister of Ammunition B.L. Vannikov, and the scientific supervisor was I.V. Kurchatov. The Minister of the Interior, Lavrentiy Pavlovich Beria, was appointed the head of SAP by the Politburo. From this moment, work on the creation of the "Nuclear shield" began developing at a tremendous speed with the involvement of all obtainable resources. And after four years, on August 29, 1949, the first Soviet atomic bomb was detonated. Later on August 12, 1953, a Soviet thermonuclear bomb was detonated. The USA's monopoly on nuclear weapons was eliminated.

The creation of nuclear weapons required tremendous effort from chemists and technologists. New knowledge was gained about the isotopes of many elements and the technologies for their production were developed. New sections appeared in chemical science: radiochemistry, radiation chemistry, nuclear chemistry, and radionuclide control. New subtle chemical technologies for radioactive elements were developed. Many thousands of chemists and technologists worked on the tasks of creating atomic and thermonuclear explosives. And all this took place in an atmosphere of strict secrecy. Very often, even colleagues from one laboratory did not know about the work of their neighbors. Nuclear industry veterans understood this completely: not a single secret flowed from SAP enterprises, and in many areas of chemical technology the Soviet Union was able to significantly overtake its rivals.

And only 50 years after the start of SAP, the leadership of the country and the Ministry of Atomic Energy and Industry of the USSR decided to partially declassify the Soviet Union's achievements in the scientific and technological issues surrounding the creation of the nuclear shield [1–3]. Over that half-century, many active participants in SAP have passed away, and information about their work and achievements must be found in the memoirs of former young employees of institutes and factories, and in separate brochures issued in small print runs (300–500 copies).

A typical example of the loss of detailed information about work in SAP is the situation regarding the remarkable rector of the M.V. Lomonosov Moscow Institute of Fine Chemical Technology, Kirill Andreevich Bolshakov (1906–1992). From the encyclopedia and Wikipedia you can find out that K.A. Bolshakov was a Soviet inorganic chemist, one of the founders of the industry of rare elements in the

USSR. It is also reported that from 1933 to 1971, he worked at the M.V. Lomonosov Moscow Institute of Fine Chemical Technology, having gone from assistant to rector. He was also awarded two Orders of Lenin, received two Stalin Prizes and a high scientific rank as a corresponding member of the Academy of Sciences of the USSR. But the details about his achievements are only in the brochure “The First Lady of Soviet Atomic Science. Collection of articles dedicated to the 100th birthday of Z.V. Ershova” [4].

It turns out that from 1930 to 1947 K.A. Bolshakov was also head of the laboratory at the State Institute of Rare Metals (*Giredmet*), and from 1947 to 1953 – the head of the department in the legendary *NII-9* (now the Academician A.A. Bochvar All-Russian Research Institute of Inorganic Materials). At *Giredmet*, he worked with Zinaida Vasil’evna Ershova to obtain metallic uranium, and then directed solving the problem of producing tritium (the heavy ^{3}H hydrogen isotope) for the first Soviet hydrogen bomb. And then never and nowhere did K.A. Bolshakov mention his participation in this work: he swore to keep these secrets for 60 years.

Kirill Andreevich Bolshakov

As his beloved student and employee Lyudmila Dmitrievna Yurchenko (dean of the faculty T, who was known at all enterprises and institutes in the uranium industry) recalled a direct question: “Kirill Andre’evich! Did you participate in the creation of the atomic bomb?” He answered: “Well what do you think, Lyusenka? Everyone participated. And two groups took away the radioactive elements technology from us. Then they sent them to Mendeleevka ...,” masterfully avoiding answering the question.

Just this one example shows how much invaluable information about the outstanding Soviet developments in chemistry and technology when creating the nuclear shield did not reach the 150th anniversary of the Periodic Table of Chemical Elements (PTCE). The author of the article has worked in the uranium industry for 56 years, the past 20 of which has been enthusiastically spent in the search for materials, memoirs, and articles about the Soviet Union’s remarkable scientific and industrial work in the field of problems with raw materials for SAP. Below, in the main section, we take into consideration some of these developments, which have expanded knowledge about the chemistry and technology of rare PTCE elements.

Atomic Bomb. Uranium, Graphite, Plutonium, Polonium

The atomic bomb (at the first stage plutonium, and then uranium) was created by the Germans, the Americans, and Soviet developers based on the use of fission energy of heavy element nuclei. The main contender, even before the start of the war, for the role of fissile material was the uranium-235 – ^{235}U isotope. However, natural uranium contains only 0.7% of the ^{235}U isotope. The remaining 99.3% is uranium-238. Uranium-238 was not suitable for use as an atomic charge explosive. The absence of a sufficient amount of natural uranium during SAP’s initial stage, the inability to quickly create technology and equipment for enriching natural uranium from the ^{235}U isotope and intelligence data on the efforts of Germans and Americans to develop a technology for producing element number 94 – plutonium-239 led I.V. Kurchatov to the decision to create a plutonium bomb at the first stage. But uranium was also needed to obtain plutonium.

The uranium problem was the most urgent and a very difficult one for SAP. By the beginning of work in 1945, the Soviet Union had only 13.1 tons of uranium ore in the form of dumps for the production of radium-226 in the town of Taboshar, Tajik SSR. No uranium in the USSR was mined or searched for before the start of SAP. First, one had to find the areas of its origin, build mines, and plants for processing ores. The first uranium for the experimental reactor and then the industrial ^{239}Pu production reactor was obtained as a trophy in Germany, which had concentrated uranium salts obtained in the Czech Republic and Belgium (from the Belgian Congo). And only then, thanks to the efforts of Soviet geologists, miners, builders, and chemical technologists, the uranium industry was created, in which at 14 plants up to 25000 tons of natural uranium of nuclear purity were produced up until the 1970s [5–11]. These grandiose successes are rightly connected with the name of the Minister of Secondary Engineering Efim Pavlovich Slavsky [12], three-time Hero of Socialist Labor and ten-time recipient of the Order of Lenin.

Slavsky came to SAP from the post of Deputy Minister of Non-Ferrous Metallurgy. He was awarded three Orders of Lenin for providing the Soviet Union with ultra-deficient aluminum and alloys based on it during the war. In September 1945, L.P. Beria introduced E.P. Slavsky to I.V. Kurchatov, who asked to make a batch of ultrapure graphite used as a thermal neutron moderator for an experimental reactor to produce plutonium from natural uranium. Today, it has become known that Germany significantly overtook the United States in solving the tasks of its nuclear project, but was not able to create a bomb because of an incident called the "Pote – Heisenberg error." Heisenberg, Hitler's favorite who led the atomic project, chose a neutron moderator from two options: carbon in the form of graphite or heavy water. On his instructions, the physicist-chemist Pote checked the possibilities of using graphite, but underestimated the importance of cleaning it from boron. Heisenberg made a mistake in measuring neutron drag. As a result, the use of graphite was rejected, and the Germans were unable to wait for heavy water since all the convoys had been sunk by the British.


Efim Pavlovich Slavsky

At the same time, it was known from intelligence that the Americans had a plutonium reactor filled with graphite, but the technology for its purification was unknown. However, E.P. Slavsky and his colleagues quickly dealt with the problem of producing the required quality graphite. I.V. Kurchatov saw in him not only a well-educated chemist-technologist and metallurgist, but also a brilliant organizer. At his behest, E.P. Slavsky was ordered by Stalin to be transferred to the atomic project.

At first, the extraction and purification of uranium from impurities was carried out at Plant No. 6 (near the city of Leninabad in the Tajik SSR) using the technology developed by Marie Curie at the beginning of the century [6]. Both the quality and the extraction of uranium from the ore were unsatisfactory. Large resources were spent on numerous uranium purification operations. Due to the urgency of the problem of obtaining natural uranium from ore materials, where its mass fraction is only 0.05 – 0.14%, at the initiative of E.P. Slavsky and by order of Stalin on April 19, 1951, a special research institute of chemical technology *NII-10*, now the All-Russian Scientific Research Institute of Chemical Technology was created. During the course of SAP, graduates were recruited into it from the following leading universities: M.V. Lomonosov Moscow Institute of Fine Chemical Technology (more than five hundred people), D.I. Mendeleev Moscow Institute of Chemical Technology (almost seven hundred people), Leningrad Institute of Technology, Faculty of Chemistry, M.V. Lomonosov Moscow State University, and others. A large young team from the All-Russian Scientific Research Institute of Chemical Technology created hundreds of new technologies to produce natural uranium of nuclear purity and many other rare metals. These are mainly ion-exchange sorption and extraction technologies, the introduction of which required new solutions in organic chemistry for the synthesis of ion-exchange reagents. Thanks to this work, the All-Russian Scientific Research Institute of Chemical Technology gained worldwide fame as a "uranium institute" and as a "sorption institute." The scientific supervisor of these studies, Boris Nikolaevich Laskorin, received a high scientific rank, full membership in the USSR Academy of Sciences.


Boris Nikolaevich Laskorin

To produce plutonium, in addition to nuclear purity graphite, metallic uranium was needed. The technology for its production on the basis of the magnesium thermal method had already been developed in 1945 by Zinaida Vasil'evna Ershova [4], who worked as the head of the *Giredmet* laboratory. By the way, Z.V. Ershova defended a top secret dissertation under the direction of K.A. Bolshakov at the Moscow Institute of

Zinaida Vasil’evna Ershova

Vitaly Grigor’evich Khlopin

Fine Chemical Technology in December 1943 on the topic of determining the ^{235}U / ^{238}U ratio in natural uranium. Z.V. Ershova received the experimental data during an internship in Paris at the laboratory of Irene Curie. I.V. Kurchatov and his colleagues respectfully called Z.V. Ershova the “Russian Madame Curie.” Among Z.V. Ershova’s important scientific achievements at the start of the nuclear project, is the creation of a technology for the separation of polonium-210 from irradiated bismuth-209. Polonium-210, a powerful source of alpha particles placed in a beryllium sleeve, was used as a starting neutron source in the “lighter” of the first atomic bombs. The neutron generation in a polonium-beryllium source is described by the equation:

$$^{9}_{4}\mathrm{Be} + \alpha \to {}^{12}_{6}\mathrm{C} + \mathrm{n}\ .$$

The formation of polonium-210 in irradiated bismuth-209 is described by the equation:

$$^{209}\mathrm{Bi} + \mathrm{n} \to {}^{210}\mathrm{Bi} \to \beta \to {}^{210}\mathrm{Po}\ .$$

Very little polonium is formed in the samples of irradiated bismuth, and its separation is carried out on the basis of fine chemical technologies. Incidentally, polonium heat sources were used on the Soviet Moonwalker 1 and 2 in 1975, after SAP’s completion.

The permanent mentor and her kind genius was Academician Vitaly Grigor’evich Khlopin, Director of the Radium Institute in Leningrad and Chief Radiochemist of SAP.

To produce plutonium-239 during SAP, a number of industrial uranium-graphite reactors and radiochemical plants were built to treat plutonium, uranium, and fission products from irradiated uranium. The formation of plutonium-239 upon neutron irradiation of uranium-238 in a nuclear reactor is described by the equation:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \to \gamma \to {}^{239}_{92}\mathrm{U} \to \underset{23.5\mathrm{min}}{\beta^-} \to {}^{239}_{93}\mathrm{Np} \to \underset{2.3565\mathrm{min}}{\beta^-} \to {}^{239}_{94}\mathrm{Pu}$$

Methods for producing plutonium from irradiated uranium-238 have been developed since 1946 in the first radiochemical laboratory of *NII-9*, the head of which was Z.V. Ershova. In the bowels of this laboratory, the U-5 semi-industrial facility was created, which played a significant role in developing the technology to produce plutonium preparations at the plant Mayak. From the beginning of 1947, uranium blocks irradiated in the first experimental reactor F-1 of the Institute of Atomic Energy began to arrive at U-5. Late at night on December 18, 1947, Z.V. Ershova, together with *NII-9’s* young radiochemists, first received weighted amounts of the plutonium preparation (73 micrograms). This work was the first to lead to the creation of a nuclear charge from plutonium.

The epoch of the creation of the first industrial reactor and radiochemical plant for the separation and purification of plutonium-239 at the Mayak or *Chelyabinsk-40* plant is described in detail in a book by Arkady Konstantinovich Kruglov [2], who was directly involved in the construction and commission of the enterprise. The complexity of the problem of plutonium production lies in the fact that in irradiated metallic uranium for a campaign of 2–3 weeks with a mass of loaded uranium of 100 tons, only 600–700 grams of plutonium-239 is formed. This is an extremely small amount. Further processing using PUREX technology (supervisor Academician V.G. Khlopin) makes it possible to isolate plutonium, uranium and send the nitric acid solution with a huge amount of highly active radionuclides, fission products of uranium-235, for long-term technological storage. These highly active liquid radioactive wastes

(HLRW) contain long-lived cesium-137 and strontium-90, which will remain highly active for thousands of years. The accumulation of large volumes of HLRW, the handling of which is still an unresolved problem, is the main drawback of SAP's plutonium choice.

The short interval of irradiation of uranium metal blocks (2–3 weeks) is caused by the fear of a large accumulation of plutonium-241, which after a short time of beta decay turns into americium-241 – a very highly active gamma emitter. The accumulation of americium-241 in plutonium charges is an unmasking factor, complicates the handling of charges, and requires constant resources for the fabrication of products. And this is the second significant drawback of plutonium bombs.

From what has been said, it is obvious that, along with intensive continuous production of plutonium charges, an urgent and very difficult task was developed to develop technologies and equipment for isotope enrichment of natural uranium in order to increase the content of the ^{235}U isotope from 0.72 to 90%. The first stage in solving this problem is the conversion of natural uranium from solid to gaseous. It is implemented in sublimation plants by the fluorination process to obtain uranium hexafluoride UF_6. At temperatures above 64.1 °C, this compound turns into gas [14].

As in the United States, of the four known methods for isotope separation, gas diffusion was preferred [14, 15]. In 1946, Academician Isaak Konstantinovich Kikoin was appointed the scientific leader of the project and the construction of a gas diffusion plant. The main idea behind the method is that a porous septum with countless holes with a diameter of less than 0.01 μm is installed in the path of the UF_6 gas flow. Uranium-235 hexafluoride is slightly lighter than uranium-238 hexafluoride, and lighter molecules should pass through the porous septum more easily. Therefore, the gas will be enriched in a light isotope on the other side of the septum. The main difficulties of the gas diffusion method were associated with the development of porous baffles and compressor pumps for gas movement. Acres of partitions and thousands of pumps were required. The development of porous partitions and diffusion machines was carried out by many organizations with the maximum usage of all the USSR's resources. The rush to prepare for the creation of enriched ^{235}U technology was mainly due to the fact that in 1946 the United States continued to improve nuclear weapons. In the same year, two atomic bombs were detonated on Bikini Atoll in the Pacific Ocean.

By 1950, a uranium enrichment plant was built in the middle of the Urals and was able to produce several dozen kilograms of uranium ^{235}U that had 90% enrichment. About 15000 diffusion machines worked at the plant, and the consumed electric power was 250 MW. From 1949 to 1964, another three diffusion plants in Siberia were built and commissioned. The use of enriched uranium removed the environmental problems of using plutonium for charges and opened up the possibility of using atomic energy for electric generation (with 3–5% enrichment), as well as for shipboard installations on submarines (with 40% enrichment) and icebreaking nuclear fleet (with 20% enrichment).

Centrifuge technology for enriched uranium was simultaneously developed along with the gas diffusion method. The principle of operating a gas centrifuge for the separation of uranium isotopes is that in a cylindrical rotor of a centrifuge filled with UF_6, at peripheral speeds of more than 400 m/s in vacuum, heavier molecules are concentrated at the rotor wall and are lowered down. In the machine, a special role is given to the magnetic suspension, which ensures that at high speeds of rotation of the rotor, the load is removed from the support needle. The centrifuge's fast-rotating rotor is capable of efficiently separating gas molecules into light and heavy parts. The main advantage of the centrifuge method compared to the diffusion method is its low energy consumption, which decreases quite a lot, and significantly larger thermodynamic efficiency.

The transition of the factories to centrifuge technology, carried out from 1966–1972, allowed the Soviet Union to increase the separation capacity of enterprises by 2.4 times and reduce the total electricity consumption by 8.2 times. At the same time, the Soviet Union managed to conceal the existence of the developed, most progressive and economical industrial method for 30 years. Now at the Ural Electrochemical Plant [16], one and a half million centrifuges are operating, the resource of which has reached 35 years of uninterrupted service; their rotor speed is 1500 rp/s. Russia supports 40% of the world's enriched uranium production [22].

Thermonuclear (Hydrogen) Bomb. Tritium, Deuterium, Lithium

A thermonuclear bomb uses the energy of helium **He** synthesis based on the reaction of the combination of hydrogen isotopes deuterium ^{2}**H** (**D**) and tritium ^{3}**H** (**T**).

$$\begin{gathered} {}^3_1H + {}^2_1H \rightarrow {}^4_2He + {}^1_0n + E_2\,, \\ \text{where } E_2 = \underset{\text{synthesis}}{3.5} + \underset{\text{neutron}}{14.1} = 17.6 \text{ MeV}\,. \end{gathered} \tag{1}$$

The deuterium tritium reaction is accompanied by the release of enormous energy and the formation of a fast neutron. However, its implementation requires an ultrahigh temperature T = 10^7–10^8 K and enormous compression (implosion). In addition, reagents are needed: heavy hydrogen isotopes – deuterium and tritium. The ingenious "explosive" was proposed back in 1949 by Vitaly Lazarevich Ginzburg: lithium-6 deuteride (^{6}**LiD**). It is a solid that can be layered in a hydrogen bomb body. If the trigger is detonated (a small atomic bomb in the same casing) then ultrahigh temperatures and implosion of explosives will be the result.

$$^{6}_{3}\mathrm{Li}+^{1}_{0}\mathrm{n} \rightarrow ^{3}_{1}\mathrm{H}+^{4}_{2}\mathrm{He}+\mathrm{E}_{1}, \quad \text{where } \mathrm{E}_{1}=\underset{\text{synthesis}}{4.8\ \mathrm{MeV}}. \tag{2}$$

The neutron flux will cause a tritium reaction and then the tritium will react with deuterium according to (1). These are the formulas for the formation of explosion energy. However, the topic of the article is to recall the achievements in chemistry and technology of lithium-6 and deuterium. In nature, there are two stable lithium isotopes: ^{6}Li (7.5%) and ^{7}Li (92.5%). During SAP, mercury technology was used to obtain pure ^{6}Li. To obtain deuterium, an effective and economical technology for low-temperature rectification of liquid hydrogen [17] was developed at the Institute of Physical Problems of the USSR Academy of Sciences under the leadership of Anatoly Petrovich Aleksandrov. The author of the idea of technology and the creator of the cryogenic Petr Leonidovich Kapitsa at that time was removed from the leadership of the institute. Highly appreciating each other's contributions, they both refused the Lenin Prize for this work, giving everything to the Institute of Physical Problems.

The technology for producing tritium according to (2) not in a bomb, but in terrestrial conditions, for the first thermonuclear charge was developed at *NII-9* beginning in 1950 under the guidance of K.A. Bolshakov in Z.V. Ershova's laboratory [18-20]. And today, after the completion of SAP, the technology for processing ceramic products from lithium-6 irradiated inside a reactor with the aim of producing tritium is used at the Mayak plant to produce the main fuel component of the international thermonuclear experimental reactor (ITER) under construction in France.

Conclusion

The brief overview of the implementation of the Soviet atomic project convincingly shows the significant contribution of SAP to the chemistry and technology of isotopes of the lightest and heaviest chemical elements of the Mendeleev Periodic Table.

The author declares no conflicts of interest.

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Dvi-manganese – rhenium is the youngest stable element in the Periodic Table

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The article was written for the 150th anniversary of the D.I. Mendeleev's Periodic Law. The history behind the discovery of dvi-manganese – rhenium by D.I. Mendeleev has been explained. Rhenium as well as its compounds' fields of application has been indicated. In addition, potential sources of rhenium in Russia have been identified.

Keywords: *Periodic Table, eka-manganese, dvi-manganese, rhenium, application, potential sources in Russia.*

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Дви-марганец – рений: самый «молодой» стабильный элемент Периодической системы элементов

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Статья написана к 150-летию Периодического закона Д.И. Менделеева. Кратко изложена история открытия предсказанного Д.И. Менделеевым дви-марганца – рения. Указаны области применения рения и его соединений. Обозначены потенциальные источники рения в России.

Ключевые слова: *Периодическая таблица Д.И. Менделеева, эка-марганец, дви-марганец, рений, применение, потенциальные источники в РФ.*

Для цитирования: Дробот Д.В., Куликова Е.С. Дви-марганец – рений: самый «молодой» стабильный элемент Периодической системы элементов. *Тонкие химические технологии.* 2019;14(6):17-21. https://doi.org/10.32362/2410-6593-2019-14-6-17-21

This report illustrates an attempt, using the history of prediction, discovery, and subsequent studies, to trace the role of the “youngest” (it has been known for less than 100 years, in comparison to gold) and the rarest (in comparison to the elements in the platinum group of metals) element in the Earth’s crust [1]. Figure 1 shows a diagram in the form of a pyramid, showing the content of the Periodic Table’s elements in the Earth’s crust (clarke), where rhenium is located at the very top of this pyramid.

D.I. Mendeleev predicted the existence of elements with atomic numbers 43 and 75, which are called eka-manganese (atomic number 43, Tc) and dvi-manganese (atomic number 75, Re), which means “the first and second analogs of manganese”[2] (Fig. 2). In June 1925, at a meeting in the Prussian Academy of Sciences, Professor Walter Noddak with employees Ida Tacke and Otto Berg made the first report about their discovering the elements, which received their names from two German provinces: No. 43, Masurium, and No. 75, Rhenium [2–4]. Later, the 43rd element was renamed technetium and was only obtained artificially in 1937.

W. Noddack, I. Tacke, and O. Berg suggested that deposits of platinum group metals and some minerals, such as columbite, may contain small amounts of rhenium: 10^{-3}–10^{-4}% in the first case and 10^{-5}–10^{-4}% in the second. In 1926, this group of scientists isolated the first 2 mg of rhenium from molybdenite.

Today, the main industrial source of Re is copper-molybdenum ores. During the burning stage, rhenium in the form of a higher oxide passes into the vapor phase and is absorbed by a solution of sulfuric acid.

The main producer of rhenium in the USSR was the Dzhezkazgan plant in Kazakhstan. Today the latter is an independent country. In the Russian Federation, there are no industrially developed primary raw sources of rhenium. It is extracted from secondary raw materials in small quantities.

The largest reserves of rhenium are in the USA (48%), Chile (27%), and Canada (16%). According to developed deposits, Chile is in first place (70%) and the USA is in second (21%). In general, the supply of international industry with proven and possible reserves of rhenium at current levels of production is about 40 years.

Rhenium is a dispersed, refractory, and rare metal. It combines unique physical and chemical properties that determine the diverse use of the metal in modern technology.

Refractoriness (melting point 3180 °C, boiling point 6000 °C), second only to tungsten, high strength, ductility at room temperature, have made it possible to create a whole gamut of heat-resistant alloys of rhenium with nickel, cobalt, molybdenum, tungsten, tantalum, titanium, and other metals used in aerospace engineering, in particular for the manufacture of jet engine blades.

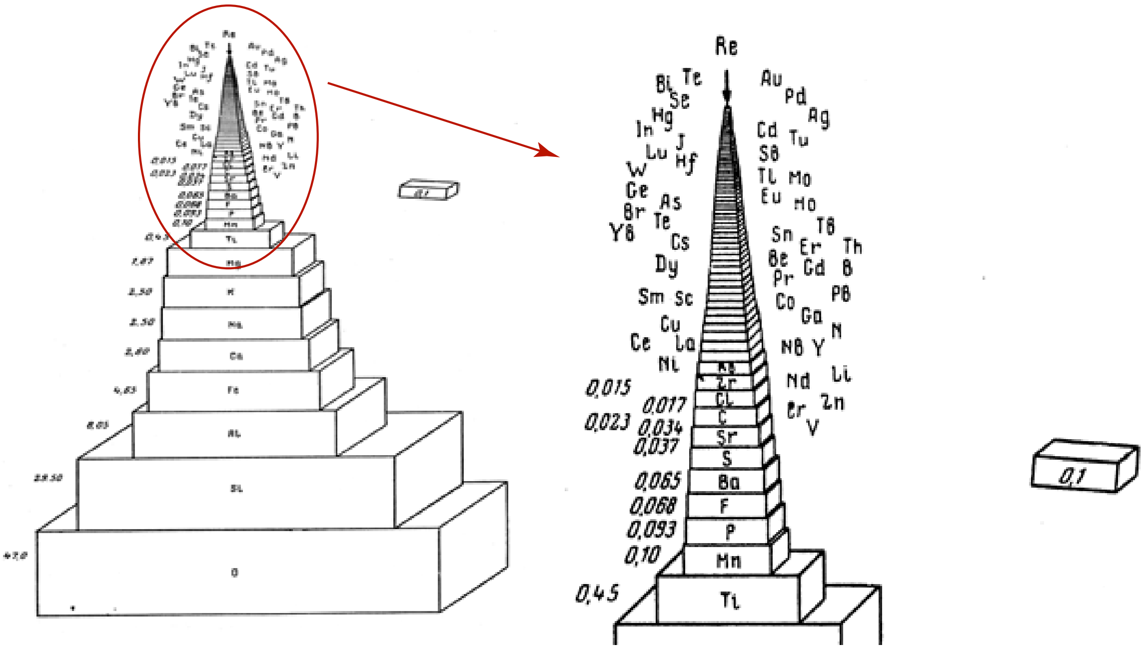

Fig. 1. Content of elements in the Earth’s crust[1].

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[1] Taken from a report by V.E. Fedorov.

[2] In publications from 1925–1930, “Eka-manganese element” and “Dvi-manganese element” can be found.

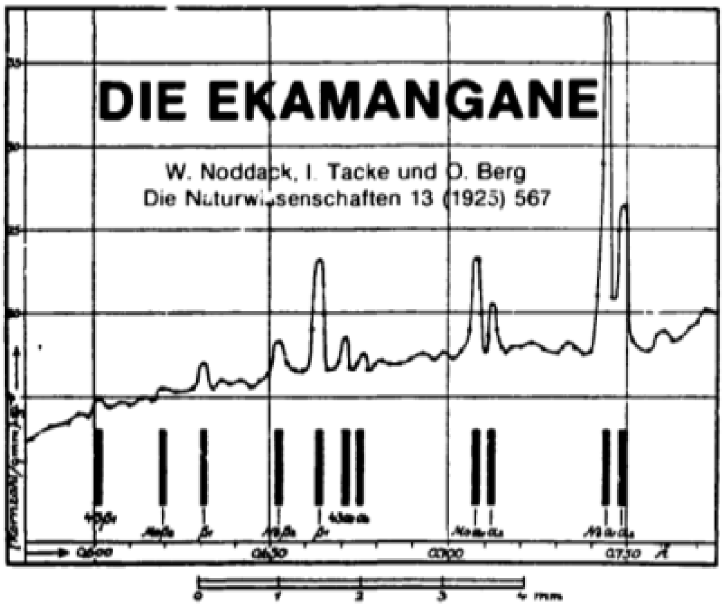

Fig. 2. Noddack W., Tacke I., Berg O. Die Ekamangane. *Naturwissenschaften*. 1925;13(26):567-574 [1].

Another critical area of application is heterogeneous catalysis in various organic industries. Figure 3 shows the applications of rhenium.

A unique source for rhenium in the Russian Federation is the Kudryavy volcano deposit (Fig. 4), discovered by the Institute of Volcanology and Geodynamics (IVG) of the Russian Academy of Natural Sciences on the Iturup island (Ministry of Natural Resources of Russia Certificate No. *YuSKh02MET10006* from July 19, 2002)[4]. In the high-temperature gases of the Kudryavy volcano, high levels of rhenium, germanium, indium, and other rare and noble metals have been confirmed. According to a decision by the Central Control Commission of the Ministry of Natural Resources of Russia dated July 8, 2002, dynamic reserves of category C_2 rhenium in the amount of 36.7 t/year, without determining the balance of ownership, were promptly obtained. The method for extracting rhenium from volcanic gases has been defended (patent No. 2159296 from November 20, 2000) and tested in laboratory experiments conducted from 1994–2002 (Institute of Volcanology and Geodynamics, Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, *GINTSVETMET*). Obtaining a rare-metal concentrate from gas, unlike traditional sources, does not incur extraction, transportation costs and concentrations of ore and may be cost-effective.

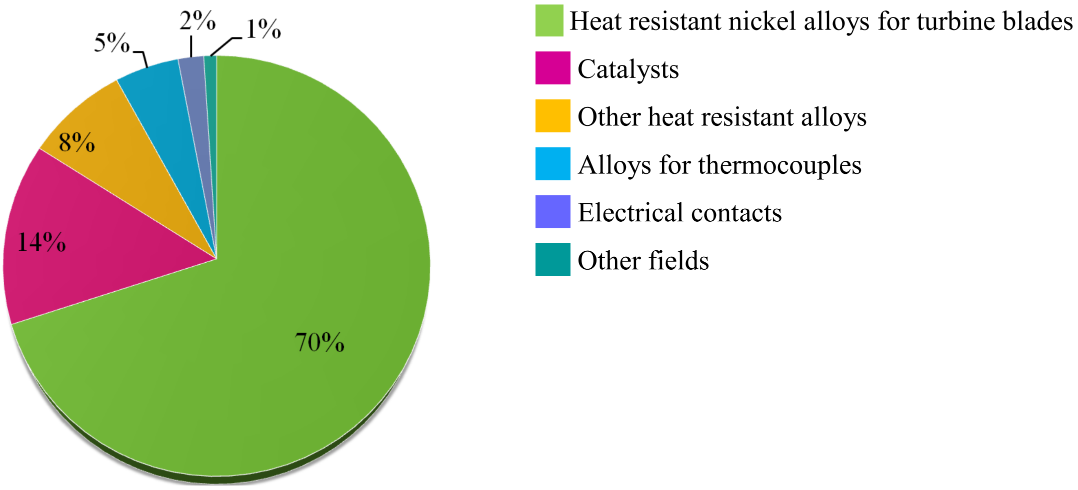

Fig. 3. Main applications of rhenium[3].

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[3] Electronic resource MetalResearch / World market of rhenium 2016 / 3rd edition. http://www.cmmarket.ru, Roskill.com, Ereport.ru

[4] The glory of this discovery belongs to the doctor of geological and mineralogical sciences, Academician of the Russian Academy of Natural Sciences G.S. Steinberg (*Snob*, April 2014, No. 4).

Fig. 4. Photo of the Kudryavy volcano.

From the standpoint of basic science, the results of studying the chemistry of rhenium compounds made a relief contribution to the chemistry of clusters, the methods of "soft chemistry," the problem of obtaining motor fuels or additives to them from renewable sources of raw materials (heterogeneous catalysis).

The term "metal-cluster" was introduced into coordination chemistry by A.F. Cotton in 1964. Although the term "cluster" is widely used in various fields, in chemical literature it defines a circle of compounds whose molecules contain a skeleton of metal atoms surrounded by ligands at distances that allow direct metal–metal interaction. Metal-cluster compounds are often characterized by complex structures, a peculiar reactivity, and unusual physical properties.

Rhenium is a cluster-forming metal. The most typical representatives of metal-cluster compounds are rhenium halide and chalcogenide complexes in which rhenium atoms are in low oxidation states. The presence of free valence electrons and coordinated unsaturation of such low-valent ions induce additional (in addition to metal–ligand bonds) interactions with each other, leading to the formation of metal clusters [5, 6].

It is clear that since electrons are needed to form the metal–metal bond, their number largely determines the type and size of the metal cluster: the more valence electrons the metal ions have (which is determined by the electronic configuration of the ion), the larger the number of M–M bonds and the larger the metal clusters will be. An alternative possibility of using free valence electrons is the formation of multiple metal–metal bonds. The simplest metal cluster is the M_2 dimer. With a larger number of metal atoms, the cluster can be triangular M_3, tetrahedral M_4, octahedral M_6, cubic M_8, or even more complex. The first cluster compound of rhenium, Re_3Cl_9, in which a rhenium atom forms a triangle with short rhenium–rhenium distances of 2.47 Å, was described in 1963.

Today, a family of mono-, bi-, and trimetallic oxoalkoxy compounds of rhenium and metals in the V–VIII groups of the Periodic system have been obtained and characterized5. These results have made it possible to create methods to produce refractory metal alloys ($T_m > 2500$ °C) at record low temperatures (< 600 °C), catalysts that make it possible to obtain motor fuels or additives from biomass [7–9].

Evaluating the retrospective, one can reasonably believe that the chemistry of rhenium and its compounds will develop dynamically and provide extraordinary and sought-after results.

These particular results describe the paradigm of the great discovery, the D.I. Mendeleev Periodic Table of Elements.

The authors declare no conflicts of interest.

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[5] A number of compounds demonstrate the presence of Re_4 clusters.

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Ruthenium: Past and Present

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This article provides information on one of the most interesting elements in the D.I. Mendeleev Periodic Table – ruthenium, discovered 175 years ago by the outstanding Russian chemist Karl Karlovich Klaus. Its most important physical properties, a variety of oxidation states, and a tendency to form countless compounds have been noted, making it unique and indispensable in all areas of science, technology, and in society. We have taken into consideration the structure of ruthenium consumption today as well as a few prospects for its future use.

Keywords: *ruthenium, ruthenium compounds, discovery, chemical properties, application.*

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Рутений: прошлое и настоящее

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В представленной статье приведена информация об одном из интереснейших элементов Периодической системы Д.И. Менделеева – рутении, открытом 175 лет назад выдающимся русским химиком Карлом Карловичем Клаусом. Отмечены его важнейшие физические свойства, многообразие степеней окисления, склонность к образованию бесчисленного количества соединений, что обусловило его уникальность и сделало незаменимым во всех сферах науки, техники и в социальной сфере. Рассмотрена структура потребления рутения в наши дни, а также некоторые перспективы применения в будущем.

Ключевые слова: *рутений, соединения рутения, открытие, химические свойства, применение.*

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One hundred and fifty years ago, the great Russian chemist Dmitry Ivanovich Mendeleev created the Periodic Table of Chemical Elements. A brilliant scientist, Mendeleev came to the conclusion that "... the size of atomic weight determines the nature of the elements." He not only arranged the 63 chemical elements known by 1869 in the order of increasing atomic weight, but also managed to make very bold predictions about the existence of yet to be discovered elements and their properties, leaving empty cells for them. Cell number 44 was occupied by the chemical element ruthenium (translated from Latin *Ruthenia* – Russia)[1], discovered 25 years before Mendeleev's invention by the Russian chemist Karl Karlovich Klaus.

The history behind the discovery of this unique element, a representative of the platinum metal family, is quite well known and has been described in detail in literature [1–3]. Therefore, there is not much point in referring to it in detail in this article. It is sufficient to mention that many famous scientists and scientific historians both in Russia and around the world contacted K.K. Klaus. On the centennial of ruthenium's discovery in 1953, Klaus's Selected Works on the Chemistry of Platinum Metals came out in the Classics of Science series. In 1926, "Materials for the Chemistry of Platinum Metals" were published in Germany. It is impossible not to mention in this article the book by the famous chemistry historian N.N. Ushakova "Karl Karlovich Klaus," published in 1972 [4, 5]. In 1984, the monograph "The Chemistry of Ruthenium" appeared (authors E.A. Seddon, K.R. Seddon) with a volume of over 1300 pages [6].

Within the framework of the present article, it is advisable to consider the main fields of ruthenium's application due to its physical and chemical properties as well as current trends in the development of ruthenium chemistry, the interest in which is not decreasing, but actually steadily increasing.

Ruthenium, like all metals in the platinum group, combines a variety of properties: heat resistance and ductility, corrosion resistance and weldability, reflectance and emission capability, heat and electrical conductivity, and high magnetic characteristics (Table 1) [7].

Due to its unique hardness and strength, ruthenium is an ideal component for imparting the same characteristics in various alloys. As a metal with a hexagonal close-packed lattice, ruthenium is used as an alloying additive. The alloy of ruthenium and platinum is a material used to manufacture fuel cells for artificial space satellites. Ruthenium greatly enhances platinum and increases the melting temperature of heat-resistant platinum alloys (the characteristic of heat resistance is creep resistance). Heat-resistant platinum alloys are unique structural materials capable of withstanding thermal and mechanical stresses in oxidizing aggressive environments for unusually high temperatures of 70–95% of melting temperature for many hundreds and thousands of hours [8]. The concentration of ruthenium in such alloys varies from 0.1 to 10%. Heat-resistant structural materials are used in aerospace engineering, also surpassing molybdenum and tungsten alloys in oxidation resistance. The refractoriness of this platinum group metal is used in the manufacture of thermocouples capable of reaching high temperatures. The smallest proportion (0.1%) of ruthenium added to titanium increases the metal's anticorrosion properties. From 1 to 5% Ru in the main alloy is sufficient to produce high-quality low-current contacts.

The discovery of ruthenium oxide's metallic conductivity in 1962 led to a comprehensive study of the properties of various simple and mixed oxides based on elements in the platinum group [9]. In 1974, N.M. Zhavoronkov, V.B. Lazarev, and I.S. Shaplygin established a correlation between the electronic configuration and the type of conductivity in simple and mixed platinum metal oxides. A semiconductor type of conductivity is shown by oxides with an external configuration d^6 d^8, while a metallic type has a configuration of d^4 and d^5. This discovery made it possible to carry out a directed synthesis of materials with specified conductive properties and ensured unprecedented progress in electronics.

Without ruthenium oxide titanium anodes ORTA and anodes containing, in addition to ruthenium dioxide, additives of iridium oxide – ORTA-I, it would be impossible to imagine the production of chlorine and chlorine-containing compounds – disinfectants, in particular sodium hypochlorite [10] today. They have increased corrosion resistance, electro-catalytic activity, as well as good and reliable polarization characteristics.

Along with the pure metal, various ruthenium compounds are also used. Some are used as powerful oxidizing agents, while others are added to the composition of glass and enamels as dyes, and yet others have fluorescent properties. The inorganic dye called "ruthenium red" deserves special attention (Fig. 1).

It is used in anatomical studies and in histology for more contrasting isolation of the tissues studied and substances when they are studied under a microscope.

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[1] If we turn to the etymology of this name, it is important to remember that Ruthenians is the traditional Latin name for Rus, the Latin distortion of the ethnonym "Rusyns", known to us from the chronicles and "Russian Truth" of Yaroslav the Wise. In German and Danish chronicles written in Latin, the Slavs of the southern Baltic coast were called Ruthenians, i.e. Rus, Rusyns [Merkulov V.I. About one of the names of Russia and Russians in sources: *Rusin*. 2006;4(6):118-122].

Table 1. Physical and chemical properties of Ruthenium [7]

Properties	Group VIII
	Ru
Nucleus charge	44
Amount of stable isotopes	7
Base state electronic configuration	[Kr]4d75s1
Usual oxidation states	+3, +4
Ion radius, nm	0.062
First ionization energy, kJ/mol	710.13
Pauling electronegativity	2.20
Type of crystal lattice	close-packed hexagonal
Density at 20 °C, g/cm	12.45
Melting temperature, °C	2334
Boiling temperature, °C	4080
Normal oxidative potential relative to the potential of a normal hydrogen electrode at 25 °C	+0.45
Electrical resistivity at 300 K, μΩ cm	7.55
Elastic properties at 300 K, GPa	485

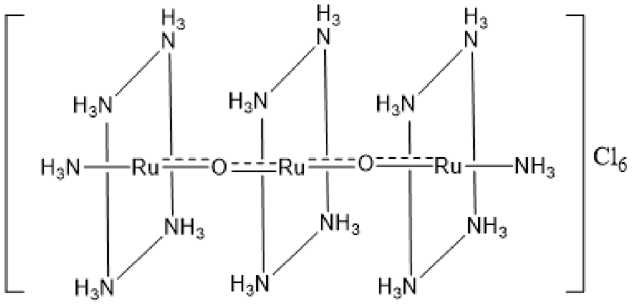

Fig. 1. "Ruthenium red" – the structure of the ammonia complex of ruthenium.

Judging by the latest market data[2], as expected from consideration of the most important properties of ruthenium, the greatest demand for this rare platinum metal is observed in industries such as electronics and electrical engineering, chemical and electrochemical industries. The total demand fluctuates at around 30 tons per year (Fig. 2).

As can be seen from the data presented, the demand for ruthenium fell by 11% due to the use of metal obtained from the processing of secondary raw materials generated in the chemical and electrochemical industries, especially in China. In 2019, according to the diagram, it grew as a result of meeting the demand for it due to available stocks. The main source of ruthenium (Clarke of ruthenium averages 5 × 10^{-7}% wt.) today are sulfide polymetallic ores, in which it is mainly present in a dispersed form. The price of ruthenium reached \$250 per troy ounce (as of December 2019).

It is advisable from our point of view to pay attention to a very promising future source of ruthenium – spent nuclear fuel (SNF): among the fission products of uranium, we see a significant amount of light metals of the platinum group – Ru, Rh, and Pd mainly in the form of a mixture of stable isotopes. It is known [11, 12] that, depending on the type of reactor, the combustion mode of the fuel, and

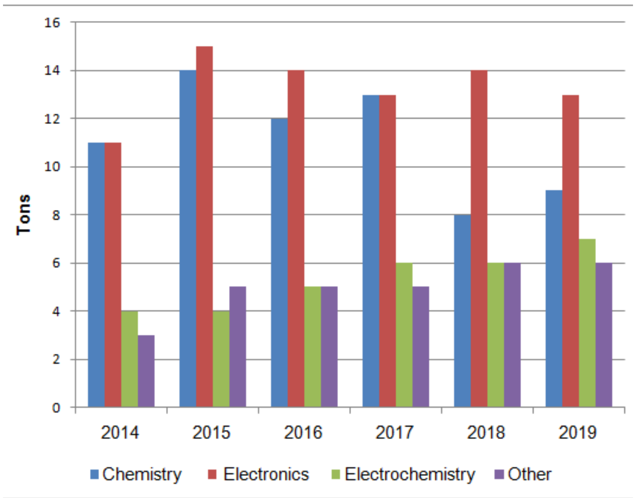

Fig. 2. Ruthenium Market Overview 2014–2018 (2019 – forecast).

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[2] http://www.platinum.matthey.com (accessed November 18, 2019).

its storage time, the concentration is from 0.7 to 29.4 g per liter of liquid waste, and the fraction of inactive ruthenium in nitric acid solutions of SNF is many times greater than the fraction of its radioactive isotopes. Therefore, current trends in improving environmental safety in the management of highly active SNF waste are the separation of platinum fragmentation metals for their subsequent transmutation and practical use.

Ruthenium is a unique element in the periodic system that has an amazing ability to manifest up to 10 different degrees of oxidation in its compounds, from –2 ($K_2[Ru(CO)_4]$) to +8 (RuO_4) (Table 2).

One of the most interesting examples is the formation of complexes with molecular nitrogen. $[RuN_2(NH_3)_5]X_2$ is the first of the known complexes obtained by Allen and Senof in 1965 by the interaction of $RuCl_3$ with hydrazine hydrate in an aqueous solution. In this case salt-like compounds of the composition $[RuN_2(NH_3)_5]X_2$ ($X = Cl^-$, Br^-, I^-, BF_4^-) [6] were isolated from the solution.

An important distinguishing feature of the chemistry of ruthenium is its ability to form nitroso complexes [6]. Nitro complexes are the only class of ruthenium compounds that are resistant to redox transformations in aqueous solutions. They have the group $(RuNO)^{3+}$, which is extremely stable even in "harsh" conditions. The discovery of the ability of nitroso complexes to enable the reversibly photoinduced transition to a long-lived metastable state provides rare opportunities for the synthesis of hybrid materials combining photoactivity with other physical properties, such as conductivity, magnetism, special optical properties, etc. [14]. Objects in which magnetic properties can reversibly change under the influence of light are of great scientific and practical interest, in particular, as materials to record information. The combination of these properties in one crystal lattice and their synergism can lead to new physical phenomena and new applications in molecular electronics.

Catalysis is one of the most common uses for platinum metals, including ruthenium. In recent decades, due to significant advances in the chemistry of coordination and organometallic compounds, for example, processes of homogeneous and heterogeneous catalysis involving catalytically active complexes "fixed" to the surface of a solid have been widely developed. Homogeneous and catalytic are the industrial processes of hydroformylation of olefins, carbonylation of alkenes, synthesis of aldehydes, etc. [6, 15]. In the electrolytic oxidation reaction of alkyl aromatic compounds, the pyridine complex Ru (IV) is used, while for the synthesis of aromatic acetaldehydes $RuCl_3$[3] is used. It was established that acidified methanol solutions of the complexes $[Ru_3(\mu\text{-}O)(CH_3COO)_6(PPh_3)_3]or[Ru_2(\mu\text{-}O)(CH_3COO)_4(PPh_3)_2]$ catalyze the hydrogenation reaction of alkenes.

It has been found [16] that the reaction for acetylene hydrochlor chlorination under conditions of homogeneous and heterogeneous catalysis selectivity (100%) and with a sufficient rate (at least 1 mol/lh h) catalyze all products formed in $RuOHCl_3$ – CH_3COOH – $(CH_3CO)_2O$, including by-products of the synthesis of the gross composition of $Ru_xO_yCl_z$, containing 40–50% ruthenium, which is of great practical importance. $[Ru_2(CH_3COO)_4Cl]$ has the highest catalytic activity in the case of direct application to activated carbon.

Table 2. Oxidation states and stereochemistry of ruthenium compounds [13]

Oxidation state	CN	Stereochemistry	Compound example
–2 (d^{10})	4	Tetrahedron	$[Ru(CO)_4]^{2-}$
0 (d^8)	5	Trigonal bipyramid	$[Ru(CO)_5]$
+2 (d^6)	4	Tetrahedron	$[RuH\{N(SiMe_3)_2\}(PPh_3)_2]$
	5	Square pyramid	$[RuCl_2(PPh_3)_3]$
	6	Octahedron	$[Ru(CN)_6]^{4-}$
	10	«Sandwich»	$[Ru(\eta^5\text{-}C_5H_5)_2]$
+3 (d^5)	6	Octahedron	$[RuCl_6]^{3-}$
+4 (d^4)	6	Octahedron	$[RuCl_6]^{2-}$
+5 (d^3)	6	Octahedron	$[RuF_6]^-$
+6 (d^2)	4	Tetrahedron	$[RuO_4]^{2-}$
	5	Trigonal bipyramid	$[RuO_5]^{4-}$
+7 (d^1)	4	Tetrahedron	$[RuO_4]^-$
+8 (d^0)	4	Tetrahedron	RuO_4

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[3] Ruthenium trichloride is well known as a catalyst for the synthesis of ammonia. The commercial drug $RuCl_3 \cdot H_2O$ is quite popular not only in catalysis, but also in preparative practice.

It was found [16] that the selectivity of ruthenium catalysts does not decrease when the CO content in acetylene exceeds 3% vol., providing the ability to work with pyrolysis acetylene.

It is impossible not to pay attention to the possibility of using ruthenium, one of the least expensive platinum group metals, in automobile exhaust gas afterburning catalysts. Ru-containing bimetallic catalysts obtained by autoclave thermolysis are effective in the oxidation of hydrocarbons [17, 18]. Table 3 shows the conversion of *n*-hexane during complete oxidation at 250–450 °C in a flow reactor using various mono- and bimetallic catalysts [17, 18]. Obviously, at 250°C on Pt, Pd, Ru, Pt–Ru, Pd–Ru and other catalysts, the conversion of *n*-hexane is ~ 50–70%, and at a temperature of ≥300 °C it exceeds 90%. In Ru catalysts, a 50% conversion of *n*-hexane is achieved at 230–250 °C, and 90% conversion is achieved at 280–335 °C, which, according to temperature characteristics, corresponds to a catalyst containing 0.2% of the mass.

It was shown [17, 18] that in the studied reaction, the Pd catalysts turned out to be significantly less active than platinum, ruthenium, and platinum-ruthenium: the temperatures of the complete conversion of *n*-hexane to them are almost 100 °C higher for each given value and are 350–370 °C and 385–390 °C, respectively, for 50% and 90% conversion. The addition of an equal amount of ruthenium to the Pd catalysts leads to a noticeable decrease in temperature (by about 50–100 °C) for both semi- and complete conversion of *n*-hexane.

Although the totality of the data presented demonstrates a significant practical effect from the use of ruthenium-based catalysts and its compounds, it certainly cannot compete with the enormous role that the achievements of the Nobel laureates in chemistry in 2001 and 2005 played and will play.

Primarily, this is a set of work carried out under the leadership of Ryōji Noyori to create chiral redox catalysts for the pharmaceutical industry. The chiral catalysis of hydrogenation reactions made possible the synthesis of enantiomers of very simple chiral molecules, which can be used as building blocks – synthons for the preparation of complex structures of natural origin [19]. Stereoselective hydrogenation methods have made available many terpenes, vitamins, amino acids, antibiotics, alkaloids, prostaglandins, and other biologically important compounds, and a number of them have begun to be produced by the industry. The scientist proposed a ruthenium (II) catalyst, BINAP (its structure is shown in Fig. 3), which hydrogenated many types of molecules with different functional groups. In particular, the Noyori complex is used as a catalyst in the production of (R)-1,2-propanediol for the industrial synthesis of the antibiotic levoflaxazine.

Moreover, the second Nobel Prize is for his contribution to the development of the metathesis

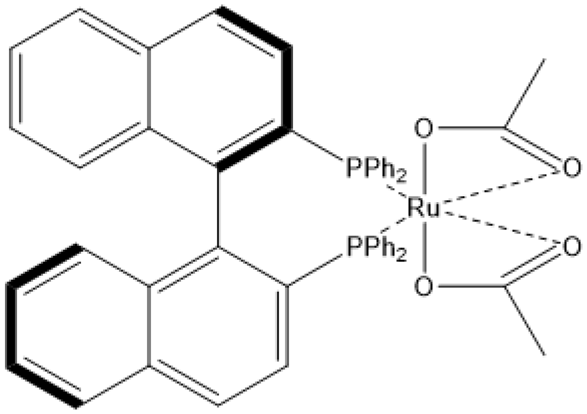

Fig. 3. Structure of the complex (R)-Ru$(OAc)_2$ (BINAP).

Table 3. Conversion of *n*-hexane during complete oxidation at 250–450 °C in a flow reactor using mono- and bimetallic Ru-containing catalysts [17]

Composition of the catalytically active phase, %	*N*-hexane conversion at temperatures, %				
	250 °C	300 °C	350 °C	400 °C	450 °C
0.2 Pt	47.2	88.2	99.5	99.9	99.9
0.1Pd	19.9	23.9	38.7	94.9	99.9
0.2Pd	8.9	27.5	51.1	99.2	99.9
0.1Ru	49.5	71.4	98.4	99.0	99.9
0.2Ru	59.1	97.8	98.6	99.0	99.9
0.1Pt–0.1Ru	47.5	94.7	97.8	98.9	99.9
0.2Pt–0.2Ru	48.0	86.6	98.6	99.4	99.9
0.1Pd–0.1Ru	4.5	92.2	98.1	99.1	99.9
0.2Pd–0.2Ru	15.4	24.0	98.9	99.2	99.9

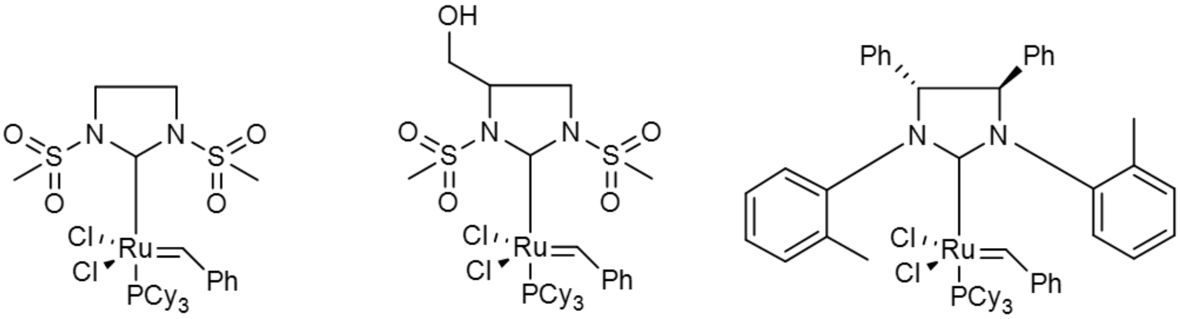

Fig. 4. Grubbs Catalysts.

method in organic chemistry. Metathesis reactions are catalyzed by ruthenium catalysts that are known as Grubbs catalysts (Fig. 4) [20]. Grubbs catalysts exhibit high reactivity in various types of metathesis and high tolerance to various functional groups. Ruthenium catalysts show low sensitivity to air, moisture, and minor impurities in solvents. They can be stored for several weeks in the open air without decomposition. Reactions with Grubbs type catalysts are often slightly slower than with ones with molybdenum, but their availability and ease of manufacture make them the most convenient for use.

In conclusion, special attention should be paid to a socially significant sphere of application for ruthenium – medicine. This should include various drugs based on ruthenium, primarily drugs for the treatment of cancer.

It should be noted that the ability to exhibit biologically active properties was stated by the great Klaus in "Neue Beiträge zur Chemie der Platinmetalle. Über das Ruthenium verglichen mit dem ihm ahnlichen Osmium" [21][4]. In it, he cited a strange — from his point of view — example of the inexplicable sensitivity of individuals to drugs of other platinum metals. In the article, he mentions the name of an assistant to the famous professor at the University of Dorpat, Ozanne, who, even after 31 years of working with platinum residues, could not enter the chemical laboratory in which platinum products were stored.

Carrying out detailed studies of the properties of ruthenium and its closest analogue, osmium, Klaus drew attention to the fact that volatile compounds of ruthenium irritate the respiratory system. In fact, the manifestation of similar and other properties of ruthenium compounds is understandable, since ruthenium in the Mendeleev Periodic Table is in the same group with iron, which are considered vital elements [22].

As a result of the study of the physicochemical and pharmacological properties of a large number of compounds synthesized to date, it was possible to identify several classes of ruthenium compounds with external sphere ligands that have antitumor activity that significantly exceeds platinum-containing preparations. In addition, ruthenium compounds are not toxic to humans, making the production of an antitumor substance based on it safe.

In 2000, clinical trials of the Ru (III) octahedral complex with imidazole (Im) and dimethyl sulfoxide (dmso) *trans*-(ImH) [Ru^{III}Cl4 (dmso)(Im)] (NAMI-A) began as the antimetastatic agent, the first of a number of ruthenium complexes (Fig. 5).

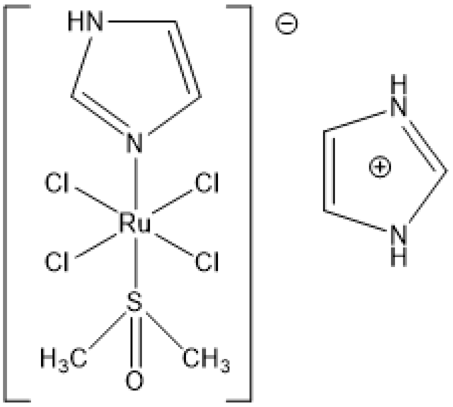

Fig. 5. Antitumor agent (NAMI-A).

We note that the ruthenium complex NAMI-A is slightly toxic to primary tumor cells and is promising in preventing the spread of cancerous tumors (metastases) [22].

Binding to biological targets is an important part of the modes of action of ruthenium complexes and organometallic compounds. As shown in the clinically

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[4] "New advances in the chemistry of platinum metals. Comparison of the properties of ruthenium and osmium" (translated from German).

studied Ru (III) complexes, they bind rapidly to serum proteins, and bind to albumin and transferrin, which is most likely especially important for selective transport into a cell. It is assumed [23, 24] that it is responsible for the selective activity of some Ru complexes and is responsible for lower side effects compared with established chemotherapeutic agents based on platinum. The latter bind relatively non-selectively to DNA, which inhibits replication and transcription and, finally, leads to the induction of controlled cell death, i.e. apoptosis. However, DNA is not necessarily the only and/or primary target for organometallic ruthenium compounds. It has recently been shown [24] that they can also act as kinase inhibitors or show preferential binding to proteins compared to DNA.

The activity and specificity of antitumor metal-containing compounds can be easily varied using the ligand environment. The introduction of a target-oriented organic fragment into the complex structure will significantly increase the antitumor properties of the compounds. In the work [24], lonidamine and bexarotene were selected as target-oriented ligands: lonidamine specifically inhibits aerobic glycolysis in cancer cells, while enhancing glycolysis in normal cells; bexarotene is known as an antagonist of the retinoid X receptor. Ru (II) compounds, leaders with high specificity for malignant neoplasms, were identified *in vivo* experiments.

This is just a small fraction of ruthenium compounds for medical applications. Both ruthenium clusters [24], and the nitroso complexes [25] mentioned above, and diruthenium complexes with amino acids [26] are being studied.

The properties of ruthenium are so unique; the chemistry of ruthenium is so multifaceted that it is impossible to cover everything in a short article, so we did not even attempt to do it. In summary, we only emphasize that the possibilities of ruthenium are endless and inexhaustible; it is unlikely to completely know about ruthenium in the future like other metals in the platinum group. Ruthenium is still waiting for its researchers, thanks to which, undoubtedly, this "Russian" elemen.

The authors declare no conflicts of interest.

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ON THE 150TH ANNIVERSARY OF THE D.I. MENDELEEV PERIODIC TABLE OF CHEMICAL ELEMENTS

К 150-ЛЕТИЮ ПЕРИОДИЧЕСКОЙ ТАБЛИЦЫ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ Д.И. МЕНДЕЛЕЕВА

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Ancient Roman technology of aluminum production: Process reconstruction

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Ancient sources indicate that aluminum was known at Ancient Rome. The article attempts to reconstruct the ancient technological process of production of metallic aluminum based on the currently available information about the properties of aluminum and modern production methods.

Keywords: *aluminum, Ancient Rome, fractional crystallization, pyrometallurgical processes, aluminothermy*

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Древнеримская технология получения алюминия: реконструкция процесса

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Античные источники свидетельствуют, что алюминий был известен еще в Древнем Риме. В статье делается попытка реконструировать древний технологический процесс производства металлического алюминия на основе имеющихся на настоящий момент сведений о свойствах алюминия и современных методах производства.

Ключевые слова: *алюминий, Древний Рим, фракционная кристаллизация, пирометаллургия, алюмотермия*

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The discovery and use of chemical elements are closely connected with the human history, and many mysteries are associated with them. In this article, we will try to unveil certain enigmas about aluminum, the 13th element of the Periodic Table.

Approximately in 25 AD, there existed an interesting story suggesting that aluminum was known by Romans already 2000 years ago [1]. This story is found in several ancient sources, and in a brief form in the works of Pliny the Elder [2]. The most comprehensive variant was written by Isidore of Seville who lived in the 7th century. In his book *Etymologiae*, volume 16, chapter 16, we read the following:

"They say that, during the reign of Tiberius, a worker invented a malleable and ductile glass alloy (*vitri temperamentum*). When he appeared before the Emperor, the worker showed him a chalice made of that material, and Tiberius threw it on the floor in indignation. The worker picked up the chalice, which was all bent as if it were a bronze vase, then took a hammer from his pocket and fixed the deformations. Then the Emperor asked, "Is there any other worker who knows the recipe of this glass?" When the worker swore that no one else knew the recipe, the Emperor ordered to behead him, fearing that the secret "would make gold not more precious than dirt, and other metals would lose value completely." Thus, the worker's secret remained unknown.

Based on the characteristics of the material mentioned in the text, such as its sheen and malleability, it must be aluminum, one of the most important metals in today's world. The indication that it was glass should be considered wrong, as there exists no such ductile glass [3].

Henri Étienne Sainte-Claire Deville recollected the story about the "silver made of clay" when he received a large subsidy from Napoleon III to build the first manufactory for aluminum production, and he spoke of generosity displayed toward him, thanking the emperor for being treated in a completely different way compared to the scientists of the Roman Empire.

Aluminum is one of the most widespread elements in nature, universally found in feldspar, mica and clay; it is the product of their weathering. Alum, the double sulfate of potassium and aluminum $KAl(SO_4)_2 \cdot 12H_2O$, according to Pliny the Elder, was known to Herodotus in the 5th century BC. Despite all this, metal aluminum was obtained much later, at the beginning of the 19th century.

Aluminum is a light metal of silvery color. Its density is 2.70 g/cm^3, the melting temperature is 660 °C, and the boiling temperature is 2270 °C. Aluminum has a face-centered cubic crystal structure. The thermal conductivity of aluminum at regular temperatures is 3 times higher than that of iron, and 2 times lower than that of copper. The electric conductivity of aluminum amounts to approximately 60% of that of copper. The heat capacity of aluminum is quite high, approximately 2.5 times higher than that of copper and 2 times higher than that of iron. The heat of fusion of aluminum is also rather high; that is why the metal, despite it having a lower melting temperature than copper, is more difficult to melt than copper. At the same time, melted aluminum remains liquid for longer than other metals.

The difficulties in production of metallic aluminum are determined by its extremely high affinity to oxygen. Aluminum oxide Al_2O_3 is naturally found in the form of corundum and emery, as well as gemstones – ruby and sapphire. A thin oxide layer covers the surface of the metal and prevents it from oxidation, even in a melted form. However, this protective layer is easily destroyed by mercury, which explains why mercury is banned from being carried onboard aircraft.

Aluminothermy, a process of interaction between aluminum powder and oxides of other metals, is well known. A lot of heat is emitted during this reaction. That is why the mixture of aluminum with iron oxide (thermite) is used for generation of high temperatures. Even the crystal form of boron may be obtained through aluminothermy.

Today, the industrial production of aluminum is based on electrolysis of aluminum oxide dissolved in melted cryolite Na_3AlF_6. Graphite electrodes are used in this process. The contents of the electrolytic baths are maintained in a liquid form by the heat generated by the electric current. The temperature of the electrolytic baths should not exceed 1000 °C. Metallic aluminum obtained on the cathode sinks to the bottom, while in the liquid form. On the anode immersed into the bath, oxygen oxidizes graphite producing carbon monoxide, which is then oxidized into carbon dioxide. The latter is also produced directly on the anode [4].

"For the first time, aluminum oxide was produced from alum by Andreas Sigismund Marggraf in 1754, later it received the name of alumina. Humphry Davy attempted (in 1808–1810) to obtain the metal from Al_2O_3 by electrolysis, but his efforts were in vain. Hans Christian Ørsted managed to produce aluminum in 1825 by reduction of anhydrous aluminum chloride (discovered by him) by potassium amalgam upon heating. This method, not always reliable, was significantly improved by Friedrich Wöhler who used pure metallic potassium instead of the amalgam (1827). Wöhler also made the first rather accurate description of aluminum, and he is usually credited with purification of metallic aluminum, since Ørsted did not have proof that he had obtained a true pure metal" [4].

Henri Étienne Sainte-Claire Deville modified Wöhler's method in 1854 by using sodium instead of potassium. Thanks to this, the production cost became 10 times lower, industrial production of aluminum was launched, and visitors of the Exposition Universelle in Paris in 1855 could already see a large ingot of "silver made of clay." At that time, aluminum remained a very expensive metal [5, 6]. It was used for jewelry making (including some extraordinary pieces) and even for making dentures.

In the present work, we attempt to reconstruct the technology used by the ancient Roman metallurgist to produce metallic aluminum. Obviously, the technique was quite challenging at that time.

Electrolysis can be excluded from consideration. Although archaeological evidence from the Middle East suggests that a galvanic cell did exist then, there are two circumstances that make electrochemical production of aluminum unrealistic. First, we can see that the relevant knowledge has been lost. Second, the conditions of electrolysis, such as high voltage and temperature, the use of a special melt, the protection from immediate oxidation, seem unachievable for the technological level of that period.

Let us consider possible pyrometallurgical processes.

The use of charcoal as a reductant was well known in ancient Rome, for example in iron production. We can hypothesize that the following reactions could be used for aluminum:

$$Al_2O_3 + 3C = 2Al + 3CO\uparrow \qquad (1)$$

$$2Al_2O_3 + 3C = 4Al + 3CO_2\uparrow \qquad (2)$$

As a metallurgical furnace is an open system, it is possible that the equilibrium in the reactions (1) and (2) is shifted to favor the products, due to the removal of the gases from the system. However, these processes are not very well suited for production of metallic aluminum. This is due to the fact that aluminum carbide is formed easily in this case.

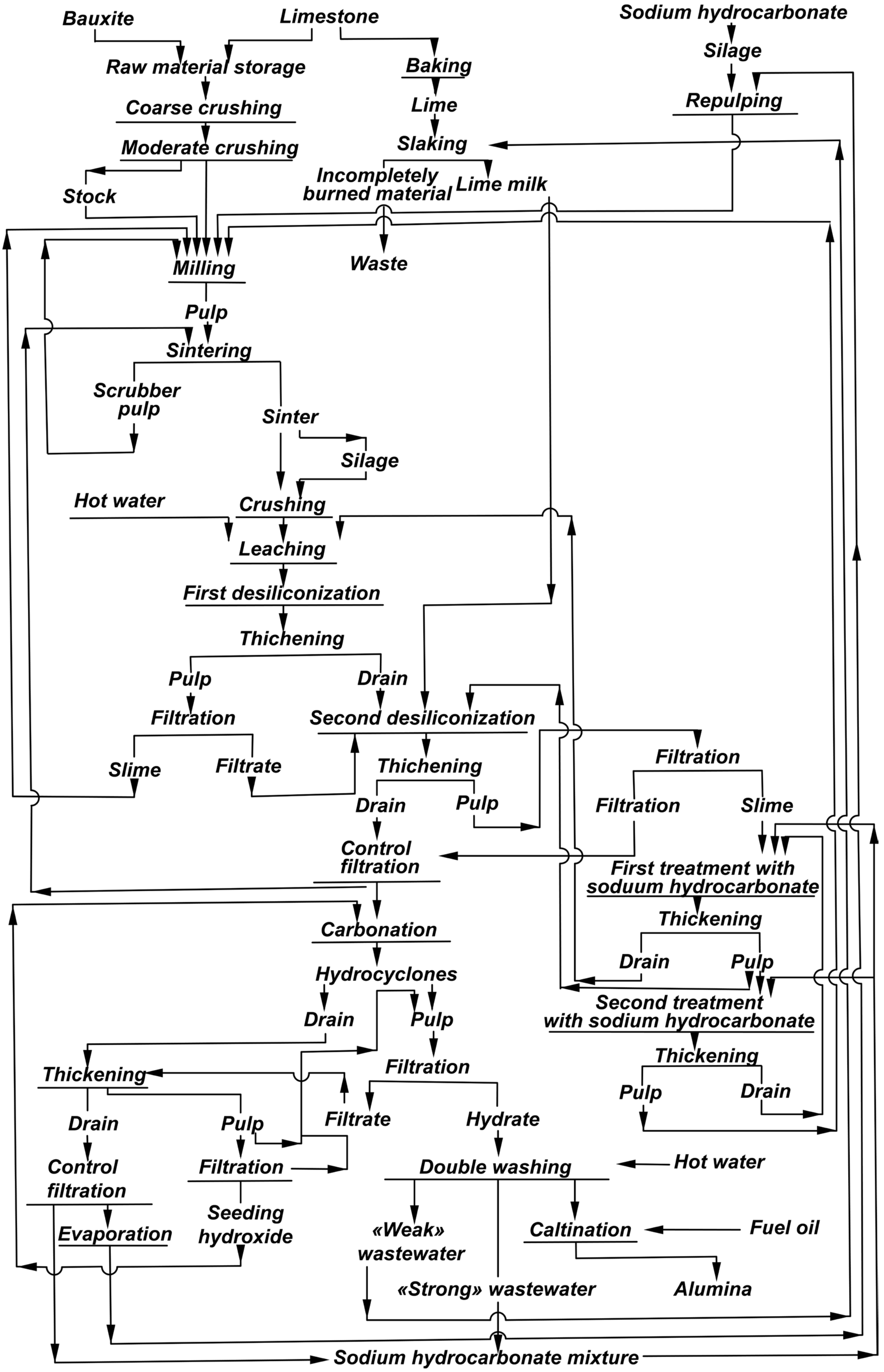
"All the attempts to replace electrolysis of a melt with thermal reduction of aluminum oxide have not been really successful so far. When carbon is used as a reductant, aluminum carbide Al_4C_3 is obtained, and this cannot be prevented" [4]. Still, it has been shown [7] that carbide formation can be minimized if the reaction is performed very quickly, and the oxide is mixed with just the exact amount of carbon. This method has been used to obtain aluminum in laboratory conditions with 93% purity. In the 19th century, there were successful attempts where alumina was reduced by carbon into metal with the use of fluxes, such as sodium chloride or borax [1].

So, in principle, carbothermal reduction of aluminum oxide into metal could be performed in ancient Rome. Let us consider now how alumina could be obtained from clay.

Currently, electrolytic production of aluminum uses alumina which is mainly obtained from bauxite. The latter is purified to remove silicon oxides, iron, titanium, etc. The process of bauxite extraction was developed by Carl Josef Bayer and is still used today. The method involves autoclaving of ore in the presence of hot sodium hydroxide solution. Since, quite obviously, there were no autoclaves in ancient Rome, we should not consider this approach as a possible one. At the same time, it is interesting to look at the technique developed by Henry Louis Le Chatelier in 1858, that is, the dry sintering of bauxite with sodium hydrocarbonate. According to a later version of the method, sintering is performed by adding limestone and spent liquor into the fusion mixture (wet sintering, Scheme 1) [8]. The sinter is leached with water and spent liquor. The aluminate solution, after desiliconization with lime milk, is saturated with carbon dioxide, and aluminum hydroxide is precipitated.

Feldspar and clay are not used in production of alumina any more. The major disadvantage of these sources is the presence of large amounts of silicates, which hamper the generation of pure alumina and produce a lot of waste. However, there is a method of nepheline (aluminosilicate of sodium and potassium) processing, developed by Alexander Fersman in the 1930s on the Kola peninsula. This technology is quite unique because it produces almost no waste. Nepheline processing involves wet sintering with limestone (see Scheme 2) [8, 9]. The process resembles the Le Chatelier method (see Scheme 1). The temperature of the sintering is in the range of 1000–1150 °C. The key chemical reaction occurring here is the following one:

$$NaKAl_2Si_2O_8 + 4CaCO_3 + 4H_2O = NaAl(OH)_4 + KAl(OH)_4 + 2Ca_2SiO_4\downarrow \qquad (3)$$



Scheme 1. Le Chatelier's scheme.

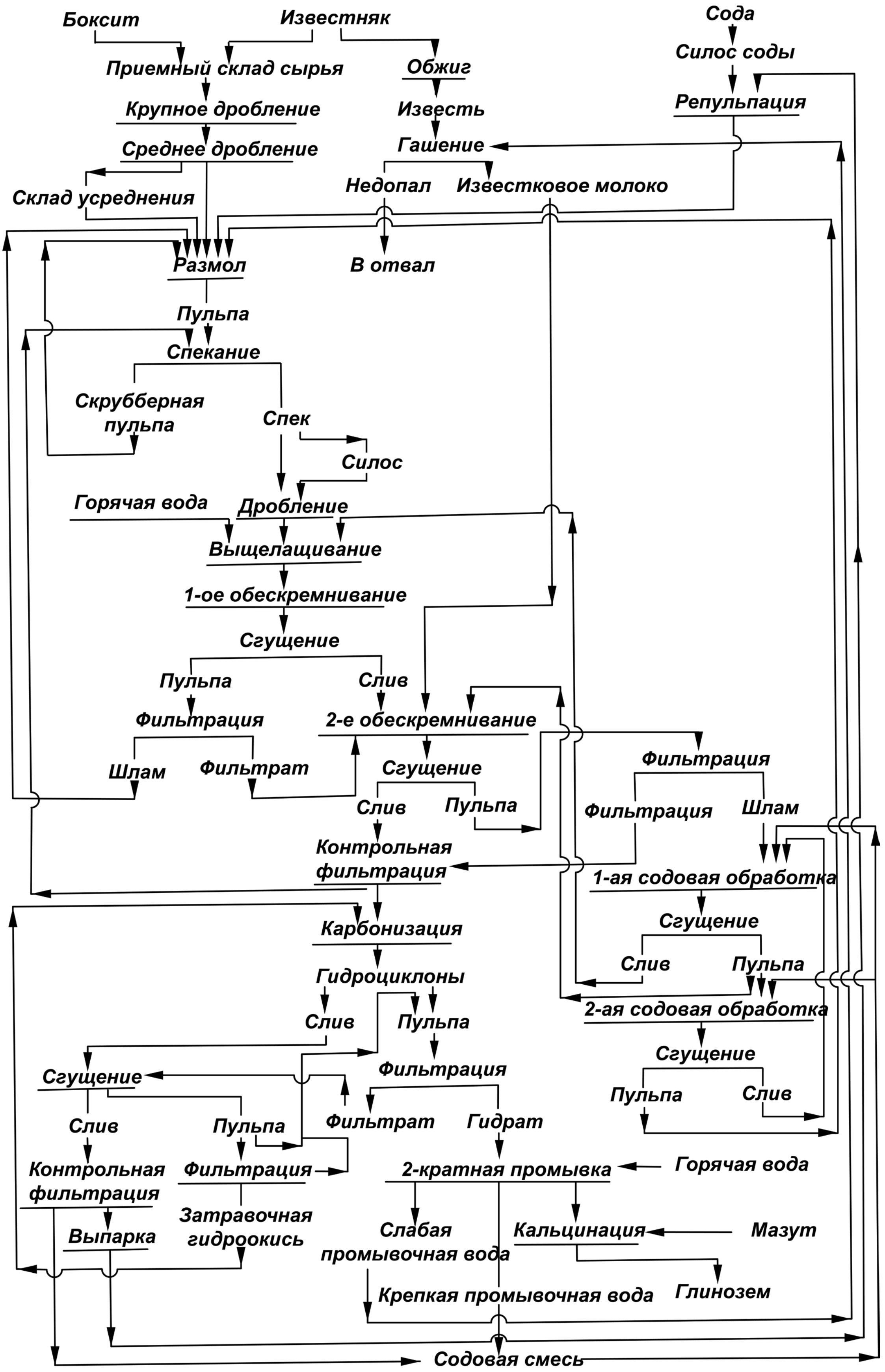
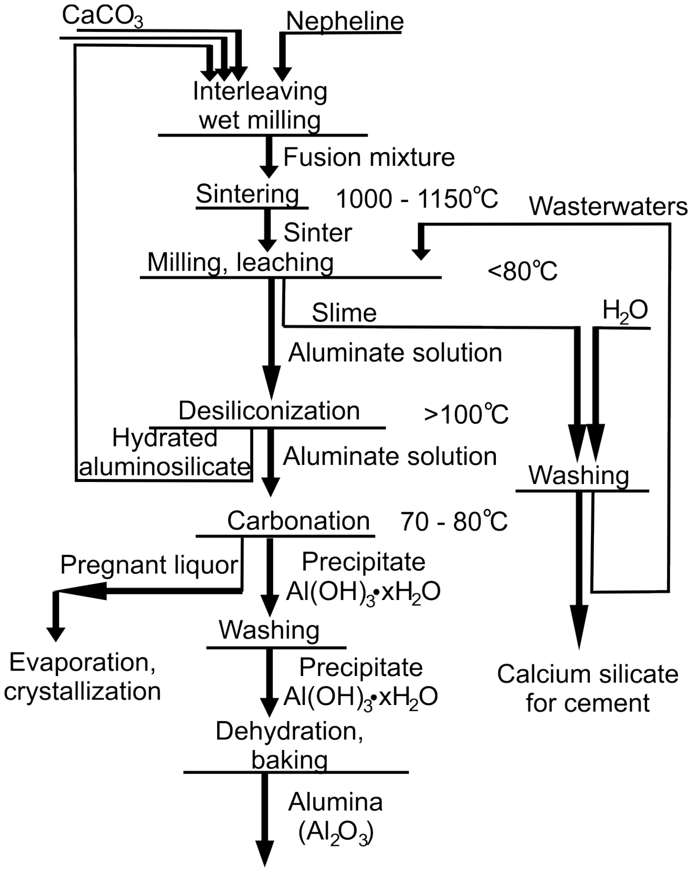


Схема 1. Схема Ле-Шателье.



Scheme 2. A.E. Fersman's scheme.

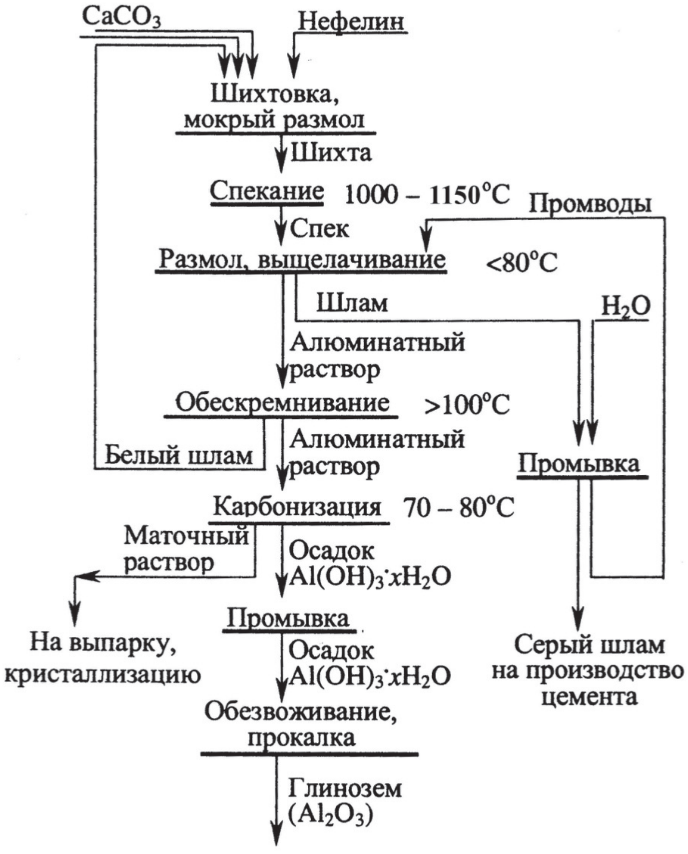


Схема 2. Схема А.Е. Ферсмана.

Calcium silicate is insoluble in water, and after washing it is used for cement production. The aluminates of alkaline metals are found in the alkaline solution. Desiliconization of the aluminate solution is carried out by heating it up to the boiling point. The hydrate of aluminosilicate, Na(K)[$AlSiO_4$]$x H_2O$, precipitates. The key stage of the process is precipitation of aluminum hydroxide. It is achieved by decreasing the pH of the solution through carbonation, just like in the Le Chatelier method. The chemistry of the process is the following:

$$2NaAl(OH)_4 + 2KAl(OH)_4 + 2CO_2 = Na_2CO_3 + K_2CO_3 + 4Al(OH)_3\downarrow + 2H_2O \qquad (4)$$

Alumina is obtained by calcination of the precipitate.

However, the most probable source of the material used for the ancient aluminum production is clay. It is a family of minerals with complex composition and structure. One of clays is kaolin, or china clay, which is a water-containing aluminum silicate whose approximate composition is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Usually, there is almost twice more silica in clay than in nepheline. Other clays also contain alkaline metals [10].

Clay processing into alumina was a significant issue in Germany.

"In Germany, it is highly important to extract Al_2O_3 from local sources, namely the abundant clays. Due to the high silicates content in the clay, alkaline processing, such as the Bayer method, is not recommended. To reduce the dissolution of silicic acid, clay is processed with acids, and the technology aims to prevent the dissolution of iron oxides, since the following separation of iron from aluminum is challenging.

In the Buchner method, also called the Nuvalon process, separation of Al_2O_3 from SiO_2, Fe_2O_3 and TiO_2 is achieved through heating the clay in an autoclave with nitric acid, at a certain concentration. Aluminum nitrate is obtained in the solution, and the main admixtures are nitrates of alkaline and alkaline earth metals, which may be separated by fractional crystallization. Nitric acid is removed when aqueous aluminum nitrate is heated, and a very clean Al_2O_3 is produced.

In the Goldschmidt method, another acid is used for the treatment of the starting material, sulfurous acid, which is significantly cheaper. However, considerable amounts of iron are found in the solution as a result. Iron forms a basic salt with aluminum that crystallizes well. Also, as long as there is not too much iron, it is possible to separate aluminum by fractional crystallization of the basic sulfite" [4].

These methods requiring acid treatment are unlikely to have been used in the ancient Roman times [6].

Let us consider another approach which employs an absolutely different strategy. It is the Haglund method; it is the most probable option to produce aluminum precursor from clay. The method was originally developed for Al_2O_3 extraction from bauxite, but later it was found to be applicable for clays, too. In this technique, oxide ore is heated with carbon and pyrite in an electric oven. Aluminum is partially transformed into its sulfide which forms a relatively fusible slag with Al_2O_3, containing, for example, 80% Al_2O_3 and 20% Al_2S_3. This slag, because of its low density, is easily removed from the iron–silicon alloy that is formed simultaneously. The solidified slag is treated with hydrochloric acid, producing H_2S that can be used for sulfur manufacturing. Besides, $AlCl_3$ and insoluble crystalline Al_2O_3 are obtained [4].

Pyrite FeS_2 is a very common mineral which was already known in the Antiquity [2]. For the purposes of our historical reconstruction, we can hypothesize that slag, obtained in a process similar to the Haglund method, could be subjected to a second reduction with charcoal. In strictly controlled conditions, this reaction would produce metallic aluminum. However, such a process would have been a challenging one in ancient Rome, since the classical Haglund method requires high temperatures that do not seem reachable for the technology of that time. The requirement comes from the fact that the components are hard to melt; the melting temperature for the iron–silicon alloy it exceeds 1200 °C.

We could suggest that the ancient Roman technology of aluminum production included the stage of clay processing, based on a method similar to Le Chatelier and Fersman processes. The technique would involve sintering with limestone and/or sodium hydrocarbonate. In ancient times, limestone was well known and it was used in cement production. Sodium hydrocarbonate was common, too [2]. The temperature of sintering, 1000–1150 °C, could be achieved in ancient Rome.

Carbonation might have been a problematic part of the process, since we can say with great confidence that carbon dioxide in pressure vessels could not exist in ancient Rome. At the same time, this gas is formed upon burning of charcoal. Even today, factories use purified emission gases for carbonation. Therefore, it is quite possible that the ancient Roman worker whose story we know thanks to Pliny the Elder and Isidore of Sevilleused carbon dioxide. As metallic aluminum is so ductile, a chalice could be made from it very easily.

However, we still cannot hypothesize what kind of equipment was actually used. The process would require a crusher, a mixer, different ovens, a sediment tank, some filtering equipment, gas supply and many more things, and we do not know what the technology of that time had to offer.

It has to be mentioned that chemistry did not quite exist as a science at the times we are discussing. This means that the worker, if he really existed, had to go into great lengths to solve very complex issues – without understanding the nature of what he was doing. Possibly, it could have caused the feeling of divine intent – quite in line with the habits of the Antiquity.

We can suggest that the place where the discovery was made was almost certainly an ironworks. Such an establishment would offer certain advantages for aluminum production. Steel was commonly used in Rome for making gladius swords. The quality of the steel was not great, but this disadvantage was compensated by low prices. Iron was obtained from ore with the help of charcoal that is required in reactions (1) and (2). The waste gases in the process contain carbon dioxide. The temperature in the shaft furnace and the finery (Scheme 2) could reach 1200 °C. We need to mention that for cast iron, the eutectic point in the iron–carbon system is 1140 °C. Experiments with clay sintering would have been natural for refractory making.

Thus, we speculate that components needed for aluminum production were plentiful in ancient Rome. However, it is not very probable that the metal was actually obtained, as it would have required great luck and talent to do so.

The authors declare no conflicts of interest.

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About chemical technology: Notes on student projects in the Mendeleev competition

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The general results of the 2018-2019 Mendeleev competitions for chemistry students have been presented and a detailed analysis of technological work of the last few years are given from the point of view of compliance of their subject and content to modern representations about chemical technology as science. An increased interest by representatives of leading companies, scientific organizations, and enterprises in the Mendeleev competition has been demonstrated. This is largely determined by the request of the chemical industry to train motivated chemical and technical specialists that possess research and implementation competencies. The possibility of forming the topics and content of students' scientific research based on the hierarchical structure of the chemical-technological system, the achievements of the theoretical foundations of chemical technology, and the principles of technology creation is shown.

Keywords: *Mendeleev competition, chemical technology, system approach, chemical-technological education, scientific work.*

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О химической технологии. Заметки на полях студенческих работ Менделеевского конкурса

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Представлены общие результаты Менделеевских конкурсов студентов-химиков 2018–2019 г.г. и дан более подробный анализ технологических работ последних лет с точки зрения соответствия их тематики и содержания современным представлениям о химической технологии как науки. Отмечен возросший интерес представителей ведущих компаний, научных организаций и предприятий к Менделеевскому конкурсу, что в значительной степени определяется запросом химической промышленности на подготовку мотивирован-

ных специалистов химико-технологического профиля, обладающих научно-исследовательскими и внедренческими компетенциями. Показана возможность формирования тематики и содержания научных исследований студентов, исходя из иерархической структуры химико-технологической системы, достижений теоретических основ химической технологии и принципов создания технологий.

Ключевые слова: *Менделеевский конкурс, химическая технология, системный подход, химико-технологическое образование, научная работа.*

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The unity of the educational and scientific processes in the higher chemical technology school has long been a prerequisite for training highly qualified personnel. Olympics for different specialties, schools for young scientists within the framework of prestigious Russian and international conferences, the possibility of obtaining individual grants and scholarships, including presidential and government ones, allow students from all courses to declare their research aspirations. One of the places to have stood the test of time is the Mendeleev Competition for chemistry students. In 2019, this competition and subsequent school-conference were held for the 29th time confirming the prestige, relevance, and attractiveness of this event in the eyes of students and potential employers. The Mendeleev Competition organizes and conducts a non-profit partnership "Promotion of Chemical and Environmental Education" with the support of universities, the Russian Academy of Sciences and technology companies. This year, the competition was supported by a grant from the President of the Russian Federation for the development of civil society provided by the Presidential Grants Foundation.

The 150th anniversary of D.I. Mendeleev's Periodic Table of Elements gave the traditional competition, bearing the name of the great Russian scientist, solemnity, significance, and a sense of involvement in the great discoveries. Looking ahead, it is appropriate to gratefully recall the lecture that was delivered to the young people by Doctor of Physics and Mathematics Sergey Nikolaevich Dmitriev, director of the Laboratory of Nuclear Reactions from the Joint Institute for Nuclear Research in Dubna. The contemporary work of Russian nuclear physicists, physicists and chemists, the technological equipping of research, the material and technical and methodological base, the openness of Russian scientists to interact with international colleagues moved the audience, filled our hearts and minds with pride. However, more about this will be mentioned later on.

The competition was hosted by the Ivanovo State University of Chemistry and Technology – a university with a rich history, a high level school of chemical technology, benevolent instructors, administration, and volunteers.

The history of the competition's creation, its rules, and the results of the competitions from 2010 to 2017 are described in great detail in an article by a professor at M.V. Lomonosov Moscow State University, a permanent member of the jury who was behind the origins of the competition's creation, Georgy Vasil'evich Lisichkin [1]. The material he presented (cities, universities, the number of works in part-time and full-time tours, the share of Moscow students in the total number of participants and award recipients) showed the formation of trends that persist today. The competition's indicators in 2018 (Novosibirsk) and 2019 (Ivanovo) complement the overall picture (Table 1).

This report is primarily devoted to the analysis of the topics and results of the chemical and technological profile work submitted to the competition over the past three years, the role of technological sections in attracting industry representatives to participate in competition events, and increasing student motivation.

A high share (36%) of students from institutes in Moscow remains strong among the participants in the Mendeleev Competition; the combined share of students from Moscow and St. Petersburg universities and the university hosting the school conference was 52.5%. The latter, in my opinion, is not a contradiction, but only strengthens the significance of the competition as an event of federal significance, since holding a competition in various Russian cities and universities helps increase the mobility of young scientists, and strengthens the scientific and educational contacts of the center and regions. Moreover, it is important to note that the competition is approaching the locations of chemical industrial facilities and, with skillful vocational guidance, can facilitate the transfer of talented young scientists from Moscow universities to those regions.

The largest teams of participants formed by universities in various Russia's cities are shown in Table 2.

Table 1. Statistical data characterizing the composition of the Mendeleev competitions of chemistry students in 2010–2019

Competition number, year	Competition city	Number of participants	Number of cities	Number of universities
XX, 2010	Arkhangelsk	129	28	41
XXI, 2011	Dubna	153	30	40
XXII, 2012	St. Petersburg	100	22	31
XXIII, 2013	Kazan	143	33	41
XXIV, 2014	Volgograd	147	31	39
XXV, 2015	Tomsk	201	40	57
XXVI, 2016	Samara	201	37	51
XXVII, 2017	Ufa	208	41	55
XXVIII, 2018	Novosibirsk	240	38	59
XXIX, 2019	Ivanovo	219	39	58

Note: data for 2010-2017 is given in [1].

As noted in [1], the nomination for “Research on chemical technology” introduced in 2005 at the initiative of Organizing Committee members and, above all, the president of the M.V. Lomonosov Moscow Institute of Fine Chemical Technologies Vladimir Savel’evich Timofeev, has allowed for the scope of the competetion to be expanded, and senior students from technological universities enrolled in master’s and specialty programs to be attracted. It seems to me that support for the competition by leading companies, especially in recent years, is to a large extent precisely connected with the possibility for future employers to evaluate not only the theoretical, but also the practical orientation and level of the specialists’ training in chemical and technological universities. This was also reflected in the new name of the category “Research and Development in Chemical Technology” in the amended Regulation about the competition.

Table 2. Statistics characterizing the largest teams of participants (at least 5 students) in the 2019 competition

City	Total number of participants	Universities	Number of participants
Moscow	79	Moscow State University, Faculty of Chemistry	25
		Moscow State University, Faculty of Materials Science	20
		Moscow State University, Faculty of Fundamental Physical and Chemical Engineering	2
		RTU MIREA (M.V. Lomonosov Institute of Fine Chemical Technologies)	24
		D.I. Mendeleev University of Chemical Technology of Russia	4
		Moscow Pedagogical State University	3
		National University of Science and Technology “MISIS”	1
Ivanovo	21	Ivanovo State University of Chemistry and Technology	17
		Ivanovo State University	3
		Lyceum No. 67	1

Table 2. Continued

City	Total number of participants	Universities	Number of participants
St. Petersburg	15	St. Petersburg State University	10
		St. Petersburg State Institute of Technology (Technical University)	2
		St. Petersburg National Research University of Information Technologies, Mechanics and Optics	2
		A.I. Herzen State Pedagogical University of Russia	1
Yaroslavl	12	Yaroslavl State Technical University	10
		K.D. Ushinsky Yaroslavl State Pedagogical University	1
		P.G. Demidov Yaroslavl State University	1
Ufa	8	Bashkir State University	6
		Ufa State Petroleum Technical University	2
Nizhny Novgorod	6	N.I. Lobachevsky State University of Nizhny Novgorod	4
		R.E. Alekseev Nizhny Novgorod State Technical University	2
Tver	6	Tver State Technical University	6
Kazan	5	Kazan (Volga) Federal University	3
		Kazan National Research Technological University (KNRTU)	2
Nizhnekamsk	5	Nizhnekamsk Institute of Chemical Technology (branch of KNITU)	5
Samara	5	Samara State Technical University	3
		Academician S.P. Korolev Samara National Research University	2

Table 3. Distribution of student works by category in the full-time round of the competition (2017–2019)

Category, section	Year		
	2017	2018	2019
Category I «Chemistry Research»	54	59	63
Inorganic chemistry and materials science	22	20	20
Organic, bioorganic and organoelemental chemistry	16	22	18
Physical and analytical chemistry	16	17	25
Category II «Research and Development of Chemical Technology»	46	46	44
General chemical technology, basic organic and petrochemical synthesis	13	12	9
Technology of biologically active compounds	7	12	8
Technology of inorganic materials	10	13	10
Technology of polymers and the materials based on them	16	9	17
Total	100	105	107

Table 4. Distribution of works acknowledged by awards from the competition (2016–2019) in the categories I and II

Reward	2016		2017		2018		2019	
	Chemistry	Chem. Tech.	Chemistry	Chem. Tech.	Chemistry	Chem. Tech.	Chemistry	Chem. Tech.
“Future of Russian Science” Medal	O.A. Khomich (Higher Chemical College, RAS, Moscow)	-	-	-	E.V. Pokochueva (Nat. Research University, Novosibirsk)	-	-	-
1st degree diploma	3	-	4	-	2	-	2	2
2nd degree diploma	9	-	5	3	5	2	8	4
3rd degree diploma	15	3	8	8	12	5	9	6
Share (%) of award recipients by category	**90.3**	**9.7**	**60.7**	**39.3**	**74.1**	**25.9**	**61.3**	**38.7**

Based on a review of student work (more than 200) over the last five years in the correspondence round, approximately half of the work is usually selected for participation in a further school conference, the distribution of which by category and section is presented in Table 3.

Certain changes occurred in 2019 with the number of chemical technology works that have earned awards in various denominations (Table 4).

This is partly due to the amendments made to the “Regulations on the Competition” concerning the independent evaluation of work in categories, but primarily with the improvement of the quality of students' chemical technology projects themselves and the aforementioned interest in them by the industry.

There are numerous special diplomas from companies and partnerships that are considered to be worth a lot: diplomas from the company *Haldor Topsoe* for work related to heterogeneous catalysis, the results of which have prospects for industrial applications (1 person); diplomas from the company *Fosagro* for high level and relevance of applied research (3 people); diploma from International Organizing Committee for the celebration of the International Year of the Periodic Table of Chemical Elements “Be in Trend!” (2 people); special certificate from the chemical and biological cluster *SCAMT* (2 people): diplomas from the Non-Profit Partnership “Promoting Chemical and Environmental Education” (5 people): for vivid presentation of scientific results; for an original technological idea; for synthetic work in the field of medical chemistry; for “The first step in science.”

Over the years, the conference has been sponsored by the following companies: *Schlumberger, KuibyshevAzot, Gazprombank, Haldor Topsoe, Solvex, AnalitProducts,* and *Acrus*. For many years, *SIBUR Holding* was the general partner of the contest. I wish to express enormous gratitude to the sponsors, but not just that. The direct participation of these sponsors and other business partners with the Mendeleev Competition in master classes, trainings, lecture programs in the person of leading scientists from the Russian Academy of Sciences and engineering companies, technologists, personnel management specialists, and strategic development of industry enterprises allows us to increase the motivation of future engineers. Unfortunately, the qualification of “engineer” has practically disappeared from educational programs and federal state educational standards, although many people understand the importance of this status: from a particular university and enterprise to state bodies that shape the priorities of the country’s scientific and technological development.

I have been working with the jury and as the head of the section “General Chemical Technology, Basic Organic and Petrochemical Synthesis” for four years. I hope my ten-year experience as rector of the M.V. Lomonosov Moscow Institute of Fine Arts and current status of the Head of the Department of Chemistry and Technology of Basic Organic Synthesis give me the right to share some of my impressions and thoughts. Quite complex and long-discussed issues were specific requirements specifically for a chemical technology profile. There are many reasons for this and most of them are subjective. In particular, contrasting the fundamental and applied nature of the works presented in different categories seems artificial to me. Purely chemical works are a theory, chemical technology works are those aimed at solving only practical problems.

Who can forget the quote by M.V. Lomonosov: "Chemistry is broadly spreading its hands into human affairs." The great Russian encyclopedic scientists Mikhail Vasil'evich Lomonosov and Dmitry Ivanovich Mendeleev knew a lot about this business and turned many of their scientific ideas into advanced technologies of their time and beyond.

And if we talk about state priorities for Russia's development as a whole along with science, engineering and technology in particular [2], and recall the list of critical technologies [3], then the relevance of the work presented in the category "Research and Development in Chemical Technology" of the Mendeleev Competition leaves no room for doubt.

The direction of "Chemical Engineering" was formed long ago all over the world and is now actively developing; the theoretical foundations of chemical technology (the core of the science of chemical engineering) and the principles of creating high-tech chemical technologies have been integrated [4, 5]. An analysis of the tender documentation requirements of the Russian Science Foundation, the Russian Foundation for Scientific Research, the Federal Target Programs of the Ministry of Education and Science and the topics of supported grants shows that the leader who clearly defines the place of specific research in fulfilling certain state priorities and realistically assesses the prospects for putting the results into practice wins. Such an approach should be implemented when choosing the subject matter for research of a chemical-technological nature: whether it is an initiative research work by a department instructor or a student's scientific qualification work. To clearly imagine the possible topics for student projects and the range of objects of study, it is sufficient to consider chemical technology from the perspective of a systematic approach [4, 6].

Any chemical technology system (CTS) can be represented in the form of a technological triad [4], including (Fig. 1):

- raw material preparation unit (I),
- chemical transformation unit (II),
- separation unit of multicomponent reaction mixtures (III).

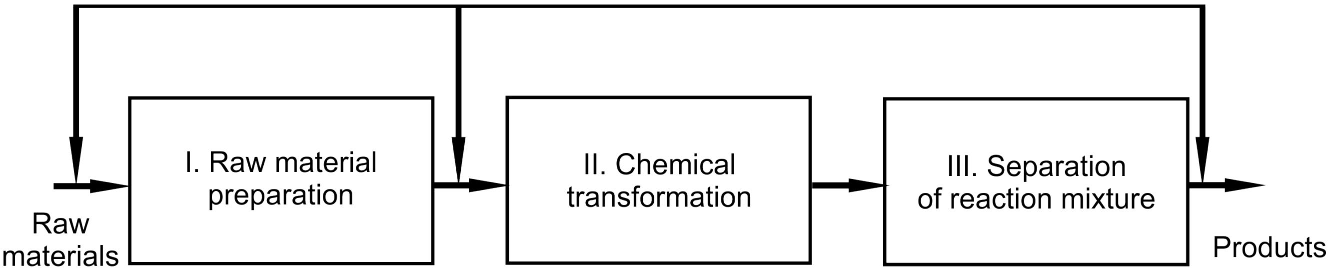

Fig. 1. Technological triad.

Such a representation of CTS, regardless of the scale of technology, immediately determines three large groups of tasks, objects, and, to a large extent, research methods that may make up the content of student scientific work. However, the competition for category II mainly presents works related to the second (chemical) unit, which is also associated with the content of special disciplines of educational programs that are traditionally focused on the chemical component of the technology. But today, the search for alternative raw materials, new methods for the deep processing of traditional raw materials, and the development of resource and energy-saving schemes for the separation of complex multicomponent mixtures obtained at the stage of chemical transformation are also relevant.

The triad's units are linked by both direct connections and feedback (recycles). The study of such systems is characterized by a certain complexity and requires the use of not only physical, but also computational experiments. But chemical technology works devoted to methods of mathematical modeling of the properties of systems and processes using modern software systems (PRO-II, ChemCad, Aspen Tech, and HYSYS) are also units.

On the other hand, the process of creating any chemical-technological system can be hierarchically divided into a number of components (subsystems), shown in Fig. 2.

In subsystems 1 and 2, many tasks relate to the establishment of "composition – property – structure" relationships, which relate to the synthesis

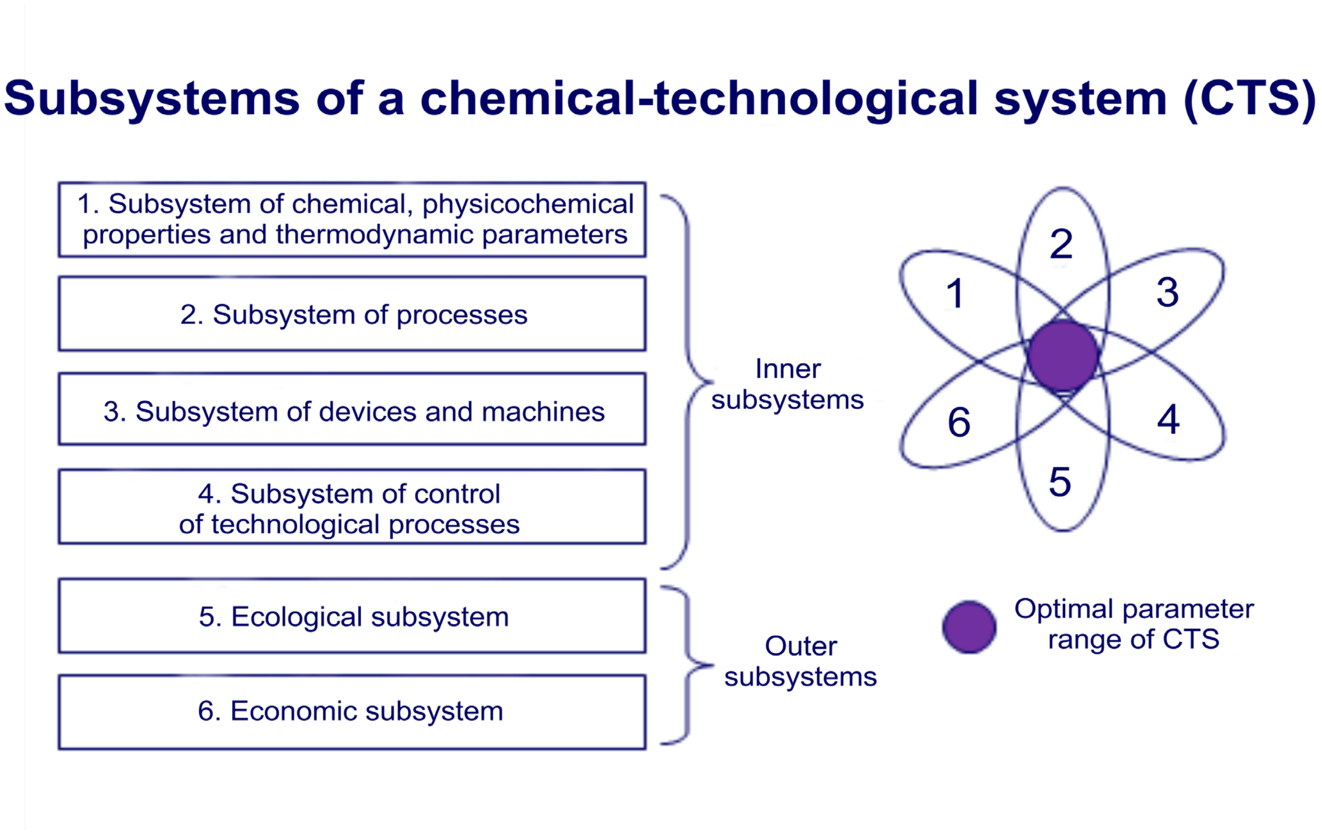

Fig. 2. Chemical-technological system structure.

of a chemical compound, production of functional materials and development of technological schemes based on phase diagram structures, etc. Incidentally, the decomposition of CTS shown in Fig. 2 perfectly illustrates the balanced curriculum for the training of specialists in the field of chemical technology, where each subsystem has a group of disciplines (chemical, physical, chemical, engineering, economic). But such an idea of the CTS also includes the possibility of choosing the topic of scientific student work and even its structure. Competitive work may contain the results of a specific chemical study, but its author should see the technological and economic prospects of the proposed solution and the possibility of its scaling and prototyping.

Unfortunately, for a long time there were no clear requirements for the content of chemical technology works submitted to the Mendeleev Competition. In 2019, a number of amendments were introduced to the Regulations on the Competition, which in a concise manner reflected at least a three-year discussion among representatives of various chemical and technological universities that implement a wide range of specialties on this issue. Today in the "Regulations on the Competition" the requirements for the work are formulated as follows:

Entries with significant scientific novelty and/or potential practical significance, corresponding to the main trends in the development of modern chemistry and carried out with the use of modern research methods are accepted for the competition in the category "Chemistry Research."

The competition in the category "Research and Development of Chemical Technology" accepts works on the development of new substances, materials and devices, various aspects of scaling up their production, the development of new processes of chemical technology, their improvement or optimization, as well as the control of production and product quality.

Below, as an example, the topics of student projects are listed that, to one degree or another, meet the requirements for technological work: development of environmentally friendly diesel fuels with bio additives and improved lubricating properties; development of a reagent for the destruction of oil-water emulsions; research and increase of the efficiency of an industrial reforming plant with mathematical modeling; the study of phase equilibrium and the development of concepts for the separation of mixtures formed in the production of cyclohexanone; investigation of the causes of degradation of the catalytic activity for sulfide catalysts of hydrogenation processes and methods of its recovery; oxidation and polymerization of vegetable oils isolated from waste oil extraction production; redistribution of narrow fractions of middle distillates during the electromagnetic processing of oil raw materials; improving the technology of chloroform purification from boiling impurities.

Work on the program to formulate the sections for category II, a number of problems remain: 1) the correspondence of the form and content of student work to the objectives of the competition, the solution of which largely depends on the supervisor of the work; 2) an adequate assessment of the work at the correspondence stage, in order to increase the objectivity of which section managers involve several reviewers, including third-party ones, for “blind” reviewing.

The positive history of the competition, the spirit of goodwill, healthy competition, and the grand mission of attracting young scientists to science allow us to hope for the further dissemination of the competition’s ideas in a university atmosphere.

In conclusion, I would like to note several aspects of this competition.

1. It would not be amiss to note with gratitude the participation of industry representatives in the competition (work in the jury; sponsorship, lectures, and master classes), which shows the interest of large companies, specific industrial enterprises, engineering firms in motivated, well-trained specialists and their orientation in a future profession.

2. The benevolent support of the competition by the administration of universities and cities testifies to the understanding of the role of the competition as a platform to promote the achievements of students of host universities, since with the positive examination results of works at the first stage, the number of such participants is not strictly limited.

3. The broad geography of the participants in the Mendeleev Competition and universities hosting an out-of-school conference allows us to raise the question of giving the Mendeleev Competition and Conference the status of an all-Russian event with international participation. And our competition, in fact, has had it for many years.

On the eve of the jubilee 30th Mendeleev contest, I would like to recall with fondness all the students participating in our intellectual competition, their advisors, and members of the jury. And to express gratitude to the inspirers and organizers of the Mendeleev Competition, the chairman of the jury, Academician of the Russian Academy of Sciences, Doctor of Chemical Sciences M.P. Egorov, Chairman of the Organizing Committee, Corresponding Member of the Russian Academy of Sciences, Doctor of Chemical Sciences O.I. Koifman, vice-chairmen of the organizing committee – Editor-in-Chief of the journal *Chemistry and Life* L.N. Strelnikova, Director of the Promoting Chemical and Environmental Education research enterprise E.S. Rotina and the scientific secretary of the jury Doctor of Chemical Sciences D.S. Perekalin.

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Yakov Syrkin: On the 125th anniversary of his birthday

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The article is dedicated to the 125th birthday of Yakov Kivovich Syrkin – Academician, Doctor of Chemical Sciences, Professor, Laureate of the Stalin Prize, and founder of the school of quantum chemistry in Russia. He was the head of the departments of Physical Chemistry at the M.V. Lomonosov Moscow Institute of Fine Chemical Technology and of Simple and Complex Compounds at the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and the Laboratory of the Structure of Molecules at the L.Ya. Karpov Institute of Physical Chemistry. Yakov Syrkin was a world-famous scientist in the field of physical chemistry, who has addressed many issues of quantum chemistry, molecules structure, chemical bonds; the mechanism of chemical reactions, kinetics and catalysis. He was a brilliant teacher and lecturer, the initiator of many scientific ideas and directions, the author of more than five hundred scientific works, a responsive man of many talents. The chronological outline of his scientific, pedagogical and life path is presented, some less well-known facts about his biography has also been highlighted.

Keywords: *Yakov Kivovich Syrkin, physical chemistry, quantum chemistry, molecular structure, M.V. Lomonosov Moscow State Institute of Fine Chemical Technologies (MITHT), L.Ya. Karpov Institute of Physical Chemistry, N.S. Kurnakov Institute of General and Inorganic Chemistry, Ivanovo State University of Chemistry and Technology, Museum of the History of the Department of Physical Chemistry of MITHT.*

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Яков Кивович Сыркин: к 125-летию со дня рождения

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Статья посвящена 125-летию со дня рождения Якова Кивовича Сыркина – академика АН СССР, доктора химических наук, профессора, лауреата Сталинской (ныне Государственной) премии, основателя школы квантовой химии в нашей стране, заве-

дующего кафедрой физической химии МИТХТ им. М.В. Ломоносова, заведующего Отделом строения простых и комплексных соединений ИОНХ им. Н.С Курнакова АН СССР, заведующего лабораторией строения молекул Физико-химического института им. Л.Я. Карпова, блестящего педагога и лектора, инициатора многих научных идей и направлений, автора более пятисот научных трудов, отзывчивого и разносторонне одаренного человека. Представлена хронологическая канва его научного, педагогического и жизненного пути, освещены некоторые менее известные факты его биографии.

Ключевые слова: *Яков Кивович Сыркин, физическая химия, строение молекул, МИТХТ им. М.В. Ломоносова, НИФХИ им. Л.Я. Карпова, ИОНХ им. Н.С. Курнакова, ИГХТУ, Музей истории кафедры физической химии МИТХТ.*

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December 5, 2019 marks the 125th birthday of Yakov Kivovich Syrkin – Academician, Doctor of Chemical Sciences, Professor, Laureate of the Stalin Prize (now the State Prize), founder of the school of quantum chemistry in Russia, the head of the departments of Physical Chemistry at the M.V. Lomonosov Moscow Institute of Fine Chemical Technology, and of Simple and Complex Compounds at the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and the Laboratory of the Structure of Molecules at the L.Ya. Karpov Institute of Physical Chemistry. He was a brilliant teacher and lecturer; the initiator of many scientific ideas and directions, the author of more than five hundred scientific works, a responsive and gifted person.

Five years ago, in December 2014, at the M.V. Lomonosov Moscow State University of Fine Chemical Technologies, jubilee readings dedicated to the 120th birthday of Academician Ya.K. Syrkin were held. They were attended by teachers, staff, graduate students, and students from Moscow State Institute of Fine Chemical Technologies, as well as representatives of the scientific community from many scientific and educational organizations, in particular, Ivanovo State University of Chemistry and Technology, the L.Ya. Karpov Institute of Physical Chemistry, N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, N.N. Semenov Institute of Physics and Technology of the Russian Academy of Sciences, and M.V. Lomonosov Moscow State University. Speakers with reports, mainly personal associates of Ya.K. Syrkin, his employees, colleagues and students, shared memories of their Teacher [1–3].

Yakov Syrkin's 120th anniversary was timed to coincide with the opening of the Museum of the History of the Department of Physical Chemistry at the Moscow State Institute of Fine Chemical Technologies, one of the oldest departments of this profile in Russia, founded in 1903 at the initiative of N.D. Zelinsky. The museum's constantly updated exposition presents documents, photographs, and artifacts that reflect its 116-year history.

The center of the museum is occupied by an exposition dedicated to Ya.K. Syrkin: a reconstruction of his office, stands with documents and material exhibits, autographs, photographs (including early ones from his personal archive), books from his scientific library systematized in a traditional catalog and electronic forms, reprints of journal articles spanning the period of his creative work from the beginning of the 1920s to the last year of his life. There are also stands with documents, photo portraits, and scientific biographies of all the heads of the department before and after Ya.K. Syrkin: S.G. Krapivin (headed the department from 1903 to 1924), Ya.I. Mikhailenko (1924–1931), M.G. Shirmazan (1974–1975), V.I. Goldansky (1975–1983), G.A. Grigoriev (1983–1988), A.A. Ovchinnikov (1988–1991), and A.P. Belov (1991–2004) [4–6].

Yakov Kivovich Syrkin was born in Minsk on November 24, 1894 (December 5, according to the new style). In 1904, he started going to the Minsk Commercial School and graduated from there in 1912. But the career of a businessman did not appeal to him, his interest in the natural sciences was stronger, and in the same year he enrolled in the Chemical Institute of Nancy University (France), where Viktor Grignard, who received the 1912 Nobel Prize in chemistry for research in the field of organometallic compounds, worked at that time.

The path to science for Ya.K. Syrkin was not easy, however. The First World War, which began in 1914, forced him to return to Russia. The chronology of his future path to higher education is described below.

In 1915–1918, Ya.K. Syrkin was a student at the Riga Polytechnic Institute (RPI), which, due to

Syrkin with his elder sister and her husband (Minsk, 1910).

Syrkin as a high school student (in the center) with his friends (Minsk, 1910).

Syrkin is in the gymnasium (Minsk, 1912).

Ya.K. Syrkin is at the Chemical Institute of the University of Nancy (Nancy, France 1913).

the threat of occupation of the Baltic States by the Germans, was evacuated first to Moscow, and then in 1918 to Ivanovo-Voznesensk (now Ivanovo), where he entered the newly organized Ivanovo-Voznesensk Polytechnic Institute (IVPI). Syrkin studied brilliantly and in 1919 he graduated with honors, successfully defending his diploma project; having received the title of process engineer and diploma No. 1 from IVPI's Faculty of Chemistry.

There is a multitude of evidence regarding Ya.K. Syrkin's contributions to science and his remarkable talent as a lecturer, teacher, and publicist [1–7]. There is just one illustration, drawing Ya.K. Syrkin as a lecturer. S.E. Shnol, professor at the Institute of Biophysics of the Russian Academy of Sciences, recalls: "At the Moscow State University's Faculty of Chemistry, lectures on the theory of the structure of chemical compounds were given by Ya.K. Syrkin. He was a wonderful lecturer; he reminded everyone of Rostand's cheerful and witty hero. He had clear logic and brilliant retreat to the side along with literary analogies and enthusiasm. And complex quantum mechanics became accessible and excitingly interesting" [8]. One of the authors of this article in the early 1960s, then a third-year student at the Moscow Institute of Fine Chemical Technology, listened to lectures by Ya.K. Syrkin about "The structure of matter" and completely agrees with its figurative comparison to Cyrano de Bergerac. Coincidentally, Rostand's play was being shown on the old stage of the Sovremennik Theater in Triumphal Square at this time.

Further on, we only give a chronological outline of his scientific, pedagogical and life path, focusing in more detail on less known facts.

After graduating from IVPI, Ya.K. Syrkin was left for pedagogical and scientific work in the Department of General Chemistry, where he held the positions of junior (1919–1921) and senior assistant (1921–1923) and then associate professor (1923–1925). In 1925, Ya.K. Syrkin was approved by the State Academic Council at the People's Commissariat of Education as a professor in the Department of Physical and Colloid Chemistry, where he worked until 1931. In 1931, Ya.K. Syrkin was invited to be the head of the Moscow Institute of Fine Chemical Technology's Department of Physical Chemistry, which formed that year, and he led it for 43 years (1931–1974). At the same time, he organized and headed the Laboratory of the Structure of Molecules at the Karpov Institute of Physical Chemistry, where he worked until his forced departure in 1952 in connection with the persecution of theoretical chemistry (Ya.K. Syrkin was an active supporter and developed the resonance theory of Nobel Prize winner Linus Pauling [9–12]).

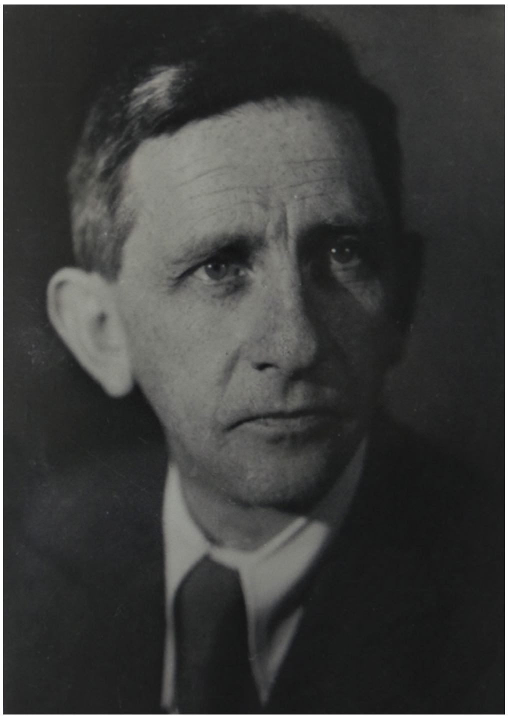
Ya.K. Syrkin (Nancy, France, 1913).

Ya.K. Syrkin as a student at the Riga Polytechnic Institute (August, 1916).

Ya.K. Syrkin (Ivanovo, 1925).

Ya.K. Syrkin at the Ivanovo-Voznesensk Polytechnic Institute (November, 1928).

Ya.K. Syrkin at the L.Ya. Karpov Institute of Physical Chemistry (1944).



Ya.K. Syrkin (Moscow, 1944).

After moving to Moscow, Yakov Kivovich over the years maintained contact with his native institute in Ivanovo.

In 1935, the All-Union Committee on Higher Technical Education conferred upon Ya.K. Syrkin the degree of Doctor of Chemistry for the totality of his scientific papers, without defending a dissertation.

During the Great Patriotic War, Ya.K. Syrkin remained in Moscow. He worked at the Karpov Institute of Physical Chemistry (the Moscow Institute of Fine Chemical Technology was evacuated to the city of Berezniki in the Perm oblast at that time) and, according to indirect information, took part in carrying out special tasks for the USSR government [12]. We have summarized the facts available that can serve as confirmation of this:

1) In 1942–1943, only seven of his scientific articles were published in the open press;

2) At a general meeting of the USSR Academy of Sciences held in November 1942, a report by Academician A.F. Ioffe mentioned the scientific school of Syrkin [13]. It is noteworthy that this session took place during the most difficult period of the Great Patriotic War, at the height of the Battle of Stalingrad;

3) In 1943, Ya.K. Syrkin was awarded the State (earlier known as Stalin) Prize, was elected a corresponding member of the USSR Academy of Sciences, was awarded the Order of the Red Banner of Labor, and later, in 1945 – the Order of the Red Star. This military order was awarded not only for military merit, but also "... for the development of military science and technology ...; for merits in strengthening the defense of the state ..." [14].

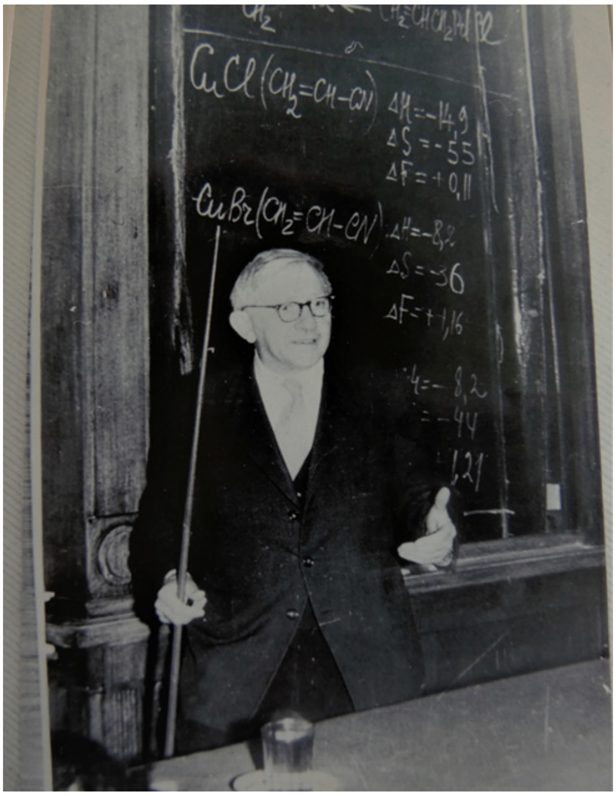
In the postwar years, Ya.K. Syrkin lectured at Moscow State University's Faculty of Chemistry on the theory of the structure of molecules until 1952, when he was removed from this activity for the same reason that he was forced to leave the Karpov Institute of Physical Chemistry [8–10].

Another place of scientific activity of Ya.K. Syrkin was the Kurnakov Institute of General and Inorganic Chemistry at the USSR Academy of Sciences (today the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences), where he was invited by academician I.I. Chernyaev. At this institute, Yakov Kivovich held the positions of senior researcher (1957–1961), head of the Inorganic Compounds Construction Laboratory (1961–1967), and head of the Department of the Simple and Complex Compounds Structure (1967–1970). However, throughout his time in Moscow, including during the period of persecution, his pedagogical activities were mainly at the M.V. Lomonosov Moscow Institute of Fine Chemical Technology.

In 1964, Ya.K. Syrkin was elected a full member of the USSR Academy of Sciences in the department of "Chemical Physics". In the same year he was awarded the second Order of the Red Banner of Labor for the development of chemistry and in connection with his 70th birthday.

Another, less well-known page in Ya.K. Syrkin's life

Ya.K. Syrkin with colleagues at the Department of Physical Chemistry (Moscow, MITHT, 1968).



Ya.K. Syrkin at a lecture in MITHT (1962).

Ya.K. Syrkin on vacation
(Uzkoe sanatorium, August, 1963).

is his home, family, and hobbies. Everyone who visited the Syrkins in their Ivanovo and Moscow apartments noted the hospitality and cordiality of Yakov Kivovich, his wife Miriam Veniaminovna, and daughter Flora. The youngest of the children – their son Alexander was born in 1930 shortly before the family moved to Moscow.

Yakov Kivovich loved and knew music, theater, and literature. He always followed book releases, and during his time in Ivanovo he had already amassed a solid library of scientific and fiction novels. In Moscow, his collection grew by leaps and bounds.

Yakov Kivovich greatly appreciated Albert Einstein as a scientist and person. A portrait of Einstein always hung in his home and office.

Nature, contrary to popular belief, did not rest on its offspring. However, the gifted children did not follow in their father's footsteps. Flora Yakovlevna (1920–2000) was a candidate of art history, historian, and a theater expert. She was also the wife of the outstanding artist A.G. Tyshler. At the end of her life, she donated the family's collection of paintings to the Museum of Private Collections (a branch of the A.S. Pushkin Museum of Fine Arts), and Syrkin's children donated his scientific library (about 700 volumes) to the Moscow Institute of Fine Chemical Technologies' Department of Physical Chemisty. Alexander Yakovlevich is also in the humanities; he graduated from the Faculty of Philology at Moscow State University, a doctor of historical sciences, orientalist, and author of several books on oriental folklore. He worked at the Institute of Oriental Studies of the USSR Academy of Sciences and currently lives and works in Israel.

According to N.I. Godnev, student of Ya.K. Syrkin, later a professor at the

Ivanovo State University of Chemistry and Technology and a family friend, in a conversation with him, Yakov Kivovich in a delicate form expressed regret that the professional vocations of his children diverged from his interests.

Yakov Kivovich Syrkin died suddenly 45 years ago on January 8, 1974. He is buried in Moscow at the Preobrazhensky cemetery.

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Dedicated to the 125th birthday of Academician Yakov Kivovich Syrkin

Quantum chemical investigation of the oxidative addition reaction of allyl carboxylates to Ni(0) and Pd(0) complexes

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Objectives. *The first allylpalladium complex was synthesized and characterized 60 years ago at the Department of Physical Chemistry of M.V. Lomonosov Moscow State University of Fine Chemical Technology (MITHT). This discovery was an important stage in the development of a new direction in chemistry – metal complex catalysis, which subsequently led to understanding the strategy for studying the mechanisms of catalysts action, and gave a powerful impetus to the study of intermediates of catalytic reactions. The key stage in many catalytic processes involving transition metal complexes is the oxidative addition stage. The study's aim was the quantum chemical modeling of the oxidative addition stage of allylic carboxylates to the Ni(0) and Pd(0) complexes.*

Methods. *Quantum chemical calculations were carried out under the Kohn-Sham method for the density functional theory using the PBE exchange-correlation functional and all-electron L11 basis set.*

Results. *As a result of theoretical study, we showed that the oxidative addition of allyl acetate to the triisopropylphosphite complex of nickel(0) and allyl formate to the triphenylphosphine complex of palladium(0) can proceed along two routes. In the first of them, in the coordinated breaking of the C–O bond and the formation of the metal–O bond, the same oxygen atom is involved, thus forming a three-center transition state. In the second route, the restructuring of relations is carried out in a five-center transition state. The chelating effect in the five-centered transition state of the second route reduces the reaction's activation barrier by 12.7 kcal/mol for allyl acetate and the nickel(0) triisopropylphosphite complex* $Ni(P(O^iPr)_3)_2$ *and by 9.9 kcal/mol for allyl formate and the palladium(0) triphenylphosphine complex* $Pd(PPh_3)$. *The presence of the second triphenylphosphine ligand in* $Pd(PPh_3)_2$ *reduces the activation barrier by only 2.6 kcal/mol.*

Conclusions. *The quantum chemical modeling performed allowed us to determine the preference for the oxidative addition of allyl carboxylates to the Ni(0) and Pd(0) complexes through a five-center transition state. The reaction's activation barriers through the "classical" three-center interaction are 9.9–12.7 kcal/mol higher, and the chelating effect is more noticeable for the Ni complex. The presence in the coordination sphere of several bulky ligands, such as triphenylphosphine, practically eliminates the chelating effect in the oxidative addition of allyl carboxylates.*

Keywords: *allyl complexes, nickel, palladium, oxidative addition, reaction mechanism, density functional theory, quantum chemical calculation.*

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К 125-летию со дня рождения академика Я.К. Сыркина

Квантово-химическое исследование реакции окислительного присоединения аллилкарбоксилатов к комплексам Ni(0) и Pd(0)

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Цели. *Первый аллильный комплекс палладия был синтезирован и охарактеризован 60 лет назад на кафедре физической химии МИТХТ имени М.В. Ломоносова. Это открытие явилось важнейшим этапом развития нового направления в химии – металлокомплексного катализа, привело к пониманию стратегии изучения механизмов действия катализаторов, дало мощный импульс исследованию интермедиатов каталитических реакций. Ключевой стадией многих каталитических процессов с участием комплексов переходных металлов является стадия окислительного присоединения. Целью работы явилось квантово-химическое моделирование стадии окислительного присоединения аллиликарбоксилатов к комплексам Ni(0) и Pd(0).*

Методы. *Квантово-химические расчеты проведены в рамках метода Кона-Шэма теории функционала плотности с использованием обменно-корреляционного функционала PBE и полноэлектронного базиса L11.*

Результаты. *В результате теоретического исследования мы показали, что окислительное присоединение аллилацетата к триизопропилфосфитному комплексу никеля(0) и аллилформиата к трифенилфосфиновому комплексу палладия(0) может протекать по двум маршрутам. В первом из них, в согласованном разрыве С−О-связи и формировании связи металл−О участвует один и тот же атом кислорода, таким образом формируется трехцентровое переходное состояние. Во втором маршруте перестройка связей осуществляется в пятицентровом переходном состоянии. Хелатирующий эффект в пятицентровом переходном состоянии второго маршрута уменьшает активационный барьер реакции на 12.7 ккал/моль для аллилацетата и триизопропилфосфитного комплекса никеля(0) $Ni(P(OiPr)_3)_2$ и на 9.9 ккал/моль для аллилформиата и трифенилфосфинового комплекса палладия(0) $Pd(PPh_3)$. Наличие второго трифенилфосфинового лиганда в $Pd(PPh_3)_2$ уменьшает активационный барьер только на 2.6 ккал/моль.*

Заключение. *Проведенное квантово-химическое моделирование позволило определить предпочтительность протекания реакции окислительного присоединения аллилкарбоксилатов к комплексам Ni(0) и Pd(0) через пятицентровое переходное состояние. Активационные барьеры реакции, протекающей через «классическое» трехцентровое взаимодействие, выше на 9.9–12.7 ккал/моль, причем для Ni-комплекса хелатирующий эффект оказывается более заметным. Наличие в координационной сфере нескольких объемных лигандов, таких как трифенилфосфин, практически нивелирует хелатирующий эффект в окислительном присоединении аллилкарбоксилатов.*

Ключевые слова: *аллильные комплексы, никель, палладий, окислительное присоединение, механизм реакции, метод функционала плотности, квантово-химические расчеты.*

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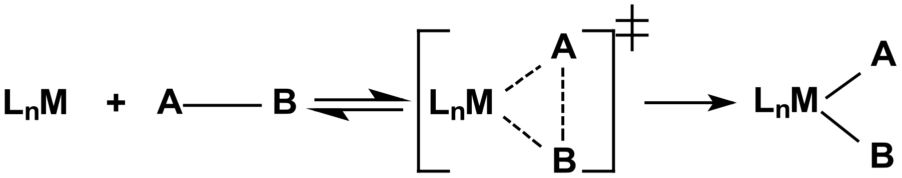
Introduction

The outgoing year 2019 has been a landmark for all chemists, not only because of the 150th anniversary of the opening of D.I. Mendeleev's Periodic Law. This year marks three more anniversary dates. This is the 125th birthday of Academician Yakov Kivovich Syrkin, an outstanding physical chemist and one of the founders of quantum chemistry in Russia, who made a huge contribution to the development of the theory of the structure of molecules and the nature of chemical bonds. His student, an outstanding technologist and catalysis specialist, academician Ilya Iosifovich Moiseev, turned 90 years old this year. The third anniversary is directly related to the names of Y.K. Syrkin and I.I. Moiseev. Sixty years ago at the Department of Physical Chemistry of M.V. Lomonosov Moscow State University of Fine Chemical Technology (MITHT) they synthesized and characterized the first allyl complex of palladium [1]. This discovery was an important stage in the development of a new direction in chemistry – metal complex catalysis, leading to an understanding of the strategy for studying the mechanisms of catalyst actions, and provided a powerful impetus to the study of intermediates of catalytic reactions. In addition, the presence of electron density delocalization in allyl fragments was a brilliant confirmation of resonance theory, actively supported and followed by Y.K. Syrkin.

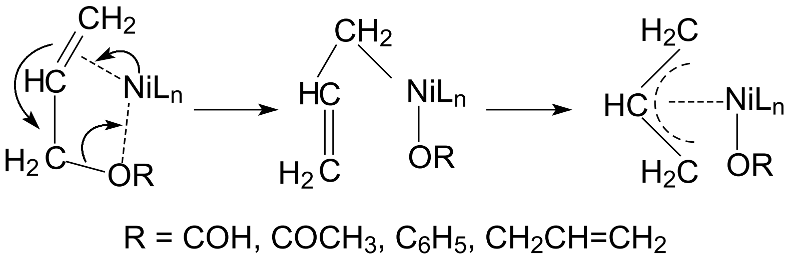
The key stage in many catalytic processes involving transition metal complexes is the oxidative addition stage [2–7]. Oxidative addition can be represented as the addition of substrate AB to a metal complex in such a way that the formal oxidation state and the coordination number of the resulting complex increase by 2 (Scheme 1). The reverse reaction may be considered as a stage of reductive elimination.



Scheme 1. Oxidative addition of AB molecule to L_nM complex (L – ligand, M – metal).

Due to the fact that in the stage of oxidative addition, the formal oxidation state of the metal increases by two, ligands that increase the electron density in the metal center will contribute to lowering the activation barrier and increasing the rate of the process. At the same time, bulky ligands, which create steric hindrances in the metal center, contribute to a decrease in the rate of oxidative addition due to an increase in the activation barrier, since they hinder the increase in the coordination number. It is assumed that the reacting system passes through a three-center transition state (Scheme 1).

Experimental studies of such reactions have been carried out since the middle of the 20th century. Of particular interest are the stages in which the C–O bond undergoes breaking. In the works of Yamamoto et al. the interaction of nickel [8] and palladium complexes [9, 10] with allyl carboxylates, allyl ethers and allyl alcohols was studied. Because of this interaction and the breaking of the C–O bond, an η^3- allyl complex is formed. Based on spectral data, a reaction mechanism has been proposed, which is shown in Scheme 2.



Scheme 2. Hypothetical mechanism of the oxidative addition of allyl containing compounds to the nickel complex (0).

Scheme 2 shows that the C–O bond cleavage in the Ni(η^2-C_3H_5OR)L_n complex initiates the η^2–η^1-rearrangement of the allyl fragment. As a result of the η^1–η^3-isomerization of the allyl fragment during the next stage, an η^3-allyl complex of Ni(II) is formed. The reaction proceeds in a similar manner on Pd(0) complexes. The interaction of allyl carboxylates with nickel and palladium complexes is an important stage in the mechanism of allylation of norbornadiene [11–14].

With the development of calculation methods, it became possible to theoretically explain the process's mechanism, revealing the structural and energy characteristics of short-lived intermediates. Therefore, it seems relevant to apply the methods of modern quantum chemistry in the study of the oxidative addition for allyl carboxylates to transition metal complexes. This study's aim was a quantum chemical modeling of the oxidative addition of allyl acetate to the triisopropylphosphite complex of nickel(0) and allyl formate to the triphenylphosphine complex of palladium(0). The modeling of these stages is also important to understand the mechanism of the allylation of norbornadiene catalyzed by systems based on $Ni(C_3H_5)_2$/P(OiPr)3/*m*-xylene [13, 14] and $Pd_3(OAc)_6/PPh_3$/ acetonitrile [11].

Materials and Methods

Quantum chemical calculations were performed in the "Priroda" program [15] using the Kohn–Sham method for the density functional theory via the PBE exchange-correlation functional [16] and the all-electron L11 basis set [17]. The contraction schemes for orbital basis sets are given in Table 1. In view of the importance of taking into account relativistic effects for palladium, the calculations of palladium complexes were carried out in scalar-relativistic approximation. This calculation technique was earlier used successfully to model reactions involving nickel and palladium complexes [18–20]. The influence of the solvent was taken into account within the framework of the polarized continuum model (PCM). For the nickel-containing system, the medium's dielectric constant was taken to be 2.35 (*m*-xylene solvent), and for the palladium-containing system – 36 (acetonitrile).

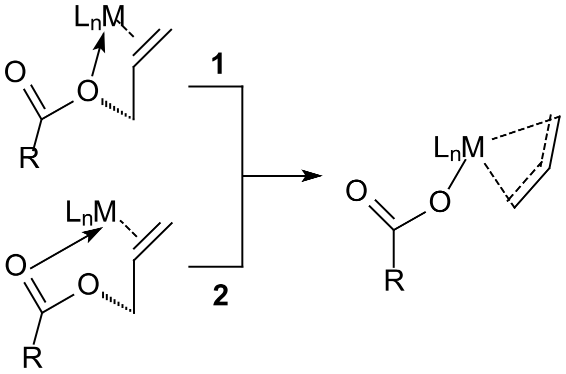
Geometry optimization was carried out without restrictions on the symmetry of the molecule. The type of critical points on the potential energy surface (minima or saddle points) was determined based on analytically calculated second derivatives of energy with regard to all coordinates. To verify the evolutionary relationship of the transition states found with local minima, a procedure to calculate the intrinsic reaction coordinate (IRC) was performed.

Results and Discussion

The results of this study showed that the oxidative addition stage of allyl carboxylates to nickel and palladium complexes can proceed along two possible routes, presented in Scheme 3. The main difference between them is the structure of the transition state. If the same oxygen atom is involved in the coordinated breaking of the C–O bond and the formation of the O–M bond, then Route 1 is realized through a three-center transition state.

Table 1. Orbital contraction schemes in L11 basis set

Element	Basis sets (contracted/uncontracted)
	L11
Pd	[26s23p16d5f]/{7s6p4d1f}
Ni	[19s15p11d5f]/{6s5p3d1f}
P	[14s11p6d]/{5s4p2d}
O	[10s7p3d]/{4s3p1d}
C	[10s7p3d]/{4s3p1d}
H	[6s2p]/{2s1p}



Scheme 3. Two possible routes for the oxidative addition of the allyl carboxylate to the transition metal complex.

If different oxygen atoms participate in the breaking of the C–O bond and the formation of the O–M bond, then Route 2 is implemented. In this case, the reacting system passes through a transition state in which five atoms participate in the coordinated stage: C–O–C–O–M. From the standpoint of the balance of bond energy, the more atoms involved in a concerted elementary act during the breaking of old and the formation of new bonds, the lower the activation barrier should be. Thus, the five-center interaction should contribute to lowering the activation barrier. However, in order to the entropy factor in the formation of the transition state of a complex structure was taken into account, conclusions about the preference of a particular route must be made based on the calculation of the Gibbs energy.

We note that at the stage of coordination of the allyl carboxylate molecule, a structure is possible in which the terminal oxygen atom of the carboxylate fragment bonds to the metal atom (Fig. 1). The resulting structure has structural prerequisites to achieve a five-center transition state and the occurrence of a chelating effect.

Oxidative addition of allyl acetate to the nickel(0) triisopropyl phosphite complex. A complex of the composition Ni(P(O^{i}Pr)$_3$)$_3$ was chosen as the initial one. Since the process of oxidative addition increases the number of ligands by 2, we simulated the substitution stage of one phosphite ligand for allyl carboxylate with the formation of structures **Ni_R1** and **Ni_R2** (Scheme 4). The optimized structures of the reagents **Ni_R1** and **Ni_R2**, the transition states **Ni_TS1** and **Ni_TS2** and the products **Ni_P1** and **Ni_P2** of allyl acetate oxidative addition to Ni(P(O^{i}Pr)$_3$)$_2$ stage are presented in Fig. 2.

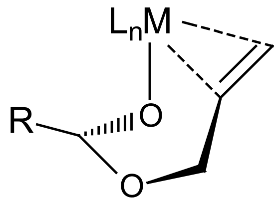
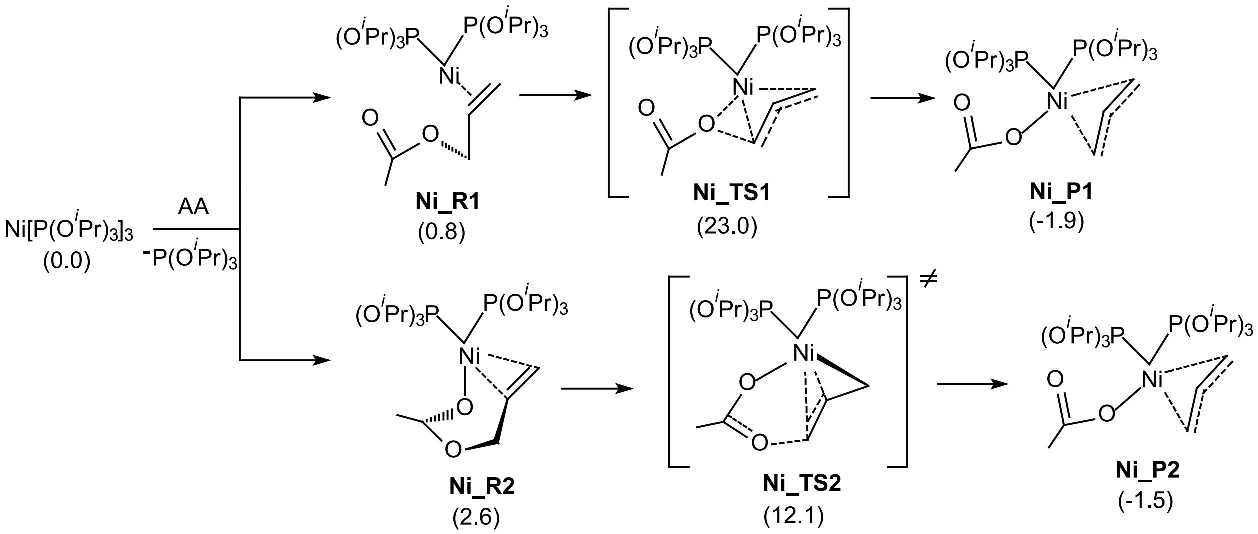


Fig. 1. Structure of the intermediate formed along Route 2, where M – Ni, Pd; L – PPh$_3$, P(O^{i}Pr)$_3$; R – H; CH$_3$.



Scheme 4. Coordination and oxidative addition stages of allyl acetate (AA) to the Ni(P(O^{i}Pr)$_3$)$_2$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.

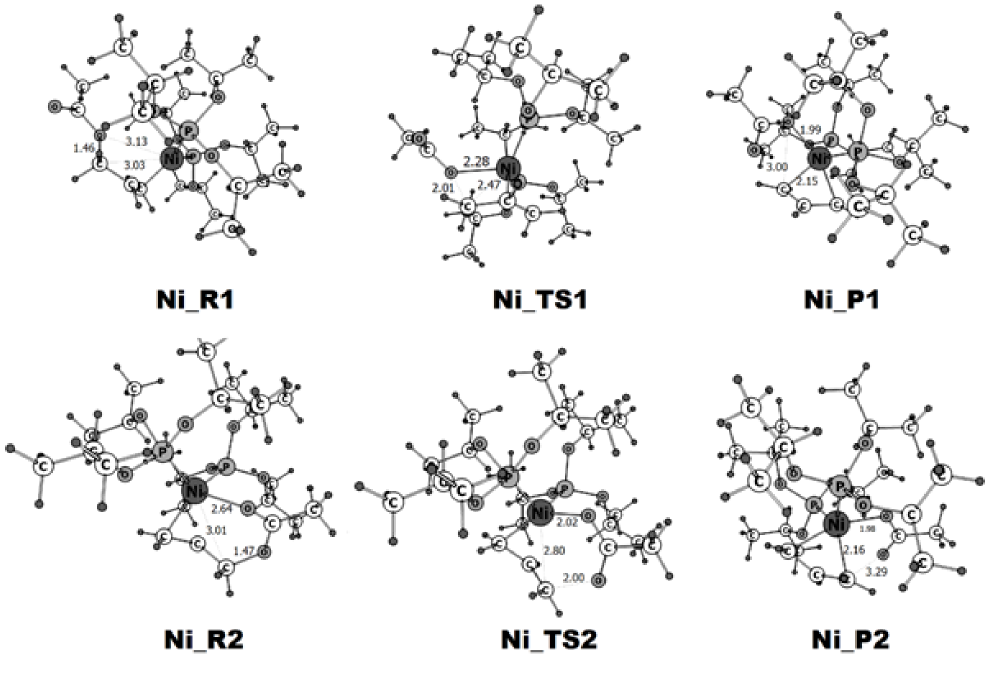
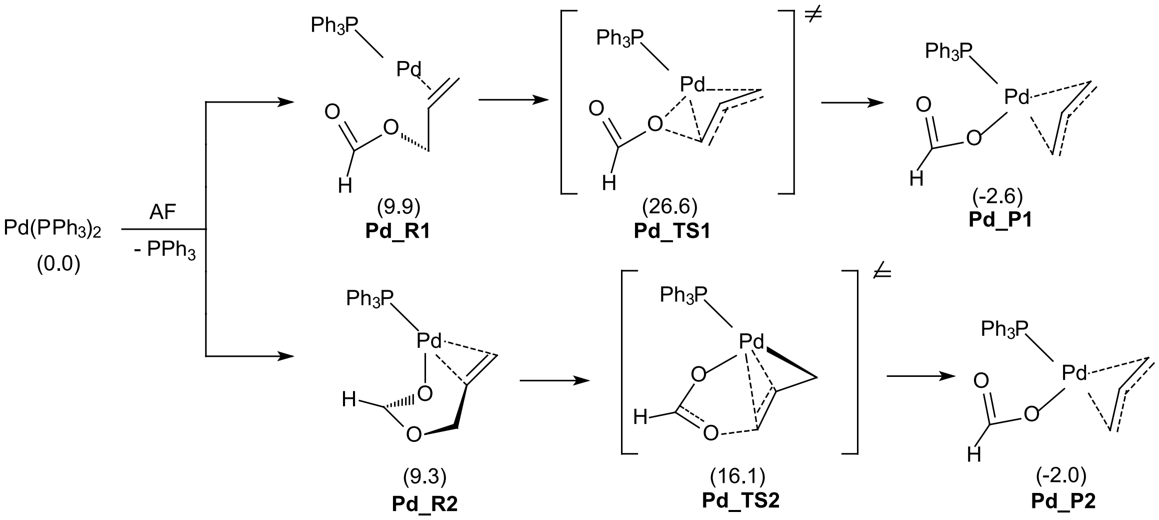


Fig. 2. Optimized structures of reagents (R), transition states (TS), and products (P) of the oxidation addition stage of $C_3H_5OCOCH_3$ to the Ni(P(O^{i}Pr)$_3$)$_2$. Interatomic distances are given in Å.

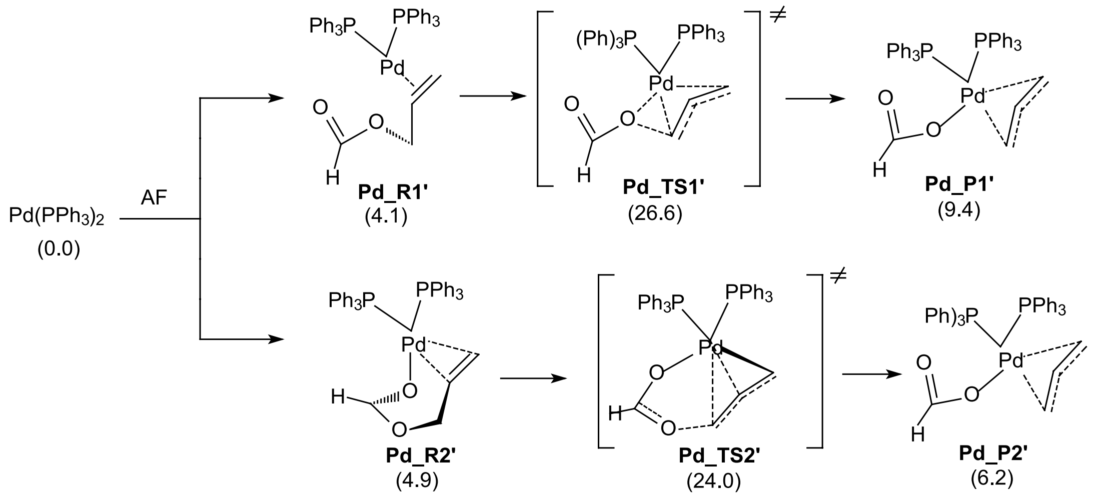
According to the calculations, despite the appearance of an additional Ni–O interaction, the Gibbs energy of the **Ni_R2** complex is 1.8 kcal/mol higher than the energy of the **Ni_R1** complex. In this case, the formation of the three-centered transition state **Ni_TS1** upon breaking the C–O bond is characterized by a higher activation Gibbs energy ($\Delta^{\neq}G_{298}$ = 22.2 kcal/mol) compared with the five-centered transition state **Ni_TS2** ($\Delta^{\neq}G_{298}$ = 9.5 kcal/mol). Figure 2 shows that the length of the formed Ni–O bond in the structure of **Ni_TS2** is noticeably shorter than that of **Ni_TS1**. Therefore, the chelating effect in the transition state of **Ni_TS2** favors the occurrence of oxidative addition.

Oxidative addition of allyl formate to the palladium(0) triphenylphosphine complex. To study the effect of the number of ligands on the activation parameters of the oxidative addition stage, quantum chemical modeling of the oxidative addition of allyl formate to the $Pd(PPh_3)_n$ was carried out for n = 1 and 2. According to our calculations, the reaction mechanism (Schemes 5 and 6) is similar to the Ni-containing system.

A comparison of the energy parameters of 4 routes (Schemes 5 and 6) showed that from the point of view of thermodynamics, the replacement of one phosphine ligand with allyl formate is not beneficial, since it leads to an increase in energy by 4.4–5.8 kcal/mol. However, from the point of view of kinetics, it is obvious that the oxidative addition of allyl acetate can proceed only to the coordination-unsaturated complex $Pd(PPh_3)$. In this case, as in the case with the nickel complex, the formation of a five-center transition state (**Pd_TS2**) leads to a significant reduction in the activation barrier (by 10.5 kcal/mol) compared to a three-center interaction (**Pd_TS1**). The optimized structures of the reagents **Pd_R1** and **Pd_R2**, the transition states **Pd_TS1** and **Pd_TS2** and the products **Pd_P1** and **Pd_P2** of the reaction of the oxidative addition of allyl formate to the $Pd(PPh_3)$ complex are presented in Fig. 3.



Scheme 5. Coordination and oxidative addition stages of allyl formate (AF) to the $Pd(PPh_3)$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.



Scheme 6. Coordination and oxidative addition stages of allyl formate (AF) to the $Pd(PPh_3)_2$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.

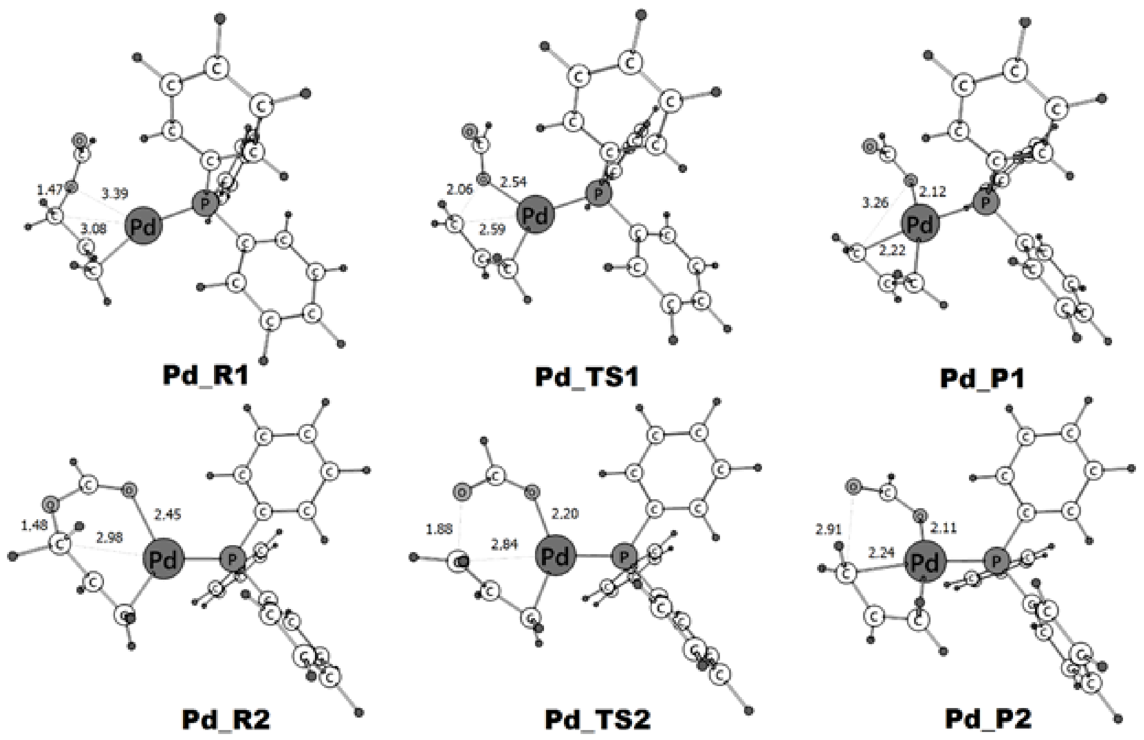


Fig. 3. Optimized structures of reagents (R), transition states (TS), and products (P) of the oxidation addition stage of C_3H_5OCOH to the $Pd(PPh_3)$. Interatomic distances are given in Å.

Table 2. Energy and structural parameters for the three- (**M_TS1**) and five-center transition states (**M_TS2**) of the oxidative addition stage of allyl acetate to the Ni(0) and allyl formate to the Pd(0)

	$\Delta E^{\neq}$, kcal/mol	$\Delta G^{\neq}_{298}$, kcal/mol	$\Delta G^{\neq}_{298,PCM}$, kcal/mol	R(M–O), Å	ν*, cm^{-1}
Ni_TS1	25.2	22.2	22.3	2.28	260.9
Ni_TS2	14.1	9.5	9.3	2.02	195.2
Pd_TS1	19.5	16.7	14.1	2.54	254.8
Pd_TS2	6.7	6.8	6.1	2.20	249.0
Pd_TS1´	25.0	22.5	18.4	2.91	141.4
Pd_TS2´	23.4	19.1	19.3	2.31	255.5

* imaginary frequency

Table 2 presents the energy, spectral, and structural characteristics of the three-center (**M_TS1**) and five-center (**M_TS2**) transition states of the oxidative addition stage of allyl acetate to the Ni(0) complex and allyl formate to the Pd(0) complex. The calculation results confirm the experimental facts about a decrease in the rate of oxidative addition in the presence of bulky ligands in the coordination sphere of the metal that create steric hindrances. Even the presence of a five-center interaction in the diphosphine transition state does not lead to a noticeable decrease in the activation barrier (**Pd_TS2´** and **Pd_TS1´**, Scheme 6). The energy gained from the chelating effect is only 2.6 kcal/mol.

The inclusion of nonspecific solvation in the calculation of the Gibbs activation energy (Table 2, $\Delta G^{\neq}_{298,\ PCM}$) leads to an insignificant correction in the results of the gas-phase calculation in the case of a nickel-containing system in *m*-xylene medium (~0.2 kcal/mol). The polarity of acetonitrile and the significant dipole moment of the three-center transition state of **Pd_TS1´** (6.9 D) lead to the greatest solvent effect for the oxidative addition stage of allyl formate to the **Pd_R1´** diphosphine complex ($\Delta G^{\neq}_{298} - \Delta G^{\neq}_{298,\ PCM}$ = 4.1 kcal/mol). Therefore, the chelating effect has a noticeable effect in coordination-unsaturated complexes and is almost imperceptible in coordination-saturated diphosphine complexes of Pd (0).

Conclusions

The quantum chemical modeling performed made it possible to determine the preferability of the oxidative addition of allyl carboxylates to the Ni(0) and Pd(0) complexes through a five-center transition state. The reaction's activation barriers through the "classical" three-center interaction are 8.0–13.0 kcal/mol higher, and the chelating effect is more noticeable for the nickel complex. The presence in the coordination sphere of several bulky ligands, such as PPh_3, completely eliminates the chelating effect in the oxidative addition of allyl carboxylates.

The authors declare no conflicts of interest.

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Dedicated to the 125th birthday of Academician Yakov Kivovich Syrkin

Phase equilibria in 4-pentyloxybenzoic acid – long-chain *n*-alkane systems

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Objective. *The work's objective is to develop methods for the thermodynamic modeling of systems of liquid crystal – organic solvent.*
Methods. *Four binary systems of nematic 4-pentyloxybenzoic acid (5OBA) with n-alkanes (hexadecane, octadecane, icosane, and docosane) were investigated via thermal analysis methods (differential thermal analysis, polarization microscopy, visual polythermal analysis, and the polytherm solubility method). The accuracy in determining phase transitions temperatures is within 0.3 K. To describe the phase equilibria, models based on the Hildebrand and Hansen solubility parameters were used. Hansen solubility parameters were estimated using the Stefanis scheme. Hildebrand solubility parameters, molar volumes, and vaporization enthalpies were calculated using a group contribution scheme.*
Results. *Phase equilibria in the systems of 5OBA with n-alkanes were studied. Four T–x diagrams were obtained by thermal analysis methods, coordinates of invariant points (eutectics and metatectics) were determined in the systems. A linear dependence of the metatectic coordinate (x_I is a fraction of 5OBA, mol. %) on the number of C atoms in the alkane (N) was established: $x_I = -0.3131 \times N + 85.467$. Solubility polytherms of 5OBA with solvents of different polarity were obtained: n-alkanes (hexane, octane), cyclohexane, aromatic compounds (benzene, toluene, and o-xylene), chlorobenzene, ethyl acetate, acetone, 1,4-dioxane, alcohols (propan-2-ol, propan-1-ol, butan-1-ol), and acetonitrile. The dependence of 5OBA's solubility on the difference in the solubility parameters of the components and the distance Ra was established.*
Conclusions. *The model for regular solutions based on solubility parameters allows us to calculate the solubility polytherms of mesogens and to select solvents for the purification of mesogens by the mass crystallization method. The best solubility of 4-pentyloxybenzoic acid at 298 K appears in chlorobenzene.*

Keywords: *liquid crystals, nematic, phase diagrams, thermal analysis, 4-pentyloxybenzoic acid, n-alkanes, solubility, thermodynamic modeling, Hildebrand solubility parameter, Hansen solubility parameter.*

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К 125-летию со дня рождения академика Я.К. Сыркина

Фазовые равновесия в системах 4-пентилоксибензойной кислоты с длинноцепочечными *н*-алканами

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Целью *работы является разработка методов термодинамического моделирования систем жидкий кристалл – органический растворитель.*

Методами *термического анализа (дифференциальный термический анализ, поляризационная микроскопия, визульно-политермический анализ и метод политерм растворимости) исследованы 4 бинарные системы нематической 4-пентилоксибензойной кислоты (5OBA) с н-алканами (гексадекан, октадекан, эйкозан, докозан). Точность определения температур фазовых переходов – в пределах 0.3 К. Для моделирования политерм растворимости 5OBA использована модель регулярных растворов на основе параметров растворимости Гильдебранда и Хансена. Параметры растворимости Хансена мезогенов рассчитаны по групповой схеме Стефаниса. Параметры растворимости Гильдебранда, мольные объемы и энтальпии испарения рассчитаны по схеме групповых вкладов.*

Результаты. *Методами термического анализа исследованы фазовые равновесия в системах 5OBA с н-алканами. Получены 4 Т–х-диаграммы, определены координаты нонвариантных точек (эвтектики и метатектики) в системах. Установлена линейная зависимость координаты метатектики (x_I – доля 5OBA, мол. %) от количества атомов С в алкане (N): $x_I = -0.3131 \times N + 85.467$. Получены политермы растворимости 5OBA с растворителями разной полярности: н-алканы (гексан, октан), циклогексан, ароматические (бензол, толуол, о-ксилол), хлорбензол, этилацетат, ацетон, 1,4-диоксан, спирты (пропан-2-ол, пропан-1-ол, бутан-1-ол), ацетонитрил. Установлена зависимость растворимости 5OBA от разницы в параметрах растворимости компонентов и приведенного радиуса.*

Заключение. *Модель регулярных растворов с использованием параметров растворимости позволяет рассчитать политермы растворимости мезогенов и подобрать растворители для очистки мезогенов методом массовой кристаллизации. Лучшая растворимость при 298 К 4-пентилоксибензойной кислоты – в хлорбензоле.*

Ключевые слова: *жидкие кристаллы, нематический, фазовые диаграммы, термический анализ, 4-н-пентилоксибензойная кислота, н-алканы, растворимость, термодинамическое моделирование, параметр растворимости Гильдебранда, параметр растворимости Хансена.*

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Introduction

This article is dedicated to the memory of Academician Yakov Kivovich Syrkin, an outstanding scientist and teacher. His research interests lied primarily in the fields of chemical kinetics and the nature of chemical bonds. On the other hand, his university course on physical chemistry was different from the standard course in this subject, mainly due to a revision of the chemical thermodynamics part [1, 2]. Research related to thermodynamic description of systems containing liquid crystals is relatively new for the Ya.K. Syrkin Department of Physical Chemistry at the M.V. Lomonosov Institute of Fine Chemical Technologies of the MIREA – Russian Technological University, however certain success has already been achieved here (see, for example, [3–5]).

Liquid crystals (LCs) are widely used in a variety of applications [6–8], especially in display technologies [8–12]. Modern liquid crystalline materials (LCMs) are multiple-component mixtures, because no individual mesogen has all the necessary properties to be used as a material for display devices. Today, there are two major tasks for those who design new materials – purification of individual LCs and creation of LCMs with a wide range of mesophase existence. The final step of mesogen purification is usually performed by multiple recrystallizations from a solution; this is why research on LC – non-mesogen (solvent) systems is needed (see, for example, [5]).

Since experimental research on LC-containing systems is rather laborious, thermodynamic modeling is in demand.

The objective of this work is to develop methods for thermodynamic modeling of systems of liquid crystal-organic solvent.

One of the most interesting types of mesogen is 4-alkyloxybenzoic acids that allow generation of supramolecular ensembles with new properties. The number of publications on systems with a mesomorphic component that forms hydrogen bonds has soared since the mid-1990s (see, for example, [13–16]). Later, 4-alkyloxybenzoic acids (nOBA) have been used most often as model objects (see, for example, [17–23]). Certain patterns are observed in this homologous series. Acids with a short alkyl chain form only a nematic mesophase. Starting with the 4-heptyloxybenzoic acid (7OBA), the mesomorphic components also have a smectic phase. A specific feature of systems with alkyloxybenzoic acids is the formation of the mesomorphic component in melts and solutions of dimers. The connection between the structure of the nOBA crystalline phases, mesophase types, and length of the mesogen alkyl chain are summarized in articles [24–26].

Materials and Methods

Thermal analysis is described in detail in [5]. The temperatures for phase transitions of individual components and mixtures were determined using standard techniques of differential thermal analysis (DTA) and polarization microscopy [5]. DTA data were confirmed by visual polythermal analysis (thermostating and heating of 0.8–1.2 g samples were performed in a TR-150 thermoreactor, Russia). The accuracy of temperature measurements for phase transitions was within 0.3 °C. The solubility polytherms were obtained by solubility studies (thermostating of saturated solutions – in a TW-2.02 thermostat (Latvia), at low temperatures (down to –30 °C) – in a TLM type microfridge).

We selected the following substances as components for studying the phase diagrams: 4-pentyloxybenzoic acid (5OBA) that forms a nematic phase, and long-chain *n*-alkanes (*n*-hexadecane, *n*-octadecane, *n*-icosane, and *n*-docosane). The 5OBA of the p.a. grade, was twice recrystallized from ethyl acetate. The presence of admixtures in 5OBA was determined by cryometry [5] and did not exceed 1 mol %. As non-mesogens, we have selected *n*-alkanes (C_nH_{2n+2}, n = 16, 18, 20, 22) which may be interesting as additives to lower viscosity [27]. The components' properties are shown in Table 1. The purity of alkanes was controlled by chromatography ("Crystal 2000M" gas chromatograph with a flame ionization detector and an HP-ultra-2 quartz capillary column (phase: polymethyl siloxane with 5% phenyl siloxane), with a length of 50 m and inner diameter of 0.2 mm). The analysis was performed in the following mode: detector temperature 250 °C, vaporizer temperature 270 °C. Retention times for *n*-alkanes were determined from chromatograms of small amounts (4–8%) of these substances dissolved in heptane. Alkane concentrations were calculated based on 3–5 chromatograms, relative to the internal standard (*n*-tridecane). The retention times (min:s) for alkanes and the internal standard were as follows: *n*-heptane – 4:16; *n*-tridecane – 15:39; *n*-hexadecane – 19:51; *n*-octadecane – 22:01; *n*-icosane – 25:00; *n*-docosane – 26:25. The amounts of admixtures in *n*-hexadecane, *n*-octadecane, *n*-icosane, and *n*-docosane did not exceed 2 mol %.

For studies of 5OBA solubility polytherms, we used organic solvents of different polarity: *n*-alkanes

Table 1. Phase transition temperatures of components

Component	Formula	Reagent grade	$T_{ph.tr.}$, °C	
			Exp.	Lit. [29]
5OBA	$C_5H_{11}O$-C_6H_4-COOH	pure analysis	K 124.3 N 152.1 I	K 124.4 N 151.4 I*
n-Hexadecane	*n*-$C_{16}H_{34}$	pure analysis	18.2	18.3
n-Octadecane	*n*-$C_{18}H_{38}$	pure analysis	28.2	28.2
n-Icosane	*n*-$C_{20}H_{42}$	pure analysis	36.4	36.8
n-Docosane	*n*-$C_{22}H_{46}$	pure analysis	44.0	44.0

* K 124.4 N 151.4 I – 5OBA crystals melt at 124.4 ºC forming a nematic (N) phase that at 151.4 ºC forms an isotropic phase.

(hexane, >99%, octane, 98%), cyclohexane, >99%, aromatic compounds (benzene, >99%, toluene, >99%, and *o*-xylene, >99%), chlorobenzene, >99%, esters (ethyl acetate, >99%, and *n*-butyl acetate, >99%), alcohols (propan-2-ol, >99%, propan-1-ol, >99%, and butan-1-ol, >99%), acetone, 99.8%, 1,4-dioxane, >99%, and acetonitrile, >99%. Extra purification of the solvents was performed using standard techniques [28].

Results and Discussion

The minimal set of non-variant equilibria in the systems studied with *n*-alkanes is represented by eutectics and metatectics. The coordinates for the non-variant points are shown in Table 2.

Let us look at the phase diagram of the system 5OBA (I) – *n*-hexadecane (II) (Fig. 1). The eutectic is close to degeneracy:

$$K_I + K_{II} \xrightleftharpoons{t_e} I$$

At the temperature of 118.9 °C (t_m), the interaction between the crystals of LC (I) and the isotropic solution leads to the formation of a boundary nematic solution through a metatectic reaction (with 5OBA content equal to 80.3 mol. %):

$$K_I + I \xrightleftharpoons{t_m} N$$

The T–x diagrams for systems of 5OBA (I) with *n*-octadecaneand *n*-docosane (II) look similar (Figs. 2–4).

The metatectic coordinate moves towards lower 5OBA content upon growth in the alkane length (n is the number of C atoms in the alkane) (Fig. 5). A linear dependence of the metatectic coordinate (x_I is a fraction of 5OBA, mol.%) on the number of C atoms in the alkane was established: $x_I = –0.3131 \times n + 85.467$.

Table 2. Metatectic and eutectic coordinates for 5OBA (I) – alkane (II) systems

System of LC (I) – alkane (II)	Temperature, °C / alkane, mol. %	
	Metatectic	Eutectic
5OBA – *n*-hexadecane	118.9 / 19.7	13.1 / >99.5
5OBA – *n*-octadecane	118.0 / 19.9	25.3 / >99.5
5OBA – *n*-icosane	117.8 / 20.8	33.9 / >99.5
5OBA – *n*-docosane	118.7 / 21.5	40.2 / >99.5

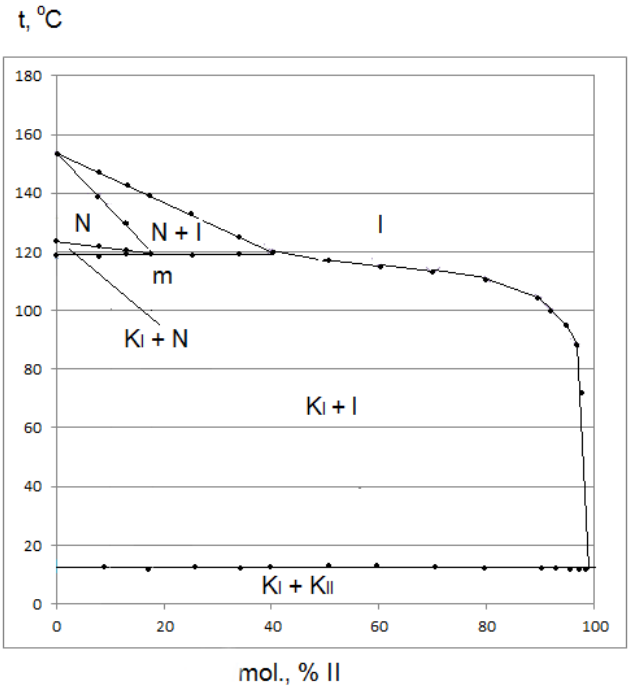

Fig. 1. 5OBA (I) – *n*-hexadecane (II)

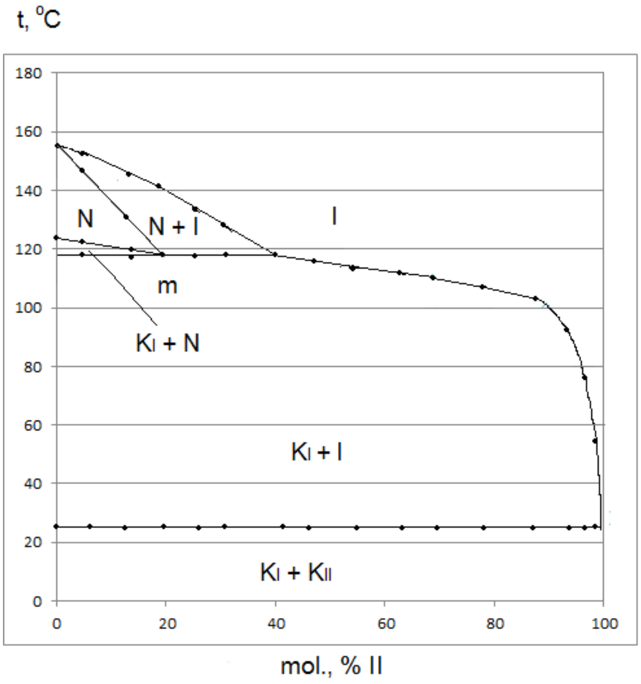

Fig. 2. 5OBA (I) – *n*-octadecane (II)

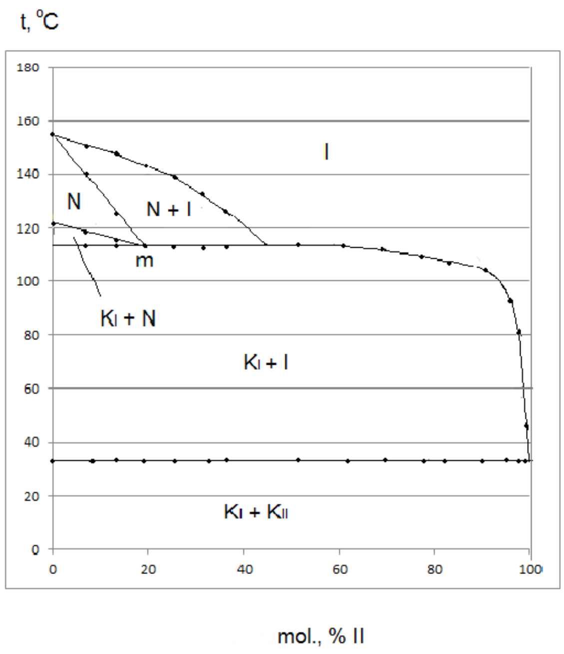

Fig. 3. 5OBA (I) – *n*-icosane (II)

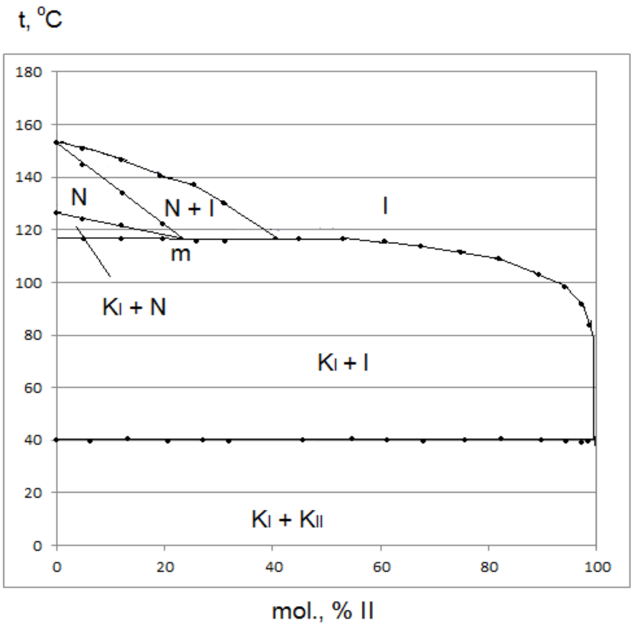

Fig. 4. 5OBA (I) – *n*-docosane (II)

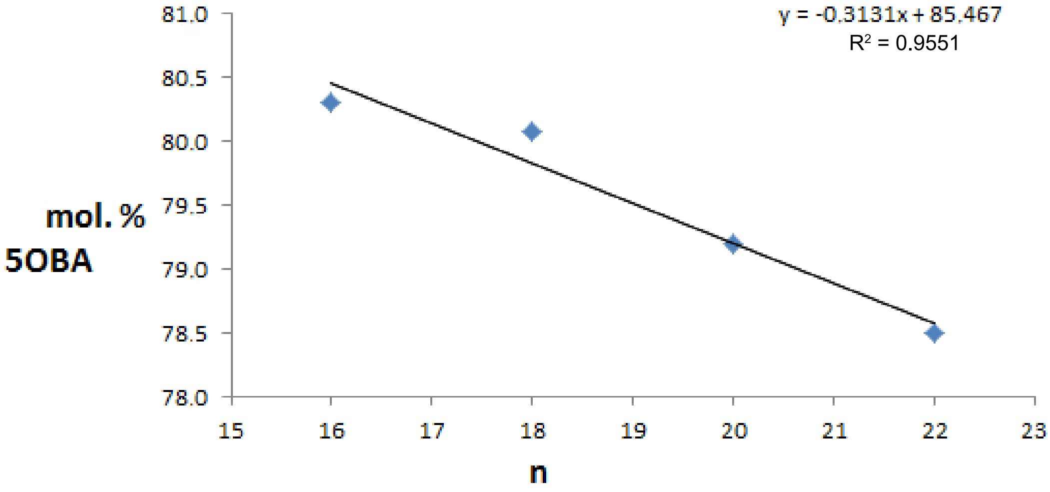

Fig. 5. Dependence of the metatectic coordinate for 5OBA – C_nH_{2n+2} systems on the number of atoms C in the alkane.

For the metatectic point, we calculated an excess Gibbs energy for 5OBA: $G^E_1 = RT_m\ln(\gamma_1)$, where R is the universal gas constant; T_m is the metatectic temperature; γ_1 is the activity coefficient of LC. This value decreases from +0.48 to 0.43 kJ/mol upon increasing the non-mesogen's chain length. Therefore, systems of 5OBA with *n*-alkanes exhibit positive deviation from the ideality, allowing us to use the model of regular solution with solubility parameters to describe such systems [5].

We have studied the solubility polytherms of 5OBA with various types of solvents. Fig. 6 shows solubility data for 5OBA in *n*-hexane, *n*-octane, cyclohexane, benzene, toluene, propan-1-ol, and ethyl acetate. It is evident that 4-pentyloxybenzoic acid dissolves the best in ethyl acetate and alcohol, and the worst in *n*-alkanes; aromatic compounds are somewhat in the middle range. The data on LC solubility (x_1 is a molar fraction) can be described well by a linear function of inverse temperature:

$$-\ln(x_1) = a - b / T$$

Coefficients a and b of the linear function are shown in Table 3.

To correlate the solubility of 5OBA at 298 K in different solvents, models based on Hildebrand and Hansen solubility parameters have been suggested that

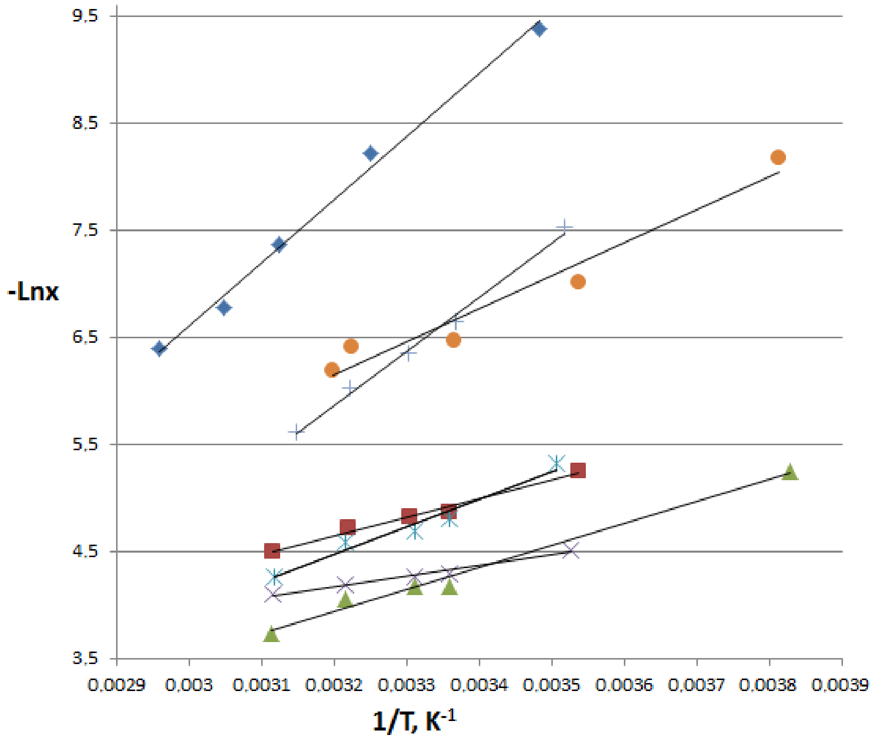

Fig. 6. Solubility polytherms of 5OBA: ◆ – *n*-hexane, ● – *n*-octane, + – cyclohexane, ■ – benzene, ⋇ – toluene, × – propan-1-ol, ▲ – ethyl acetate.

Table 3. Parameters for 5OBA polytherm solubilities

№	Solvent	*b*	*a*	R^2
1	Hexane	5861.5	–10.963	0.9933
2	Octane	3067.9	–3.662	0.9512
3	Cyclohexane	5043.2	–10.268	0.9943
4	Benzene	1730.3	–0.894	0.9837
5	Toluene	2577.8	–3.781	0.9634
6	Ethyl acetate	2065.0	–2.673	0.9880
7	Propan-1-ol	993.4	0.990	0.9784

are widely used for systems with positive deviation from the ideality (see, for example, [30–32]):

$$\delta = \sqrt{\frac{\Delta H_{v,298} - RT}{V}}$$ – Hildebrand solubility parameter,

where $\Delta H_{v,298}$ is an evaporation enthalpy, V is a molar volume of the component.

$\delta_i = [\delta_{id}^{\ 2} + \delta_{ip}^{\ 2} + \delta_{ih}^{\ 2}]^{0.5}$ – Hansen solubility parameter, where δ_{id} is a dispersion component, δ_{ip} is a polar component; δ_{ih} is a component that takes into account the possibility of hydrogen bond formation.

Hildebrand and Hansen solubility parameters for solvents were taken from the reference book [31], and calculations for 5OBA were performed using the scheme of Stefanis group components [32]: $\delta_d = 18.46$, $\delta_p = 6.91$, and $\delta_h = 5.93$ MPa$^{1/2}$.

Fig. 7 shows the dependency of 5OBA solubility (ln X_1) at 298 K on the solvent solubility parameter (δ_2, MPa$^{1/2}$). It is evident that the expected peak value (maximal solubility) is the same as the calculated Hildebrand solubility parameter for 5OBA (22.3 MPa$^{1/2}$). When the difference in solubility parameters for the components is lower, 5OBA solubility is higher.

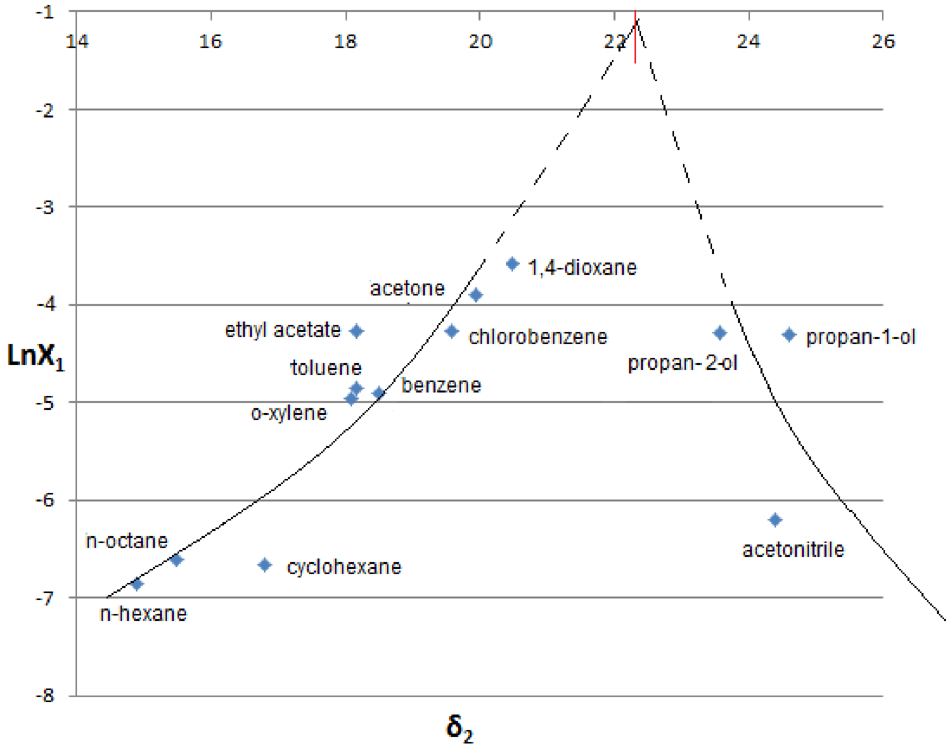

Fig. 7. Solubility plot of 5OBA (ln) vs. δ_2 at 298 K.

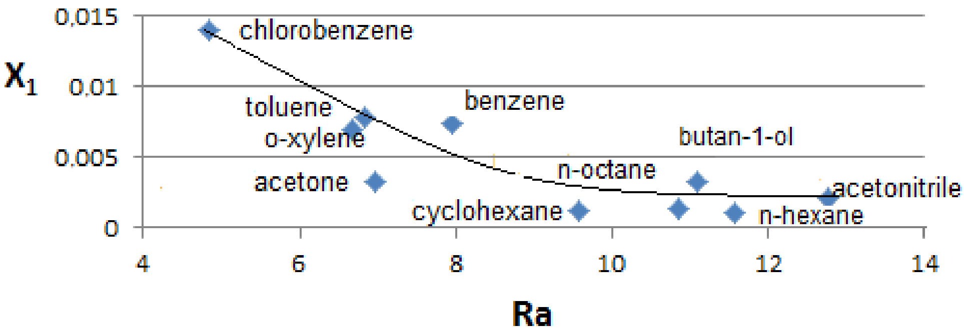

Fig. 8. Solubility plot 5OBA (X_1) vs. R_a at 298 K.

Figure 8 shows the dependency of 5OBA solubility (molar fraction X_1) at 298 K on an equivalent radius (R_a). The formula for calculation of the equivalent radius is as follows [31, 32]:

$$R_a^2 = 4.(\delta_{d(1)} - \delta_{d(2)})^2 + (\delta_{p(1)} - \delta_{p(2)})^2 + (\delta_{h(1)} - \delta_{h(2)})^2,$$

where $\delta_{d(1)}$ and $\delta_{d(2)}$ are parameters of dispersion interaction; $\delta_{p(1)}$ and $\delta_{p(2)}$ are parameters of polar interaction between the LC and the solvent; $\delta_{h(1)}$ and $\delta_{h(2)}$ are parameters of components which take into account hydrogen bond formation upon interaction between the LC and the solvent.

When choosing a solvent for purification of individual LCs, it is necessary to have data on solubility and mutual miscibility of the components [5]. The graph showing the dependency of LC solubility on equivalent radius (Fig. 8) demonstrates that, when the difference in solubility parameters increases, solubility decreases; and when the R_a decreases, LC solubility increases, respectively. This is line with the basic assumptions of the Hansen theory [31] and it allows us to estimate the LC solubility in various types of solvents *a priori*.

Conclusions

1) T–x diagrams for the systems of 4-pentyloxybenzoic acid with *n*-alkanes (C_{16}, C_{18}, C_{20}, C_{22}) contain at least two non-variant points: metatectic and eutectic. In the systems studied, the eutectic is close to degeneracy. The metatectic

coordinate depends on the number of carbon atoms in the alkane, in a linear manner.

2) We have demonstrated the possibility of estimating the solubility of the mesomorphic 4-pentyloxybenzoic acid in various types of solvents, using Hildebrand and Hansen solubility parameters. Calculations based on the solubility parameters allow us to select solvents for mesogen purification by mass recrystallization. The best solubility at 298 K for 4-pentyloxybenzoic acid appears in chlorobenzene.

The authors declare no conflicts of interest.

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Carbon monoxide oxidation by oxygen in water–acetonitrile solutions of palladium(II) bromide complexes in the presence of Co(II), Fe(II) and Mn(III) phthalocyaninates

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Objectives. *The objective of this paper was to compare acetylene oxidative dicarbonylation that leads to maleic anhydride with a side reaction of CO oxidation by oxygen in a $PdBr_2$–LiBr–H_2O–CH_3CN system and in the presence of insoluble (Co) and soluble (Co, Fe, and Mn) phthalocyaninates (PcM).*
Methods. *To study the oxidation of CO to CO_2, a kinetics method was used; UV and IR spectroscopy was used to determine the concentrations of initial and intermediate compounds.*
Results. *The kinetics of CO to CO_2 oxidation were investigated and the reactivity series of PcM in CO oxidation and maleic anhydride synthesis was characterized. A satisfactory correlation was observed between reaction rates and PcM concentration, as well as the nature of metal, in both processes. The IR measurements of concentrations of Pd(II) and Pd(I) intermediate carbonyl complexes, and CO_2 concentrations, have made it possible to hypothesize the mechanism of CO_2 generation. The effect of PcM concentration on the concentrations of Pd(II)(CO) in CO oxidation has been shown.*
Conclusions. *Based on the data regarding CO oxidation and acetylene oxidative dicarbonylation, certain conditions have been proposed to effectively produce double-labeled maleic anhydride with ^{13}C (from ^{13}CO).*

Keywords: *metal complex catalysis, palladium carbonyl complexes, maleic anhydride, carbon monoxide, carbon dioxide, transition metal phthalocyaninates.*

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Окисление монооксида углерода кислородом в водно-ацетонитрильных растворах бромидных комплексов палладия(II) в присутствии фталоцианинатов Co(II), Fe(II) и Mn(III)

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Цели. *Сравнение результатов изучения процесса окислительного дикарбонилирования ацетилена до малеинового ангидрида (МА) с закономерностями побочной реакции окисления СО кислородом в системе $PdBr_2$–LiBr–H_2O–ацетонитрил в присутствии нерастворимых (Co) и растворимых (Co, Fe и Mn) фталоцианинатов (PcM).*

Методы. *Использованы кинетический метод для изучения реакции окисления СО до CO_2 и УФ- и ИК-спектроскопия для контроля за концентрациями исходных и промежуточных соединений.*

Результаты. *Изучена кинетика образования CO_2. Установлены ряды активности PcM в реакции окисления СО и получения МА и показана удовлетворительная корреляция характера зависимостей скоростей R_{CO2} и R_{MA} от [PcM] и от природы металла в обоих процессах. По результатам измерения концентраций промежуточных карбонильных комплексов Pd(II) и Pd(I) и концентраций CO_2 в ходе процесса методом ИК-спектроскопии предложены гипотезы о механизме образования CO_2, а также установлено влияние [PcM] на концентрацию $[Pd^{II}](CO)$ в стационарных условиях в ходе каталитического процесса окисления СО.*

Заключение. *По результатам изучения модельной реакции окисления СО и закономерностей окислительного дикарбонилирования ацетилена предложены рекомендации по условиям эффективного процесса получения дважды ^{13}C-меченного малеинового ангидрида (из ^{13}CO).*

Ключевые слова: *металлокомплексный катализ, карбонильные комплексы палладия, малеиновый ангидрид, монооксид углерода, диоксид углерода, фталоцианинаты переходных металлов.*

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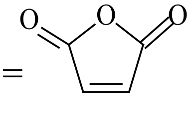
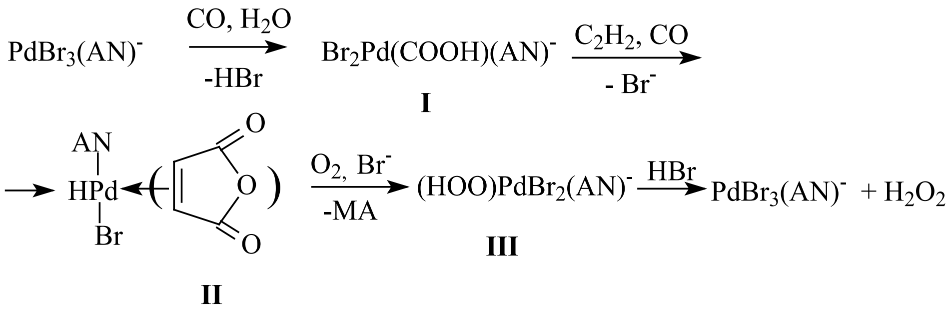
Introduction

Oxidative carbonylation processes, including those for alkynes, have been long known in the field of catalysis with metal complexes, and have been described in reviews [1–7] and monographs [8–10]. One of the most important oxidative carbonylation reactions for acetylene (and alkynes) is oxidative dicarbonylation that leads to maleic anhydride (MA):

$C_2H_2 + 2CO + 1/2O_2 =$  (1)

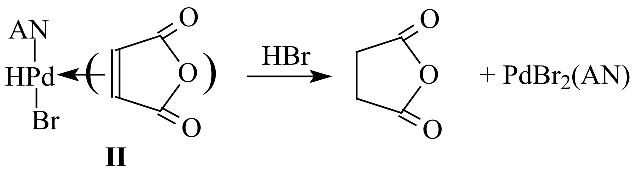
This reaction may be used to obtain MA labeled with ^{13}C for medical diagnostic purposes [11]. The reaction occurs efficiently in the catalytic system of $PdBr_2$–LiBr–acetonitrile (AN)–H_2O. To lower the partial pressure of oxygen, a second catalyst is used to activate O_2–metal phthalocyaninates (PcM) [12]. It has been shown that in the presence of the insoluble PcCo and soluble $(C_4H_9)_2SO_2N)_4$PcFe, the partial pressure of O_2 can be lowered to 0.05 bar in an acetonitrile–H_2O system.

A simplified scheme for the reaction mechanism (Scheme 1) shows the main steps of acetylene dicarbonylation that takes place, for example, in the presence of the $PdBr_3(AN)^-$ complex.



Scheme 1

Oxidation of hydride intermediates of type **II** (Scheme 1) with oxygen [13–21] or the oxygenyl complex PcM(O_2) [12] results in the regeneration of Pd(II). The formation of H_2O_2 upon oxidation of CO has been noted in the papers [22, 23]. The synthesis of succinic anhydride (SA) is one of the side reactions (2) [24]:



(2)

Another side reaction (3) is CO to CO_2 oxidation via oxygen through Intermediate **I**:

$$\underset{\mathbf{I}}{Br_2Pd(COOH)(AN)^-} \xrightarrow[-CO_2]{} HPdBr_2(AN)^- \xrightarrow{O_2,\ HBr} PdBr_3(AN)^- + H_2O_2 \tag{3}$$

Depending on a solution's composition, Pd(0) complexes may be produced instead of hydride complexes; the former may also be oxidized by O_2 or oxygen complexes of PcM [14–16]. Optimization of MA synthesis in the $PdBr_2$–LiBr–PcM–AN–H_2O catalytic system requires an understanding of a simpler process – the side reaction of CO oxidation. The latter includes stages that are also involved in MA synthesis, namely the generation of Intermediate **I** and oxidation of palladium hydride complexes. In order to investigate the process of CO oxidation, we used kinetics, infrared (IR) spectroscopy, and ultraviolet (UV) spectroscopy.

The kinetics for the homogenous oxidation of CO were thoroughly studied for aqueous solutions of Pd(II) complexes with various oxidants: $CuCl_2$ [25–28], $CuCl_2$ + O_2 [29], Fe(III) [29–31], Fe(III) + O_2 [32], heteropolyacids [29, 33], para-quinones [35–37], and oxygen (in certain aqueous–organic solvents [23, 24]). However, for the catalytic system of $PdBr_2$–LiBr–PcM–AN–H_2O used in MA synthesis, the kinetics of CO oxidation were not studied.

Materials and Methods

The following reagents were used: $PdBr_2$ (*Pure*, TU-6-09-05-905-83), acetonitrile (HPLC grade, 99.9%, *Macron* GAS-75-05-8, Poland), tetrahydrofuran (99.95%). Prior to use, tetrahydrofuran (THF) was stored in the presence of NaOH and distilled in the presence of Na. Commercial cobalt phthalocyaninate was additionally purified by reprecipitation from sulfuric acid. Tetra-dibutylsulfamoyl derivatives of cobalt phthalocyaninate [$(C_4H_9)_2SO_2N)_4$CoPc] and iron phthalocyaninate [$(C_4H_9)_2SO_2N)_4$PcFe] (termed Pc*Co and Pc*Fe, respectively), and phthalocyaninate of manganese acetate PcMnOAc have also been used in this work.

CO oxidation was studied at 40 °C in a gas flow reactor with complete mixing. A magnetic stirrer was used to mix the solution. The flow of the incoming gas was measured using a rheometer. The flow of the outgoing gas was measured with a Mariotte vessel or by introducing an inert gas (nitrogen or helium) into the gas reaction mixture. The CO oxidation rate ($\boldsymbol{R}_{CO2}$) was calculated using the stationary areas of the curves of CO_2 accumulation.

In the first step, all components of the catalytic system were loaded into the reactor prior to execution of the experiment (Method A). Then the loading sequence was changed; this was necessary because of the low CO oxidation rate. To elevate the CO_2 portion in the outgoing gas flow ($[CO_2] \approx 2–9$ vol %), the initial gas mixture was put through the reactor at a low speed (3–6 mL/min while the contact solution volume was 5 mL). It is not possible to rapidly fill up the reactor with the gas mixture after reagent loading when working with low speeds of gas flow. This is why a technique was developed whereby PcM was loaded into the reactor first then the reactor was filled up with the gas mixture; 2.5 mL of the solvent was added with a syringe; and then stirring was turned on. Contact solutions containing $PdBr_2$, LiBr and AN (THF) were prepared separately. The experiment started with the introduction of 2.5 mL of the contact solution into the reactor. The loading of the solvent and contact solution was controlled by weighing the syringes (Method B). The behavior of carbonyl complexes during CO oxidation was studied in a closed reactor, while loading the reagents according to Method B. The ratio of LiBr and $PdBr_2$ concentrations is termed α. The composition of the gas mixture and purity of the individual gases were determined by gas adsorption chromatography using an LKHM-8MD chromatograph. Separation of the gases occurred in two sequential packed columns, each 3 m in length. The first column was packed with AG-3 activated charcoal (with a separation temperature of 128 °C), the second column was packed with a 13X molecular sieve (with a separation temperature of 25 °C). The following conditions were used: detector (katharometer) temperature of 160 °C, detector current 70 mA, argon as a carrier gas (1.5 L/h). The concentration of water in the contact solution was determined by gas adsorption chromatography using an LKHM-8MD chromatograph. The following conditions were used: packed column, 3 m in length, 3 mm in diameter, and packed with sorbent Polisorb-1; a separation temperature of 170 °C; evaporator temperature of 200 °C; a detector (katharometer) temperature of 180 °C; detector current 120 mA; helium as a carrier gas (1.2 L/h). Concentrations of MA and SA in the contact solution were determined by gas-liquid chromatography according to the aforementioned method [12, 24].

The IR spectroscopy of contact solutions was performed using a *Specord* M-82 spectrophotometer. For analysis, a portion of the contact solution was taken out of the reactor with a syringe and then it was loaded into 0.25 mm cuvettes, with NaCl windows. Ultraviolet (UV) and visible spectra were recorded using the *Specord* M-40 spectrophotometer, in 1 mm, or 0.1 mm, or 0.01 mm quartz cuvettes.

Results and Discussion

Oxidation of CO using oxygen

It had earlier been shown that the rate of CO oxidation in the catalytic system of $PdBr_2$–LiBr–AN–H_2O was much lower than in the systems of $PdBr_2$–LiBr–THF or $PdBr_2$–LiBr–1,4-dioxane [22]. Because of this to evaluate the experimental setup and analyze low concentrations of CO_2, and to find the conditions for the reaction to occur at a considerable rate, the preliminary experiments in this work were carried out in THF and in the mixture of THF and AN, in a flow reactor. The results of these experiments, with varying concentrations of LiBr and water, as well as temperature, are shown in Table 1.

The preliminary data demonstrate that the rate of CO oxidation in the catalytic system increases with the growth in water concentration (Table 1, exp. 1–3). A partial replacement of tetrahydrofuran with acetonitrile leads to a lower rate of CO_2 production (Table 1, exp. 4, 5). When THF was absent in a $PdBr_2$–LiBr–AN solution, it was impossible to detect CO_2 (Table 1, exp. 6). It is worth mentioning that Experiments 6 and 7 were performed in two stages: first, the gas mixture was put through the $PdBr_2$–LiBr–AN solution, and second, $PcCo_{solid}$ was added into the reactor and the reaction was performed for 1–1.5 h. The addition of $PcCo_{solid}$ into the contact solution in Experiment 6 did not lead to the production of CO_2. A small amount of CO_2 was detected in the $PdBr_2$–LiBr–AN contact solution in Experiment 7, which was carried out at 40 °C, with a lower LiBr concentration (0.025 M) and in a closed reactor.

A change in color was observed in the solution before CO_2 was detected. After contact with CO, an orange color cleared up and went on to become greenish. The greenish color could be due to the reduced forms of palladium. By the 60th minute of the reaction, 0.067 mmol CO_2 was detected, which is ~25% of the $PdBr_2$ amount. Therefore, in Experiment 7, CO_2 production occurs due to the reduction of $PdBr_2$ in the absence of $PcCo_{solid}$, potentially through reaction (4):

$$PdBr_2 + CO + H_2O \rightarrow Pd^0 + CO_2 + 2HBr. \qquad (4)$$

The introduction of $PcCo_{solid}$ in the 60th minute of the reaction resulted in a higher rate of CO_2 production (Fig. 1). The initial rate of this process, in the presence of $PcCo_{solid}$, was 0.17 (M/h). The lower rate of CO_2 production towards the end of the reaction was due to the lower reagent concentration or the higher product concentration, in the closed reactor.

The next experimental series was carried out in a gas flow reactor at 40°C, with α = [LiBr]/[$PdBr_2$] = 0.5. All the components of the catalytic system ($PdBr_2$, LiBr, AN, $PcCo_{solid}$, and water) were loaded into the reactor prior to the reaction. The unsubstituted $PcCo_{solid}$ almost did not dissolve in the contact solution; this is why the process took place in a three-phase catalytic system.

The contact solution's volume and amount of $PcCo_{solid}$ were varied, and the conditions that allowed the kinetic reaction to occur were found.

During the first stage, the process was investigated at [$PdBr_2$] = 0.05 M, [LiBr] = 0.025 M (α = 0.5). The catalytic system would become unstable at lower values of α. The reaction rate had a weak maximum of CO concentration in the gas phase (at O_2 concentration of ~50 vol %) and almost did not depend on [O_2] in the 20–70% range (at a CO concentration of 30 vol %).

Table 1. Results of preliminary experiments*

Exp.	Concentration, M		Temperature, °C	Solvent	Initial gas composition, vol %		R_{CO2}, M/h
	LiBr	H_2O			CO	O_2	
1	0.050	0.5–0.8	30	THF	34.3	53.3	0.170
2	0.050	0.6	30	THF	55.3	38.1	0.100
3	0.050	0.3	30	THF	46.3	51.6	0.010
4	0.050	0.6	30	THF + AN	35.7	60.5	0.038
5	0.050	0.9	30	THF + AN	46.5	51.8	0.034
6**	0.050	0.9	30	AN	44.4	52.8	0
7**	0.025	0.9	40	AN	42.0	56.4	0.170

* Conditions: $[PdBr_2]$ = 0.05 M; Experiment 7 was performed in a closed reactor and the duration of the experiments was 2 hours with a contact solution volume of 5 mL.

** Experiments with addition of $PcCo_{solid}$ into the contact solution.

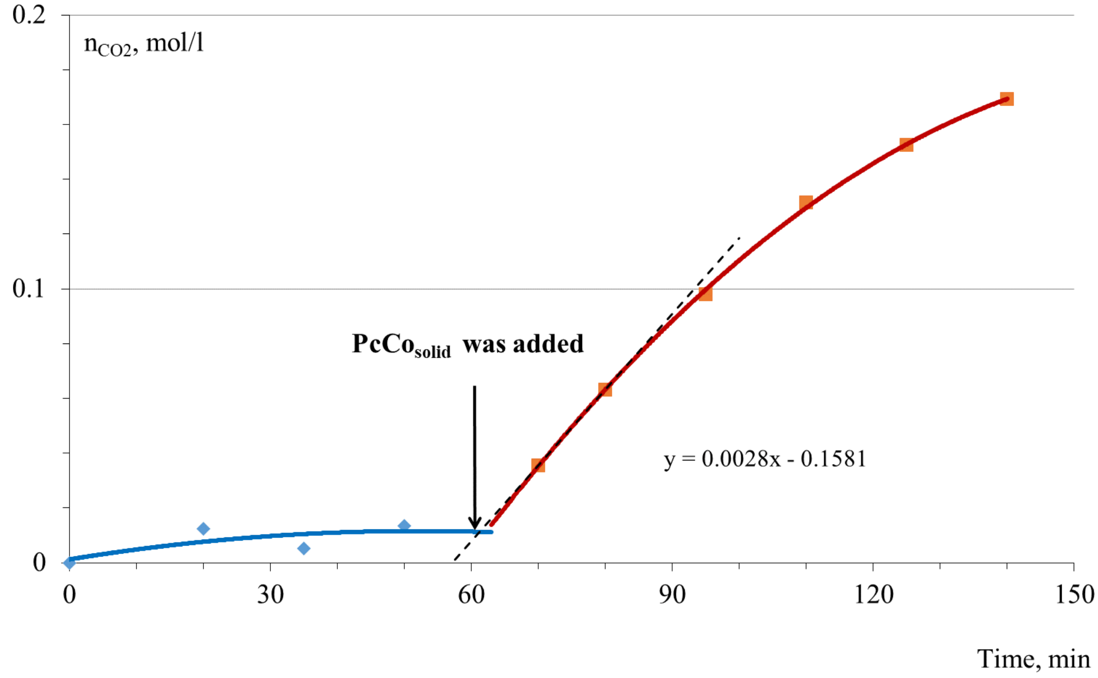


Fig. 1. CO_2 production in Experiment 7. Conditions: $[PdBr_2]$ = 0.05 M, [LiBr] = 0.025 M, $[PcCo_{solid}]$ = 0.025 M, and closed reactor.

The independence of R_{CO2} from $[O_2]$ may be due to the complete coverage of $PcCo_{solid}$ surface by oxygen in this concentration range, and also due to the participation of $PcCo(O_2)$ complexes in the rapid stage of oxidation of palladium hydride complexes, beyond the limiting stage of the process. The reaction rate is a linear function of water concentration in the 0–1.6 M range (Fig. 2).

The effect of the amount of PcM on the rate of CO oxidation was studied at lower concentrations of the components: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.0125 M (Method B) (Fig. 3). The concentration of water in the contact solution was 0.5–0.7 M. Figure 3 shows that only in the case of $PcCo_{solid}$, R_{CO2} is a linear function of the amount (concentration) of PcM. The R_{CO2} curves for soluble PcM are saturation curves.

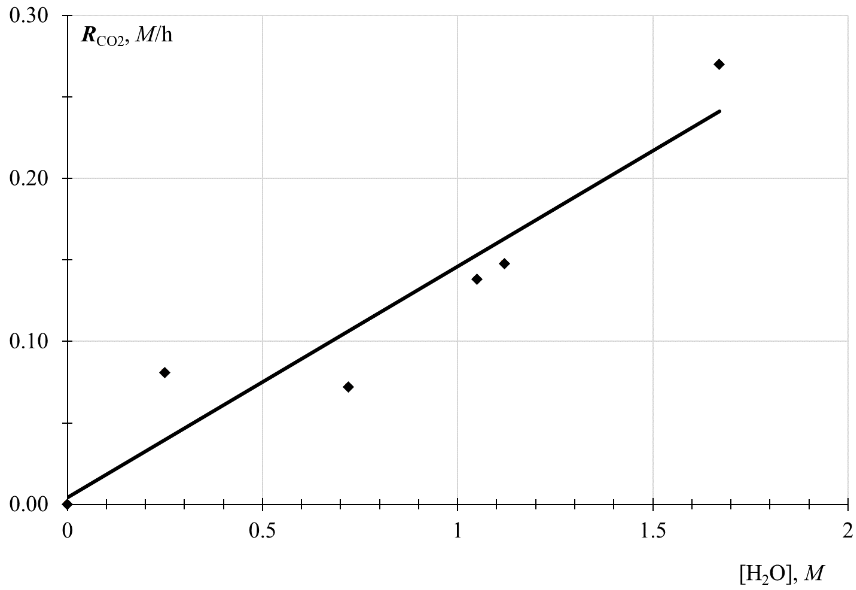


Fig. 2. Dependence of R_{CO2} on H_2O concentration.
Conditions: [$PdBr_2$] = 0.05 M, [LiBr] = 0.025 M. Method A.

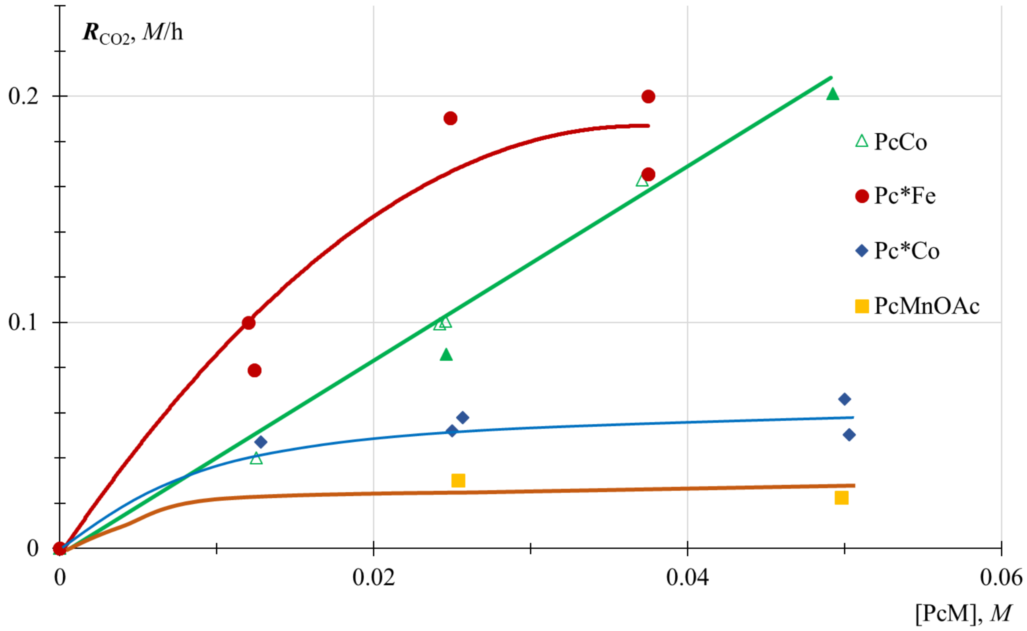


Fig. 3. Dependence of R_{CO2} on amount of $PcCo_{solid}$ and Pc*Co, Pc*Fe concentrations.
Conditions: [$PdBr_2$] = 0.025 M, [LiBr] = 0.0125 M, [H_2O] = 0.5–0.7 M,
a contact solution volume of 5 ml (closed dots), and contact solution volume of 10 ml (open dots).

Interaction between components of the catalytic system during CO oxidation and MA synthesis

To study the mechanisms of component interaction, $PdBr_2$–LiBr–$PcCo_{solid}$–AN and $PdBr_2$–LiBr–$PcCo_{solid}$–adiponitrile (ADN) systems were used. The choice of ADN was due to its well-known use as a solvent in MA synthesis [12]. In addition, ADN allows us to study the behavior of $PcCo_{solid}$ in a solution via spectral methods, because $PcCo_{solid}$ is insoluble in acetonitrile, but its solubility in adiponitrile is approximately 0.001 M, if the solution is incubated with the solid substance for 24 hours at 25 ºC.

a) According to data in [38], in the $PdBr_2$–LiBr–AN system, palladium bromide is mainly found in the form of $[PdBr_2(AN)]_2$ complex (even when α = 2), and in the form of small amounts of anionic complexes $PdBr_3(AN)^-$ (λ_{max} = 273 nm), $PdBr_4^{2-}$ (λ_{max} = 253 and 343 nm), $Pd_2Br_6^{2-}$, and cationic bromide-acetonitrile complexes of palladium. The equilibrium constant of dimeric neutral complex formation, 5.7×10^5 M^{-1}, is approximately 10^3 times higher than all other equilibrium constants, and the concentration of the sum of cationic complexes is 3–4% of $[Pd]_\Sigma$. The predominant formation of $PdBr_4^{2-}$ complex is only observed when $\alpha > 200$ [38].

Palladium bromide was shown to dissolve in nitriles in the absence of bromide anions. For example, $PdBr_2$ solubility at 25 °C is 0.021 M in acetonitrile and 0.07 M in adiponitrile. The UV spectroscopy analysis of $PdBr_2$ solution in AN without LiBr showed that the spectrum contained intensive absorption bands at 273, 208 and 218 nm, and a significantly less intensive band at 322 nm (Fig. 4).

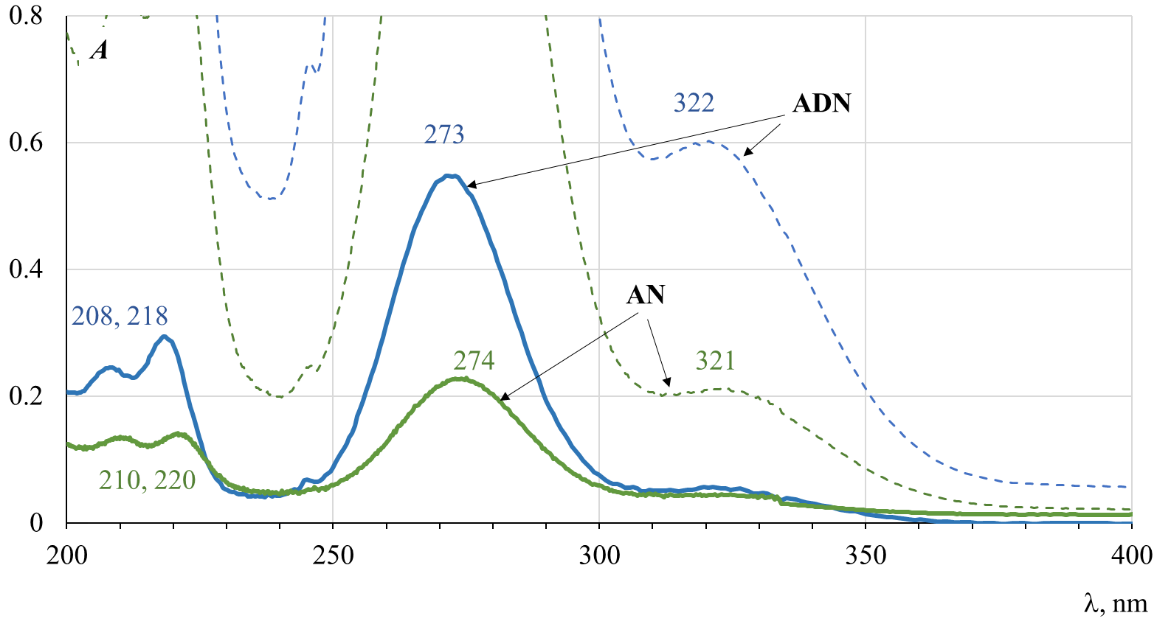


Fig. 4. UV spectra of $PdBr_2$–AN and $PdBr_2$–ADN solutions, in 0.01 mm cuvettes (solid line) and 0.1 mm cuvettes (dashed line).

The dilution of the $PdBr_2$ solution in AN with AN showed (Fig. 5) that, in accordance with the Beer–Lambert law, the absorbance was a linear function of palladium bromide concentration, at 208, 218, 273, and 322 nm, thus suggesting that there was just one predominant form of Pd(II) complex in the solution during the range of concentrations analyzed. When $\alpha = 2$ [38], the predominant form is the dimer $[PdBr_2(AN)]_2$ that has bromide bridges. In the absence of lithium bromide, this form seems even more likely to exist.

Replacement of the solvent with adiponitrile did not lead to considerable changes in the spectrum of palladium bromide.

A shift of all absorption bands by 1–2 nm was observed, which agrees with the idea that the solvent is incorporated into the coordination sphere of the palladium complex. Similarly, absorbance was a linear function of the concentration upon dilution of $PdBr_2$ in adiponitrile at 210, 221, and 274 nm.

Slow evaporation of the saturated (at 25 ºC) $PdBr_2$ solution in AN for 48 hours produced dark-brown crystals. X-ray crystallography[1] showed that these crystals were formed by monomeric complexes of *trans*-$PdBr_2(AN)_2$ that were described previously [39]. Dissolution of the crystals in acetonitrile resulted in the emergence of absorption bands at 208, 218, 273, and 322 nm in the UV spectrum, which is characteristic for a more soluble dimeric complex.

In order to explain the exceptional stability of bromide dimeric complexes upon addition of LiBr, and to interpret the absorption bands observed, one can use the following experimental technique [40] that is employed for palladium chloride complexes $[PdCl_2(AN)]_2$. It has been shown that the addition of excess LiCl to a $PdCl_2$ solution ($[LiCl]/[PdCl_2] < 4$) leads to a higher absorption intensity at 208 and 333 nm, whereas absorption intensity at 244 nm does not change. This fact, according to the

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[1] The analysis was performed by F.M. Dolgushin (D.Sc. in Chemistry) – a Senior Research Fellow at the Laboratory of X-Ray Crystallography, A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

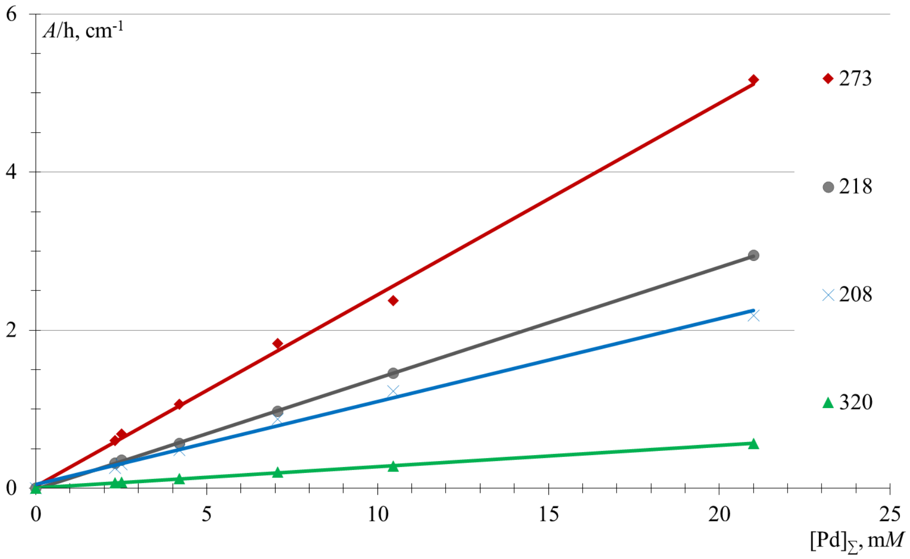

Fig. 5. Change in absorption intensity (the ratio of A to cuvette path length) upon variation of $PdBr_2$ concentration in AN.

authors of [40], agrees with the presence of terminal and bridging Cl^- ligands in the dimeric complex, and with the unchanged concentration of bridge complexes at low Cl^- concentrations. A further increase in Cl^- concentrations causes the disintegration of dimeric complexes and the formation of monomeric complexes.

In this work, similar experiments were carried out, with solutions containing 0.106 mM $PdBr_2$ and 0.08, 0.16, 0.21, and 0.42 mM LiBr. The addition of LiBr led to a higher absorption intensity at 208 and 218 nm, while absorption intensity at 273 nm remained unchanged. An additional absorption band was detected at 235 nm.

b) Cobalt phthalocyaninate $PcCo_{solid}$, dissolved in ADN, had a characteristic absorption band at λ_{max} = 668 nm, with a clear oscillating satellite at λ_{max} = 605 nm. Lithium bromide increased the solubility of $PcCo_{solid}$ in nitriles and shifted the absorption band into the range of longer wavelengths (for ADN, λ_{max} = 664 and 599 nm). In acetonitrile containing 0.1 and 0.2 mmol LiBr, cobalt phthalocyaninate had a major absorption band at 661 nm and a satellite at 598 nm.

c) The experiments with the soluble Pc*Co $[CoPc(SO_2N(C_4H_9)_2)_4]$ showed that this phthalocyaninate, when in acetonitrile, is an associate with a half-width value of 1530±20 cm^{-1} for the main absorption band at λ_{max} = 661 nm. The mixing of equivalent volumes of PcCo (0.001 M) and $PdBr_2$ (0.004 M) solutions in AN led to an almost two-fold decrease in optical density, in the absorbance range of Pc*Co and $PdBr_2$, without significant shifts in the absorption band of Pc*Co (Fig. 6). Similar results were observed for ADN solutions. Therefore, in the case of the soluble phthalocyaninate, no noticeable interaction was detected between the two components of the catalytic system.

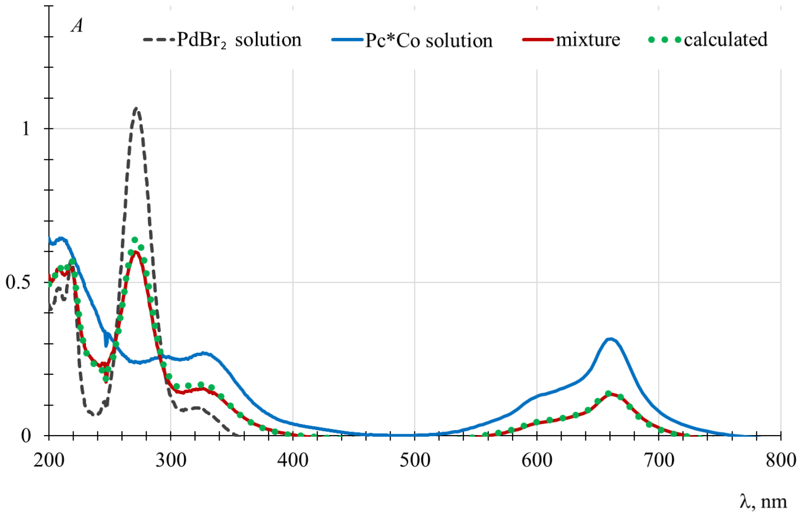

Fig. 6. Calculated and experimental data for solutions obtained by mixing of equal volumes of $PdBr_2$–AN (0.004 M) and Pc*Co–AN (0.001 M).

d) The introduction of LiBr into the Pc*Co solution in AN led to a 1.25 times higher optical density, and a decrease in the half-width of the band at 661 nm to 790 cm^{-1}. The addition of LiBr to the mixture of Pc*Co and $PdBr_2$ in AN resulted in a 1.4 times higher D_{661}, with a decrease in the half-width of the band from 1290±20 to 776 cm^{-1}. This means that bromide ions destroy the Pc*Co associates, both in the presence and in the absence of $PdBr_2$. One of the reasons for the disintegration of associates might be the oxidation of Pc*Co into Pc*Co^{III}Br by the dissolved oxygen.

IR studies of carbonyl complexes of Pd(II) and Pd(I) in various systems

The IR spectra for a number of carbonyl complexes of Pd(II) [41, 42] and Pd(I) [42–45], as well as structures of some complexes [41, 42, 45–49], has already been described. In order to investigate the possible intermediates of CO oxidation, the contact solutions were analyzed using IR spectroscopy. The absence of intensive absorption bands in the 1600–2200 and 2320–2400 cm^{-1} ranges in acetonitrile permitted the investigation of carbonyl complexes of palladium and CO_2 content (absorption band at 2341 cm^{-1}) in the contact solution.

CO oxidation was performed in a closed reactor. The components of the catalytic system ($[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M) were loaded into the reactor according to Method B. Introduction of the contact solution into the reactor led to CO absorption and the formation of a carbonyl complex with an absorption band at 2121 cm^{-1}, which is characteristic for carbonyl complexes of Pd(II) [41, 42, 45]. At low water concentrations (less than 0.1 M), the amount (mol) of CO absorbed in the $PdBr_2$–LiBr–AN–H_2O system (α = 2) was almost equal to the amount of $PdBr_2$. It agrees with the formation of carbonyl complexes, where for each palladium atom there is one CO molecule. The intensities of the absorption band at 2121 cm^{-1}, observed in experiments with different $PdBr_2$ concentrations, were used in order to determine the extinction coefficient for the carbonyl complex of Pd(II). Carbon dioxide is quite soluble in the contact solution. The extinction coefficient for the dissolved CO_2 was determined using the intensities at 2341 cm^{-1}, for solutions where CO_2 concentration did not exceed 0.02 M.

An increase in water concentration in the solution of $PdBr_2$–LiBr–AN up to 0.4 M led to a decrease in the intensity at 2121 cm^{-1} (Pd(II) carbonyl complex) and appearance of absorption bands at 2341 cm^{-1} (CO_2), 1908 cm^{-1}, and 1966 cm^{-1}. Other absorption bands in the contact solution were not detected.

The existing data on the structures of $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ complexes with different cations (Pr_4N^+ [44], NBu_4^+ [46], NH_4^+ [47], PBu_4^+ [48]), as well as the IR spectral data for solutions of the following complexes: $(Pr_4N)[Pd_2(\mu\text{-}CO)_2Br_4]$ [42] and $Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ [43], have been analyzed. Based on this information, it can be assumed that the absorption bands at 1906 cm^{-1} and 1966 cm^{-1} might be associated with the carbonyl complexes of Pd(I). The first band is more intensive and might be associated with asymmetrical oscillations of the CO bridge, whereas the second band, which is less intensive, might appear due to symmetrical oscillations of the CO bridge [48]. The extinction coefficient for the carbonyl complex of Pd(I) was determined by the intensity of the 1906 cm^{-1} band. To do so, the mass balance of the catalyst (assuming that carbonyl complexes of Pd(0) have a low concentration [45]) was taken into account, and formation of a dimeric carbonyl complex of palladium(I) was also taken into account. The resulting extinction coefficients for carbonyl complexes of Pd(II), Pd(I) and CO_2 are 850, 980, and 425 M^{-1} cm^{-1}.

It is important to note that when the 1906 and 1966 cm^{-1} bands were assigned to the carbonyl bromide complexes of Pd(I), the following data was taken into account. In THF solutions of palladium bromide complexes that are obtained through replacement of Cl$^-$ by Br$^-$ in Pd(I) dimeric complexes, or through reduction of $PdBr_4^{2-}$ by CO, a band at 1908 cm^{-1} is observed (CO bridge) in the mixture of Pd(I) and Pd(0) dimeric complexes, and a band at 2106 cm^{-1} is observed (terminal CO) in Pd(0) complexes [45].

CO_2 concentration in the gas phase was determined by chromatography. During the experiment's first 3 to 5 hours, the temperature was 40 °C, and for the remaining 40 to 50 hours the temperature was 25±3 °C.

A. $PdBr_2$–LiBr–AN–H_2O in CO atmosphere

In this series of experiments, the stoichiometric oxidation of CO by bromide complexes of palladium(II) in an AN–H_2O system was investigated, in solutions containing $[PdBr_2]$ = 0.025 M and [LiBr] = 0.05 M (α = 2). After the first introduction of water ($[H_2O]$ = 0.41±0.02 M), a small amount of CO_2 appeared in the solution, and the concentration of Pd(II) carbonyl complex decreased insignificantly throughout the 20 hours (Fig. 7). After the addition of more water ($[H_2O]$ = 0.70±0.02 M), a higher rate of CO_2 production and a dramatic drop in the concentration of Pd(II) carbonyl complex were observed, while a Pd(I) complex was formed. The latter's concentration decreased as the experiment continued for 50–70 hours, due to the participation of the compound in CO_2 production, and, potentially, in formation of palladium(0) complexes with CO bridges and terminal CO groups, as described previously [45]. The total amount of CO_2 corresponds to 60% conversion of palladium. Metallic palladium was not detected even after the addition of the second portion of water.

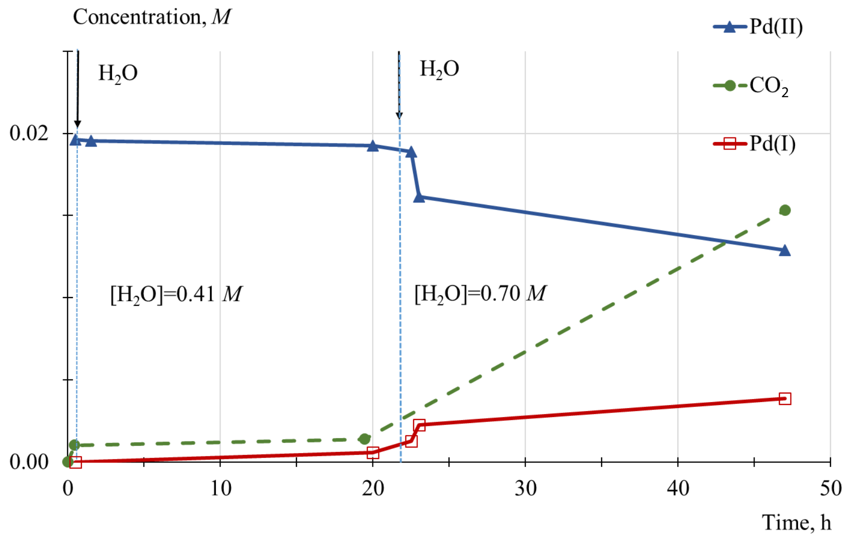

Fig. 7. Changes in concentrations of CO_2 and carbonyl complexes of Pd(II) and Pd(I) during stoichiometric CO oxidation. Conditions: $[PdBr_2] = 0.025$ M, $[LiBr] = 0.05$ M.

The first stage of the process may be represented by reactions (5–9), with carbonyl bromide acetonitrile complex of Pd(II) that is formed upon interaction of CO with the dimeric complex.

Reactions (9) and (10) illustrate two mechanisms for the formation of a Pd(I) carbonyl complex. The reversibility of the reaction (10) may lead to the disproportionation of $Pd_2(CO)_2(AN)Br_2$. The processes that take place after 20 hours and the addition of extra water (5–9) result in a higher rate of CO_2 production, and the emergence of a second possible CO oxidation – reaction (11), which is followed by the participation of hydride intermediates in reactions (8) and (9).

B. $PdBr_2$–LiBr–AN–H_2O in CO/O_2 atmosphere

The same catalytic system and the same method were used to perform experiments with a mixture of gases, CO+O_2 (1:1) (Fig. 8). During the first 20 hours, the rate of CO_2 production was much higher than in the absence of oxygen (Fig. 7). The consumption rate for Pd(II) carbonyl complex was higher, too, but only the addition of extra water triggered the catalytic process, resulting in dramatically faster CO oxidation, while the concentration of Pd(II) carbonyl complex only decreased by 25%. By hour number 40 of the experiment, the catalyst turnover number was only 2.4.

It is important to note that in these conditions, the formation of a Pd(I) carbonyl complex was not observed. It is likely that the intermediates, which formed in reactions (7) and (8), as well as the hydride complexes in reaction (11), were oxidized by oxygen [13–21].

According to the data, hydrogen peroxide is not degraded in the system studied and may participate in the oxidation of all forms of the reduced palladium, including hydride complexes.

Mechanisms with direct involvement of palladium hydroperoxide complexes in forming reaction products can be found among the oxidation mechanisms of unsaturated substances [50]. In the case of CO, such a mechanism may be represented by reactions (15) and (16).

$$Pd_2Br_4(AN)_2 + CO + AN \rightarrow Pd(CO)(AN)Br_2 + PdBr_2(AN)_2 \quad (5)$$

$$Pd(CO)(AN)Br_2 + H_2O \leftrightarrow Br(AN)Pd(COOH) + HBr \quad (6)$$

$$Br(AN)Pd(COOH) + CO \rightarrow HPd(CO)(AN)Br + CO_2 \quad (7)$$

$$HPd(CO)(AN)Br \rightarrow Pd(CO)(AN) + HBr \quad (8)$$

$$HPd(CO)(AN)Br + Pd(CO)(AN)Br_2 \rightarrow HBr + Pd_2(CO)_2(AN)_2Br_2 \quad (9)$$

$$Pd(CO)(AN) + Pd(CO)(AN)Br_2 \leftrightarrow Pd_2(CO)_2\ (AN)_2Br_2 \quad (10)$$

$$Pd_2(CO)_2(AN)_2Br_2 + H_2O = HPd(CO)(AN)Br + HPd(AN)Br + CO_2 \quad (11)$$

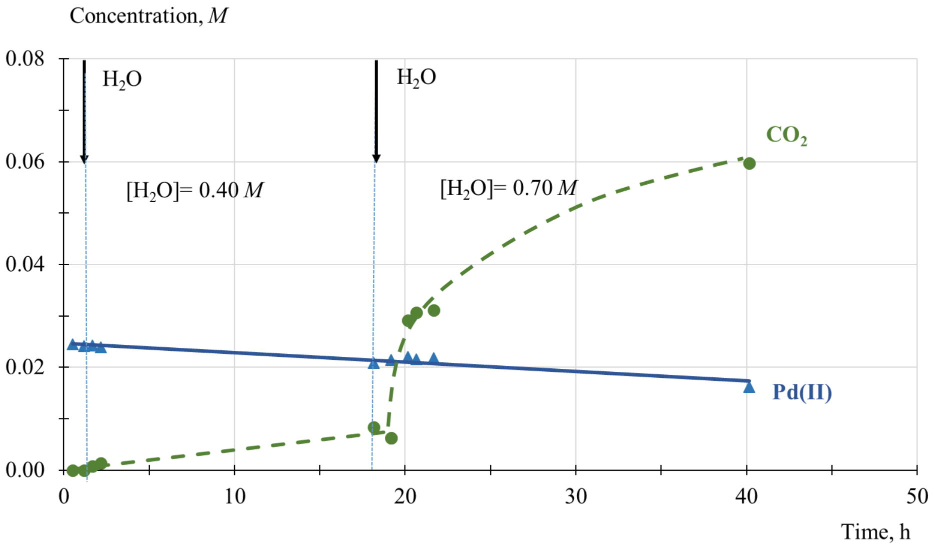

Fig. 8. Changes in concentrations of CO_2 and Pd(II) carbonyl complexes during CO oxidation using oxygen. Conditions: $[PdBr_2] = 0.025$ M, $[LiBr] = 0.05$ M.

$$HPd(CO)(AN)Br + O_2 \rightarrow HOOPd(CO)(AN)Br \text{ (slow)} \tag{12}$$

$$HOOPd(CO)(AN)Br + HBr \rightarrow H_2O_2 + Pd(CO)(AN)Br_2 \tag{13}$$

$$Pd(CO)(AN) + O_2 \rightarrow Pd(CO)(AN)(O_2) \xrightarrow{2HBr} Pd(CO)(AN)Br_2 + H_2O_2 \tag{14}$$

$$HOOPd(CO)(AN)Br + CO \rightarrow HOOCOPd(CO)(AN)Br \tag{15}$$

$$HOOCOPd(CO)(AN)Br + HBr \rightarrow CO_2 + Pd(CO)(AN)Br_2 + H_2O. \tag{16}$$

C. $PdBr_2$–LiBr–AN–H_2O–$PcCo_{solid}$

The same catalytic system was used to perform experiments with added $PcCo_{solid}$ ($[PcCo_{solid}] = 0.025$ M) (Fig. 9). During the first 25 hours, the reaction was performed only with CO, then 20 mL O_2 (~35%) was added into the reactor. No changes were detected in the composition of products and intermediates during the first 5 hours without the addition water. The production of 13% CO_2 was observed, compared to the used palladium, potentially due to oxygen admixtures in CO and a small amount of oxygen on the surface of $PcCo_{solid}$.

After 5 hours, water was added ($[H_2O] = 0.55 \pm 0.02$ M) and the formation of CO_2 was observed; the amount of the latter did not exceed the stoichiometric amount of Pd. The rate was not much higher than in the absence of $PcCo_{solid}$. A decrease in the concentration of Pd(II) carbonyl complex and an increase in the concentration of Pd(I) carbonyl complex were detected. Adding oxygen made the process almost quasi-stationary: concentrations of carbonyl complexes changed from 0.019 M to 0.0154 M for Pd(II), and from 0.0054 M to 0.0073 M for Pd(I). The rate of CO_2 formation increased significantly, and in the first 2 hours after the introduction of oxygen, it was 0.019 M/h. The catalyst turnover number was 4.3.

Oxidation in the presence of $PcCo_{solid}$, as illustrated in Fig. 9, agrees with the results of Experiment 16 in the flow system as shown in Fig. 1. Since oxidation of CO using oxygen leads to the production of hydrogen peroxide, it was interesting to check if it was possible for CO to be oxidized by peroxide in the same system and in the same conditions (in the absence of O_2). After introducing the first portion of H_2O_2 (0.30 mmol, 0.07 M) at $[H_2O] = 0.53 \pm 0.02$ M, the CO_2 concentration reached 0.04 M after 20 hours. The concentration of Pd(II) carbonyl complex decreased from 0.025 M to 0.0167 M, and the concentration of Pd(I) carbonyl complex increased from 0 to 0.012 M. After introducing the second portion of H_2O_2 (0.15 mmol, 0.04 M) and a simultaneous increase in water concentration to 0.82 ± 0.03 M, the CO_2 concentration reached 0.054–0.059 M. By the 45th hour of the reaction, concentrations of carbonyl complexes became almost equal, around 0.01–0.012 M. As mentioned earlier, hydrogen peroxide may partake in the oxidation of hydride complexes of palladium for HPd(CO)Br type, $[Pd^0](CO)$ complexes, and also can be directly involved in CO_2 production through the HOOPd(CO)Br intermediate, according to reactions (15) and (16). There is no doubt that it is possible to form a hydroperoxide intermediate through reaction (17).

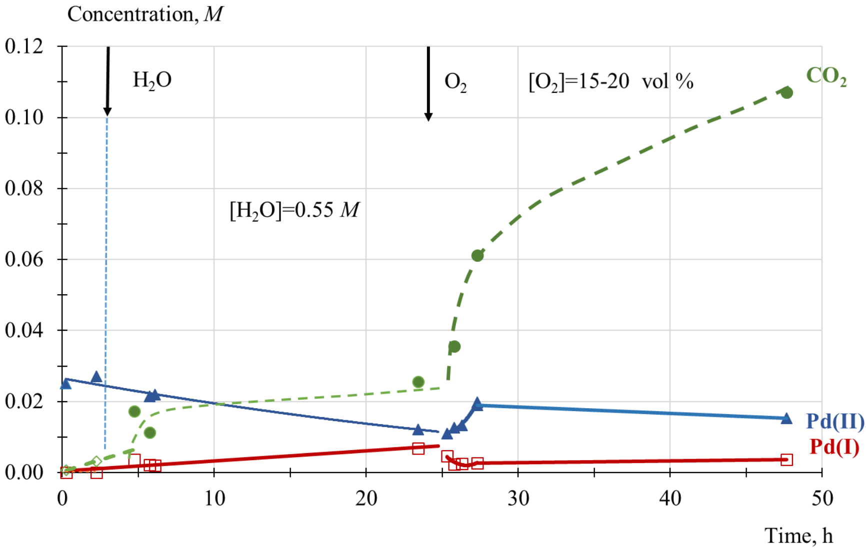

Fig. 9. Effect of $PcCo_{solid}$ on CO oxidation. Conditions: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M, $[PcCo_{solid}]$ = 0.025 M.

$$Pd(CO)(AN)Br_2 + H_2O_2 \rightarrow HOOPd(CO)(AN)Br + HBr \quad (17)$$

The oxidation of Pd(I) carbonyl complex by hydrogen peroxide does not appear to occur, because its concentration increases monotonously during the process.

Comparison of PcM activity in oxidation of CO and MA synthesis

The study of acetylene oxidative dicarbonylation in the presence of phthalocyaninates of different metals (Co, Fe, and Mn) showed that the production rate and MA selectivity by CO, as well as the share of MA in the total of anhydrides in solutions of PcMnOAc, were lower than in the presence of $PcCo_{solid}$ and Pc*Fe (Table 2).

A comparison between CO oxidation kinetics, and the existing kinetics data [12] for oxidative dicarbonylation of acetylene to MA, shows that kinetics are determined by the nature of PcM and do not depend on the type of process. For example, in the case of $PcCo_{solid}$, the rates for both processes increase linearly when its concentration in a solution increases. "Saturation" curves with the substituted Pc*Fe are observed for both processes as well. One of the reasons for the reaction rates to decrease at elevated concentrations of soluble PcM might be the formation of associates in the solution, as well as possible binding of $PdBr_2$ by metal phthalocyaninates (see below).

When the rates of CO_2 and MA production are compared it is necessary to take into account the differences in study conditions. Despite this, the reactivity series of PcM at [PcM] = 0.05 M are identical.

For $\boldsymbol{R}_{MA}$: $PcCo_{solid}$ > Pc*Fe > Pc*Co >> PcMnOAc.

For $\boldsymbol{R}_{CO2}$: $PcCo_{solid}$ > Pc*Fe > Pc*Co >> PcMnOAc.

The low activity of PcMnOAc complexes may be explained, according to theoretical calculations

Table 2. Synthesis of maleic anhydride (MA) and succinic anhydride (SA) via acetylene dicarbonylation reaction

Exp.	PcM	[PcM], M	α	$[O_2]_{exit}$,%	***R***, M/h		MA selectivity, %	
					MA	SA	MA + SA	CO
8	–	–	2	10	0.12	0.36	25.0	27.8
9	$PcCo_{solid}$	0.05	2	10	0.60	0.020	96.8	~ 100
10	Pc*Fe	0.04	2	10	0.39	0.01	97.5	82.6
11	Pc*Co	0.02	2	10	0.38	0.19	79.8	90.5
12	Pc*Co	0.05	2	20	0.43	0.01	97.3	85.0
13	PcMn(OAc)	0.025	1	15	0.08	0.03	72.7	28.0
14	$PcCo_{solid}$	0.05	1	22	0.58	0.054	91.4	83.4

*Conditions: $[PdBr_2]$ = 0.05 M, $[H_2O]$ = 0.1–0.2 M, T=40 °C.

(method DFT)[2], by the greater stability of superoxide manganese complexes, in comparison with $PcCoO_2$ and $PcFeO_2$. Whereas for PcFe and PcCo the changes in the Gibbs energy upon formation of $PcFeO_2$ and $PcCoO_2$ are similar, –0.6 and 0.2 kcal/mol, the ΔG^0_{298} is –6.7 kcal/mol upon formation of $PcMn(OAc)O_2$. This indicates that the connection between oxygen and manganese is too strong, which may be manifested through elevated activation barriers of oxidation stages for hydride complexes and Pd(0) complexes. A comparative quantum chemical analysis was performed for unsubstituted phthalocyaninate complexes PcFe, PcCo, and PcMn(OAc) to understand whether they could partake in the re-oxidation of Pd(0) and hydride complexes of Pd(II). The calculations suggest that for $PcFeO_2$, $PcCoO_2$, and $PcMn(OAc)O_2$ complexes, the mechanisms of interaction with $Pd(CO)_2(AN)_2^0$ (used as an example) are quite similar. During the first stage, an intermediate with the M–O–O–[Pd] fragment is formed. Then, the O atom (closest to Pd) is protonated. Finally, the O–O bond is destroyed, leading to the formation of oxo complexes of metal phthalocyaninates and $Pd(CO)_2(OH)Br$. Reduction of the intermediate oxo phthalocyaninate PcMn(OAc)=O by carbon oxide in PcMn(OAc) also has a very high barrier, 20 kcal/mol.

The differences between PcMn(OAc) and other PcM were observed in experiments where the effect of PcM concentration on the concentration of Pd(II) carbonyl complex was analyzed (Fig. 10). The system contained $[PdBr_2]$ = 0.025 M, [LiBr] = 0.0125 M (α = 0.5), $[H_2O]$ = 0.5–0.7 M, and CO/O_2 = 1:1. Pc*Co, Pc*Fe, and $PcCo_{solid}$ were found to decrease the $[Pd^{II}](CO)$ concentration almost to the same extent, as their own concentrations increased. The same effect was observed in the presence of PcMn(OAc), but the decrease in $[Pd^{II}](CO)$ concentration was less dramatic and led to a slightly higher concentration at high [PcM], which agreed with the lower oxidation rate of CO.

In order to explain certain peculiarities in Fig. 10, it is necessary to note that these experiments were carried out at α = $[LiBr]/[Pd]_\Sigma$ = 0.5, like the experiments that demonstrated high rates of CO oxidation (Figs. 1 and 3), and in contrast with the experiments at α = 2 (Fig. 9), at the same palladium concentration, $[Pd]_\Sigma$ = 0.025 M. For example, the initial rate of CO_2 production is 0.17 M/h in Fig. 1, but for $PcCo_{solid}$ and Pc*Fe, the rate is 0.1 and 0.15 M/h, respectively (Fig. 3). When α = 2 (Fig. 9), the initial rate, depending on the reaction time, 2.4 or 3.9 hours, at the same PcM concentrations, $[PcCo_{solid}]$ = 0.025 M, is 0.004 or 0.009 M/h.

It is necessary to note that at higher oxidation rates (Fig. 3), at α = 0.5, the concentration of Pd(II) carbonyl complex (Fig. 10) is 5 times lower than at α = 2 (Fig. 9), at the same PcM concentration, 0.025 M.

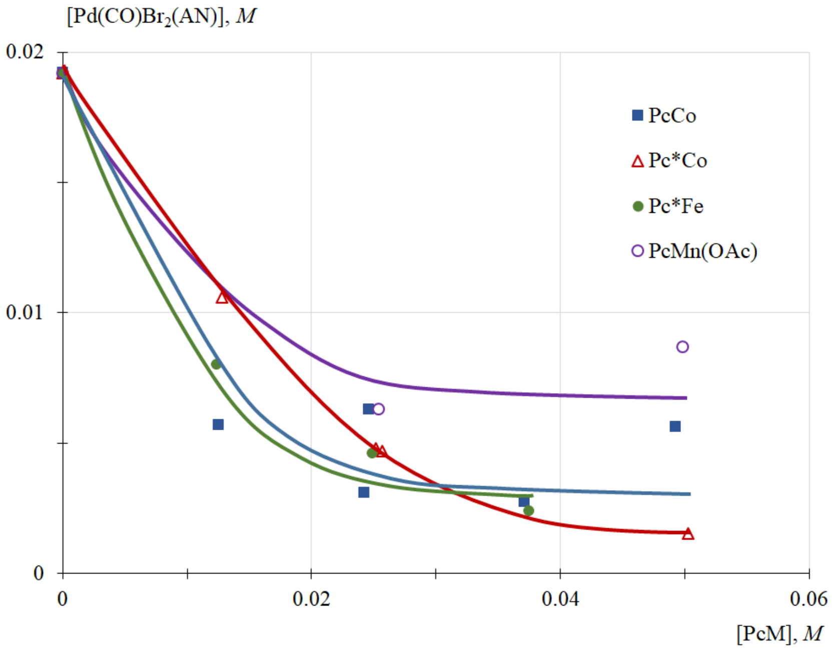

Fig. 10. Effect of PcM nature and concentration on $[Pd(CO)Br_2AN]$ concentration in the contact solution after two hours.

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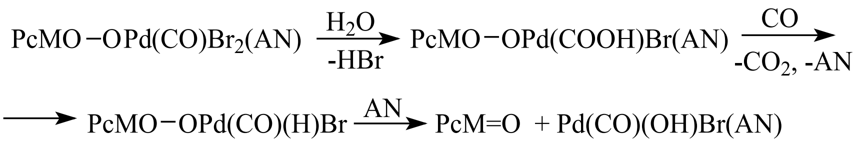
[2] R.S. Shamsiev, O.L. Kaliya and others; unpublished data. The paper by R.S. Shamsiev, which contains the results of the quantum chemical calculations was submitted to the *Russian Chemical Bulletin* in 2019.

Therefore, at lower [LiBr] concentrations, the rates for the following processes increase: CO oxidation; formation and transformation of intermediates, including Pd(II) regeneration. At the same time, the concentration of Pd(II) carbonyl complexes decreases. A logical explanation for this trend is that Co/Fe/Mn phthalocyaninates, while accelerating CO oxidation (up to [PcM] = 0.03 M), not only participate in the oxidation of intermediates – complexes of Pd(0), [Pd]–H and Pd(I), but also in CO_2 formation (directly), i.e. in a new direction of CO oxidation. For example, the formation of an intermediate complex upon interaction between $PcM(O_2)$ and Pd(II) carbonyl complex could facilitate a nucleophilic attack by H_2O on the carbonyl, due to the higher electrophilicity of the C atom and a lower concentration of $[Pd^{II}](CO)$ (see Scheme 2):



$$PcMO{-}OPd(CO)Br_2(AN) \xrightarrow[\text{-HBr}]{H_2O} PcMO{-}OPd(COOH)Br(AN) \xrightarrow[\text{-}CO_2,\ \text{-AN}]{CO}$$

$$\longrightarrow PcMO{-}OPd(CO)(H)Br \xrightarrow{AN} PcM{=}O + Pd(CO)(OH)Br(AN)$$

Scheme 2

The quantum chemical modeling (see Footnote 2) confirms that PcM–O–O–[Pd] (Scheme 2) and PcM–[Pd] complexes may be formed. This creates grounds for the second hypothesis, at least for the soluble PcM: binding of the initial Pd(II) complexes by metal phthalocyaninates or their oxygenyl complexes $PcMO_2$ decreases the concentration of those complexes that form Pd(II) carbonyl complexes.

Summary

The importance of transition metal phthalocyaninates in the catalysis of maleic anhydride synthesis has been demonstrated. For example, under comparable conditions, with $\alpha = [LiBr]/[PdBr_2] = 2$, $P_{O2} = 0.1$ bar, $[CO]/[C_2H_2] = 2$, and in the absence of $PcCo_{solid}$, the rate of MA synthesis is 0.12 M/h, while selectivity is 25% by MA. In the presence of $[PcCo_{solid}] = 0.05$ M, in the same conditions, $\boldsymbol{R}_{MA} = 0.60$ M/h, while selectivity is 96.8% (Table 2). The major advantage of phthalocyaninate catalysts is that they boost the selectivity of MA synthesis, at low amounts of oxygen in the gas mixture, $P_{O2} \geq 0.05$ bar. It is particularly important for syntheses that involve acetylene. For instance, in the presence of $PcCo_{solid}$, at $P_{O2} = 0.05$ bar (6.5 vol % of O_2), MA synthesis occurs with a rate of $\boldsymbol{R}_{MA} = 0.35$ M/h and selectivity of 91%.

PcM complexes also boost the rate of the side (model) reaction of CO oxidation into CO_2 (Fig. 3). For example, at $\alpha = 0.5$ and $P_{O2} = 0.38$ bar, the rate of CO oxidation in the absence of PcM is 0.013 M/h, and in the presence of 0.025 M $PcCo_{solid}$ the rate is 0.17 M/h, i.e. it is 13 times higher.

A comparison of two processes, CO_2 synthesis and MA synthesis, in the presence of PcM has made it possible to determine the reactivity series for Co(II), Fe(II) and Mn(III) phthalocyaninates, soluble or insoluble in acetonitrile. The reactivity series were similar for both processes. Based on the results of the present study, the following recommendations may be given to optimize MA synthesis, accelerate the reaction and boost the selectivity, as well as to improve the stability of the catalytic system:

(1) to catalyze the synthesis of maleic anhydride, it is recommended to use $PcCo_{solid}$ and the soluble Pc*Fe, at concentrations of 0.3–0.4 M;

(2) the concentration of LiBr should be in the following range: $[LiBr]/[PdBr_2] = 0.5–2.0$. This would provide the catalytic system with stability, a high oxidation rate and a low rate of CO_2 production (rate of ^{13}CO consumption in the synthesis of diagnostic molecules);

(3) water concentration should not exceed 0.1–0.2 M in order to slow down the side reaction – production of CO_2.

Conclusions

1. Based on the study of the kinetics of CO oxidation using oxygen, and oxidative dicarbonylation of acetylene into maleic anhydride, and based on the comparison of the reactivity series of metal phthalocyaninates in both reactions in the same catalytic system, it has been shown that CO oxidation is indeed a suitable model for acetylene oxidative dicarbonylation.

2. The kinetics of CO_2 production were analyzed. The PcM reactivity series, for CO oxidation and MA synthesis, was determined. It has been shown that there is a satisfactory correlation between the rates ($\boldsymbol{R}_{CO2}$ and $\boldsymbol{R}_{MA}$) and [PcM], as well as the nature of the metal in phthalocyaninate complexes for both processes.

3. Analyses of Pd(II) complexes dissolved in acetonitrile and adiponitrile were performed, using electron spectroscopy in UV and visible ranges. The important role of the dimeric $[PdBr_2(AN)]_2$ complexes in CO oxidation were demonstrated.

4. The concentrations of intermediate carbonyl complexes of Pd(II) and Pd(I), as well as CO_2

concentrations were measured throughout the course of the reaction, using IR spectroscopy. Based on this data, the mechanism of CO_2 formation was hypothesized. Also, the effect of [PcM] on $[Pd^{II}](CO)$ concentration in stationary conditions during the catalytic oxidation of CO was determined.

5. Improvements to conditions of maleic anhydride synthesis have been suggested for the effective synthesis of maleic anhydride double-labeled with ^{13}C.

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Synthesis and properties of Cu- and Pd-complexes of cyclen conjugates with pheophorbide and bacteriopheophorbide

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Objectives. *Chlorin and bacteriochlorin photosensitizers are effective agents for cancer photodynamic therapy and fluorescence imaging. They are also excellent chelators forming stable metal complexes. Besides, ^{64}Cu and ^{109}Pd isotopes can serve as emitters for nuclear medicine. Chelation of these metals with cyclen conjugates with chlorin and bacteriochlorin photosensitizers can become a simple and universal strategy for the synthesis of diagnostic and therapeutic radiopharmaceuticals for nuclear medicine. This article reports on the synthesis of similar Cu and Pd complexes of cyclen conjugates with pheophorbide and bacteriopheophorbide and the study of their photophysical properties.*

Methods. *Metalation of cyclen conjugates was carried out with palladium and copper acetates. For bacteriochlorins, 6-O-palmitoyl-L-ascorbic acid was additionally used as a reducing agent. MALDI mass spectrometry, which was carried out on a time-of-flight mass spectrometer Bruker Ultraflex TPF/TOF and a Bruker Daltonics Autoflex II confirmed the structure of the compounds obtained. Electronic absorption spectra were obtained on a Shimadzu 3101 spectrophotometer. Fluorescence and phosphorescence spectra were obtained on a FluoTime 300 PicoQuant spectrofluorometer.*

Results. *Photophysical studies of metal complexes showed that the introduction of palladium cations quenches fluorescence and increases the quantum yield of singlet oxygen generation to 0.98 for the chlorin conjugate. Besides, it decreases the quantum yield of fluorescence to 0.10 and increases the quantum yield of singlet oxygen generation to 0.72 for the bacteriochlorin conjugate. Introducing a copper cation to cyclen conjugates with pheophorbide and bacteriopheophorbide leads to photophysical characteristics quenching.*

Conclusions. *Due to the stability of the synthesized metal complexes in acidic media, as well as the short metalation time (5, 20, 10, and 15 minutes) it is reasonable to expect the successful development of effective imaging agents for positron emission tomography and radionuclide therapy. In addition, the residual fluorescence of bacteriochlorins makes it possible to use fluorescence diagnostics in combination with these methods.*

Keywords: *metal complexes, bacteriochlorins, chlorins, theranostics, cyclen, palladium, copper, photodynamic therapy.*

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Синтез и свойства Cu- и Pd-комплексов конъюгатов циклена с феофорбидом и бактериофеофорбидом

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Цели. *Фотосенсибилизаторы на основе хлоринов и бактериохлоринов являются эффективными агентами для фотодинамической терапии и флуоресцентной визуализации рака. Кроме того, они представляют собой отличные хелаторы, образующие стабильные металлокомплексы, а изотопы* ^{64}Cu *и* ^{109}Pd *могут служить в качестве излучателей для ядерной медицины. Хелатирование таких металлов с конъюгатами циклена с хлориновыми и бактериохлориновыми фотосенсибилизаторами может стать простой и универсальной стратегией синтеза диагностических и терапевтических радиофармацевтических препаратов для ядерной медицины. В настоящем исследовании сообщается о синтезе подобных Cu- и Pd-комплексов конъюгатов циклена с феофорбидом и бактериофеофорбидом и исследовании их фотофизических свойств.*

Методы. *Металлирование конъюгатов циклена проводилось ацетатами палладия и меди, для бактериохлоринов дополнительно использовали 6-O-пальмитоил-L-аскорбиновой кислоты в качестве восстановителя. Структуру полученных соединений подтверждали с помощью MALDI-масс-спектрометрии, которую проводили на время-пролетном масс-спектрометре Bruker Ultraflex TPF/TOF и Bruker Daltonics Autoflex II. Электронные спектры поглощения регистрировали на спектрофотометре Shimadzu 3101. Спектры флуоресценции и фосфоресценции были получены на спектрофлуориметре FluoTime 300 PicoQuant.*

Результаты. *Фотофизические исследования металлокомплексов показали, что введение катионов палладия приводит к тушению флуоресценции и увеличению квантового выхода синглетного кислорода до 0.98 для хлоринового конъюгата, а также уменьшению квантового выхода флуоресценции до 0.10 и увеличению квантового выхода синглетного кислорода до 0.72 для бактериохлориного конъюгата. Введение катиона меди к конъюгатам циклена с феофорбидом и бактериофеофорбидом приводит к тушению фотофизических характеристик.*

Заключение. *Устойчивость синтезированных металлокомплексов в кислых средах, а также небольшое время металлирования (5, 20, 10 и 15 мин соответственно) позволяет ожидать успешное создание эффективных визуализирующих агентов для позитронно-эмиссионной томографии и радионуклидной терапии, а остаточная флуоресценция бактериохлоринов делает возможным применение флуоресцентной диагностики в комбинации с данными методами.*

Ключевые слова: *металлокомплексы, бактериохлорины, хлорины, тераностика, циклен, палладий, медь, ФДТ.*

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Introduction

Various physical methods can be used for the molecular imaging of malignant neoplasms. Among them, an important place is occupied by single photon emission computed tomography (SPECT), positron emission tomography (PET), magnetic resonance imaging (MRI), and fluorescence diagnostics (FD). Each of these image processing methods has both merits and demerits. Combining different methods makes it possible to overcome the existing limitations. Compounds possessing different, but complementary physical properties play an important role in this. In this case, it is possible to combine two modal units, for example, a fluorescent dye and a chelator containing Gd, with the formation of a bifunctional agent for simultaneous use in FD/MRI. This type of agents is designed for 1:1 ratio (e.g., a bimetallic complex with a 1:1 Gd/Cu ratio) [1]. In the case of MRI and PET, due to the different sensitivity of the methods, this system can be used only upon diluting the radioactive isotope with "cold" copper ions. Tei et al reported the synthesis of a heterodimeric polyaminocarboxylate ligand DO3A-AAZTA (1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid – 1,4-bis(carboxymethyl)-6-[bis(carboxymethyl)]amino-6-methylperhydro-1,4-diazepine) and its hetero-ditopic Gd(III)-Ga(III) complex for use as a contrast agent in MRI/PET [2]. Guerin and coworkers described the synthesis of a series of new bimodal probes combining zinc phthalocyanine (ZnPc) to form fluorescence and ^{68}Ga/1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid (DOTA) or ^{64}Cu/1,4,7-triazacyclononane-1,4,7-triacetic acid (NOTA) for PET images [3]. Kim et al describe the synthesis of a bimodal Gd(III)/^{125}I-RGD-DOTA probe for SPECT/MRI [4]. Desbois and colleagues obtained dimeric ligands with two different chelating macrocycles: one based on a DOTA derivative for Gd(III) complexation to enhance the contrast in the MRI method and another using a corrin macrocycle for ^{64}Cu chelation in radionuclide visualization [1]. Waghorn et al used ^{109}Pd as a radioisotope for radionuclide therapy (RT) in their work. They showed that hematoporphyrin with ^{64}Cu and ^{109}Pd isotopes has significant tropism regarding tumors, mainly those localized in mitochondria [5].

Interestingly, a chelating DOTA-like tetraazamacrocycle can be used for the complexation of various metal ions usually leading to stable heterobimetallic complexes. For example, the gadolinium complex of DOTA is currently used as an extravascular contrast agent for MRI [6].

Various chelating ligands were suggested for copper radionuclides, such as polyaminocarbonoxylates, cyclic polyamines, tetraazamacrocycles and bis-thiosemicarbazones [7]. Selection of the reagents depends on the stability of the formed complexes. Acyclic chelates do not have sufficient kinetic stability. Therefore, macrocyclic ligands are preferred [8]. The thermodynamic stability of the respective classes of ligands for Cu(II) complexes decreases in the following order: hexa aza cages > tetraazamacrocycles > polyaminophosphonates > polyaminocarboxylate macrocycles > acyclic aminocarboxylates [7]. DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) is the most commonly used macrocyclic chelator of metals, including ^{64}Cu, in radiopharmaceutical studies [9]. However, DOTA is not an ideal ligand for ^{64}Cu because of the slow reaction kinetics [10]. 1,4,7-Triazacyclononane-1,4,7-triacetyl acid, as well as cross-bridged 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid are more stable as compared to DOTA, but they require harsh conditions of radioactive labeling [11]. The most common ^{64}Cu complex is diacetylbis(*N*-4-methylthiosemicarbazone) (ATSM) [12]. The lipophilic molecules of this complex are selectively absorbed by hypoxic tissues and therefore may be used to detect such areas with cardiac system disorders.

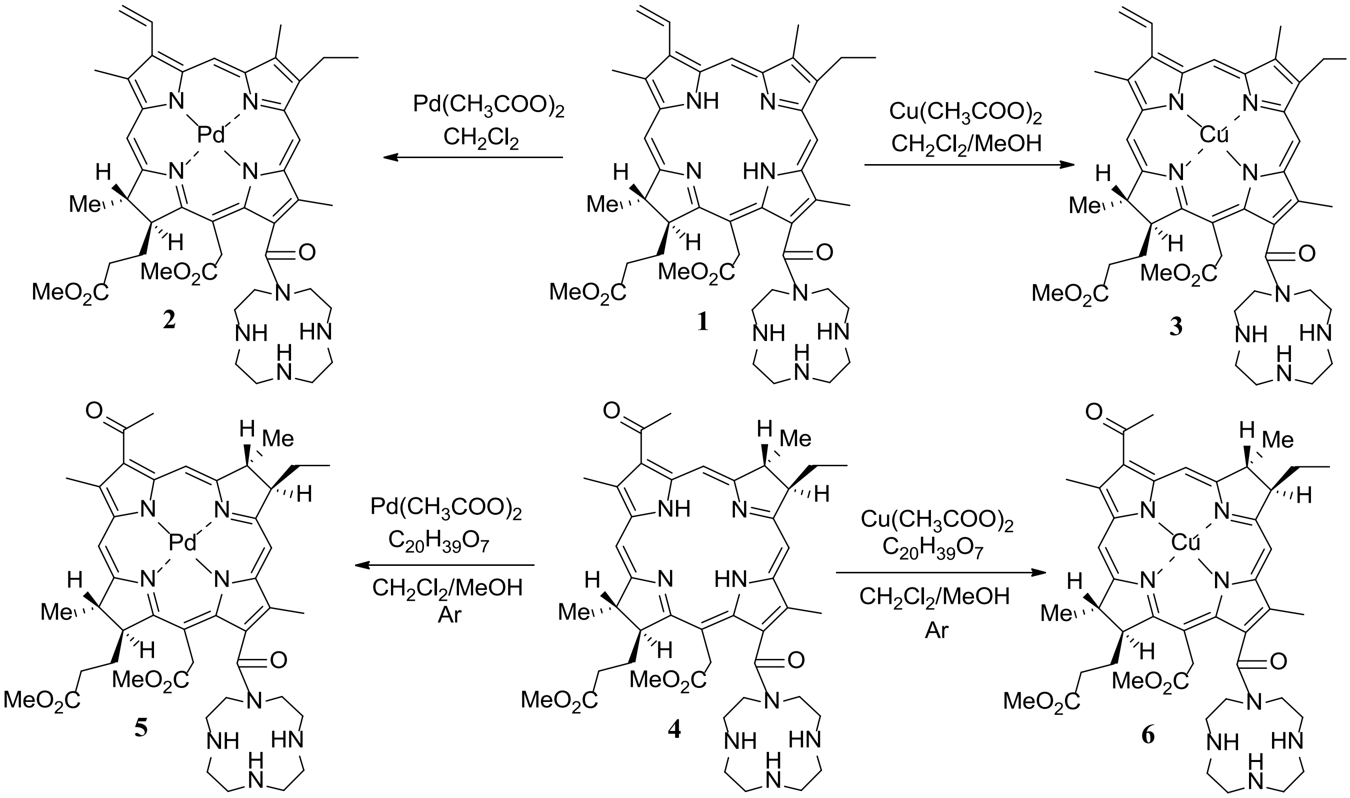
On the other hand, the rapid complexation of metal ions with a ligand is an important criterion in the development of radiopharmaceuticals, because in some cases the lifetime of a radioisotope is comparable with the time of the complex's preparation and use. This is a serious limitation of many radioactive labeling techniques, in which long incubation times (up to 1 hour) and an excess of the ligand are used to achieve a sufficient complexation yield. In some cases, the presence of an excess of the ligand in the compositions is undesirable, because many target agents have their own biological activity.

An extensive class of natural and synthetic porphyrins occupies a prominent place among numerous chelating ligands. This is due to the high affinity of these compounds to various metals and increased tropism for malignant neoplasms [13]. The metal complexes of porphyrins and of their hydrogenated analogues (chlorins and bacteriochlorins) are widely used in photodynamic therapy (PDT) for cancer. The well-known photosensitizer Padeliporfin (a Pd complex of bacteriochlorin) is used for the fluorescence diagnostics and therapy of various tumor types [14]. Porphyrins and their hydrogenated analogues are promising chelators and vehicles to deliver copper radioisotopes to diseased tissues [15]. They have the ability to chelate metal ions through a system of four nitrogen atoms in the macrocycle with an ionic radius of about 70 pm (the ionic radius of Cu^{2+} is 72 pm). Although the complexes are characterized by the high values of stability constants, they have relatively poor formation kinetics. This limitation was removed by using a mechanism including a SAT (sitting-a-top) complex formation [16]. The chelating properties are substantially independent of the type and number of substituents in the ring, which allows using a suitable amphiphilic conjugate for PET-imaging.

In this work, we developed methods for the preparation of palladium and copper complexes with derivatives of natural chlorins with DOTA, the synthesis of which we previously described [17], as potential diagnostic and therapeutic radiopharmaceuticals for nuclear medicine. The use of ^{109}Pd and ^{64}Cu isotopes in the porphyrin macrocycle followed by the introduction of Gd or Ga into the cyclic cavity will make it possible to obtain multifunctional probes for combining diagnostic and therapeutic methods (PD/RT/PET, PD/MRI/PDT, etc.).

Results and Discussion

The introduction of metal cations into chlorin and bacteriochlorin macrocycles fundamentally changes the properties of the structures and is a promising direction to generate contrast agents for diagnostics and therapy. It is known that the bathochromic shift of the main absorption band Q in the series porphyrins–chlorins–bacteriochlorins is accompanied by a decrease in the intrinsic fluorescence of these compounds. The introduction of metals into porphyrins and chlorins, but not into bacteriochlorins, extinguishes fluorescence, which greatly limits the possibility of studying such structures in further biological tests. As shown previously, the presence of two coordination cavities in conjugates **1** and **4** makes it possible to obtain homo- and heteronuclear metal complexes. The latter can be in demand in fluorescence diagnostics, magnetic resonance, and positron emission tomography as well as in radionuclide therapy and photodynamic therapy for cancer [17].



Scheme. Introduction of metal ions into the coordination sphere for conjugates of methylpheophorbide *a* and methylbacteriopheophorbide *a* with cyclen.

A regioselective introduction of the palladium cation into the chlorin macrocycle of conjugate **2** was carried out under mild conditions without heating using palladium acetate (Scheme). The reaction's progress and the formation of metal complex **2** were monitored by the hypsochromic shift of the absorption band from 664 to 624 nm. Similarly, the reaction was carried out to obtain copper complex **3**. The formation of the metal complex was monitored by the hypsochromic shift of the absorption band from 664 to 640 nm (Fig. 1).

The presence of palladium and copper cations in conjugates **2** and **3** was clearly confirmed via MALDI mass spectra by the presence of molecular ions and signal groups corresponding to the main isotopes of palladium and copper.

It follows from Table 1 data that when the Pd^{2+} cation is introduced into the chlorin macrocycle, the initial conjugate **1** fluorescence is significantly suppressed, while the photosensitizing activity of the metal complex **2**, which was estimated on the basis of the quantum yield of singlet oxygen generation

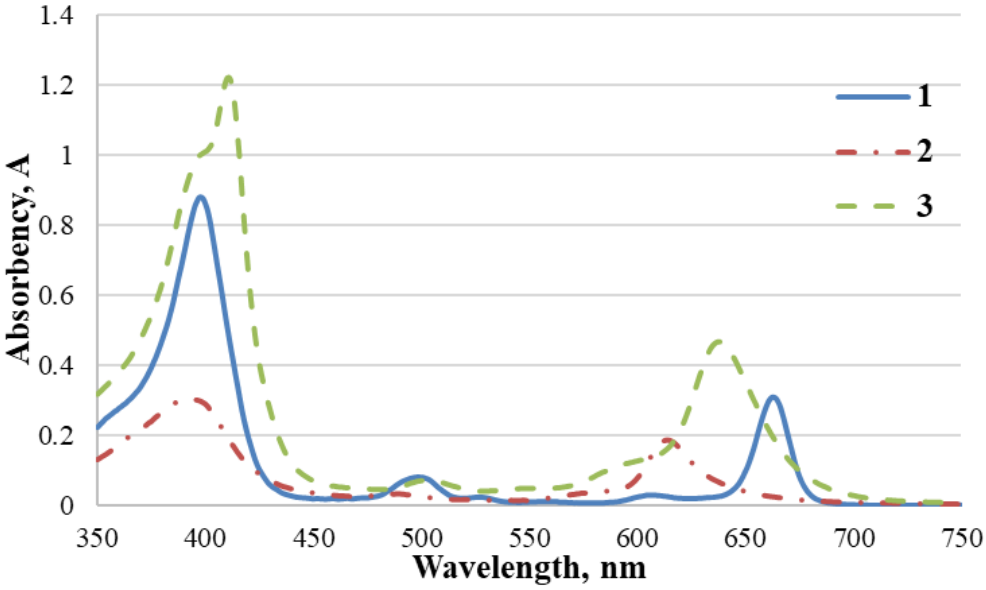


Fig. 1. Absorption spectra for methylpheophorbide *a* conjugate with cyclen (**1**), Pd complex of chlorin-cyclen conjugate (**2**), and Cu complex of chlorin-cyclen conjugate (**3**).

(Φ_Δ) using 1,3-diphenylisobenzofuran (DPIBF) as a chemical trap, it increased to 98%. This makes it possible to conclude that the photodynamic potential of this metal complex is high. The introduction of Cu^{2+} cation, in turn, results in the characteristic suppression of the main photophysical characteristics, Φ_Δ and Φ_F.

Table 1. Quantum yields for fluorescence (Φ_F) and singlet oxygen generation (Φ_Δ) of the chlorin-cyclen conjugate and its Pd complex

Compound	Fluorescence quantum yield Φ_F	Singlet oxygen generation quantum yield Φ_Δ
1	0.266±0.005	0.71
2	0.0005	0.98
3	–	–

Next, we obtained the palladium and copper complexes of bacteriopheophorbide *a* conjugate with cyclen **4**. Previously, Scherz with coworkers showed that the introduction of a metal into bacteriochlorins is much faster in the presence of reducing agents [18]. Using these data, we treated conjugate **4** with palladium acetate in the presence of 6-*O*-palmitoyl-L-ascorbic acid. The reaction was controlled spectrophotometrically by the hypsochromic shift of the main absorption band from 522 to 515 nm, as well as by the reduction of fluorescence intensity, which indicated the formation of Pd complex **5**. Similarly, metalation was performed with copper acetate. The bathochromic shift of the spectrum in the band from 758 to 767 nm as well as the almost complete absence of fluorescence, indicate the formation of Cu complex **6** (Fig. 2, Fig. 3).

The presence of palladium and copper cations in conjugates **5** and **6** was clearly confirmed via MALDI mass spectra by the presence of molecular ions and groups of signals corresponding to the main isotopes of palladium and copper.

It follows from the data of Table 2 that introducing the Pd^{2+} cation into the bacteriochlorin macrocycle results in a slight decrease in conjugate **5** fluorescence, and the fluorescence lifetime remains unchanged. The combination of such parameters in Pd complex **5** maintains its therapeutic and diagnostic potentials. In turn, the introduction of the Cu^{2+} cation quenches the photophysical characteristics of complex **6** while maintaining residual fluorescence with a maximum identical to compound **4**, which is due to the partial introduction of copper according to the SAT mechanism [5].

Conclusions

Due to the stability of the synthesized metal complexes in acidic media, as well as the short metalation time (5, 10, 20, and 15 min., respectively) it is reasonable to expect successful development of

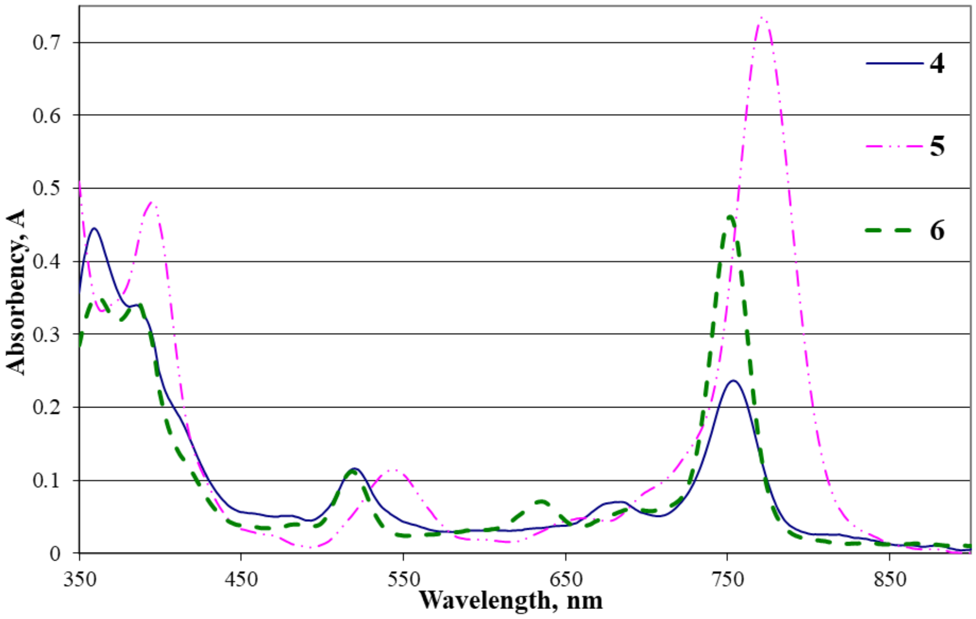


Fig. 2. Absorption spectra of methylbacteriopheophorbide *a* conjugate with cyclen (**4**), of the Pd complex of bacteriochlorin-cyclen conjugate (**5**), and of the Cu complex of bacteriochlorin-cyclen conjugate (**6**).

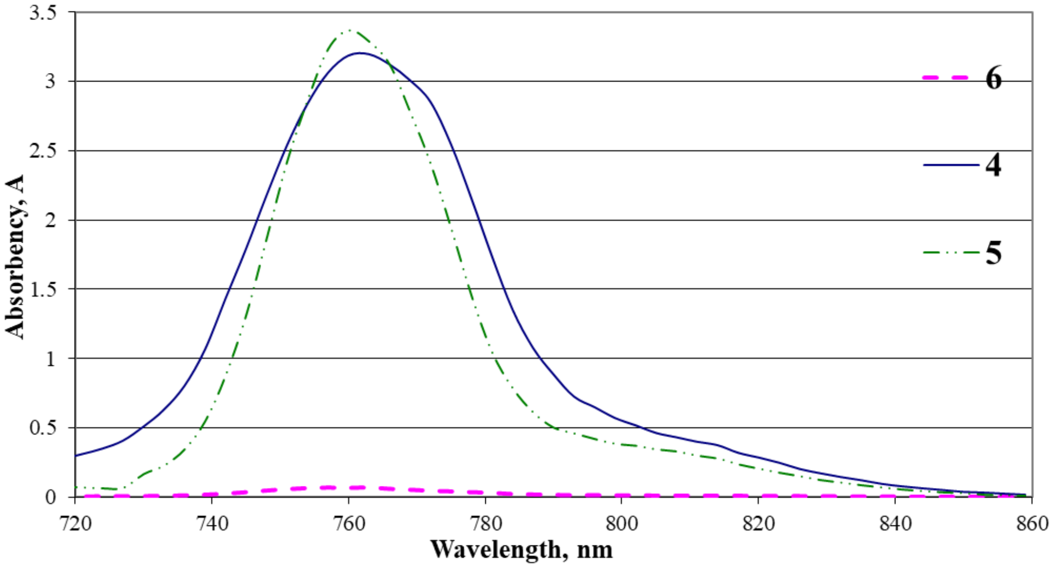


Fig. 3. Fluorescence spectra of methylbacteriopheophorbide *a* conjugate with cyclen (**4**), of the Pd complex of bacteriochlorin-cyclen conjugate (**5**), and of the Cu complex of bacteriochlorin-cyclen conjugate (**6**).

Table 2. Quantum yield of fluorescence (Φ_F), of singlet oxygen generation (Φ_Δ) and fluorescence lifetime (τ_S) for methylbacteriopheophorbide *a* conjugate with cyclen (**4**), for the Pd complex of bacteriochlorin-cyclen conjugate (**5**), and for the Cu complex of bacteriochlorin-cyclen conjugate (**6**)

Compound	Fluorescence quantum yield Φ_F	Fluorescence lifetime, τ_S, ns	Singlet oxygen generation quantum yield Φ_Δ
4	0.13	1.75	0.68
5	0.1	1.79	0.72
6	0.0013	–	–

effective visualizing agents for PET and radionuclide therapy (RT). At the same time, the virtual absence of fluorescence excludes the use of the compounds **2**, **3**, and **6** in the fluorescence diagnostics.

Therefore, the combination of physicochemical, photophysical, and spectral characteristics along with the short time of cyclen conjugates with pheophorbide and bacteriopheophorbide metalation with palladium and copper promotes the further study of metal complexes of natural chlorins for use in nuclear medicine.

Materials and Methods

Electronic absorption spectra were obtained on a *Shimadzu* 3101 spectrophotometer. Fluorescence and phosphorescence spectra were obtained on a *FluoTime 300 PicoQuant* spectrofluorometer. Mass spectra were obtained on *Bruker Ultraflex* TPF/TOF and *Bruker Daltonics Autoflex* II time-of-flight mass-spectrometers using the MALDI method; 2,5-dihydroxybenzoic acid (DHB) and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene] malononitrile (DCTB) were used as matrices.

Solvents were purified and prepared according to standard procedures. All reactions were carried out using degassed solvents under protection from direct light in an argon atmosphere. For preparative TLC, silica gel 60 (*Merck*) 20×20 cm plates with a layer thickness of 1 mm were used. Analytical TLC was performed on Kieselgel 60 F245 plates (*Merck*).

Pd complex of pheophorbide *a* methyl ester with cyclen (2). Twenty-five mg of methyl pheophorbide a with cyclen (**1**) and 10 mg of palladium acetate were dissolved in 4 ml of CH_2Cl_2. The reaction's progress was monitored spectrophotometrically by recording the reaction's mixture absorbance spectrum every 5 min. After the completion, the mixture was transferred to a separating funnel with water and extracted with DCM (2×20 ml) to remove excess metalation agent. The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in the vacuum of a water-jet pump. The resulting product was dissolved in a minimal amount of DCM and purified by preparative TLC using a DCM/methanol mixture (v/v 30:1). The purified conjugate was recrystallized from hexane. Yield: 23.75 mg. Electronic spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $M^{-1}cm^{-1}$): 390 (100), 500 (10), 621 (18). Mass spectrum (MALDI), *m/z*: 893.157 (M^+).

Cu complex of pheophorbide *a* methyl ester with cyclen (3). Twenty-five mg of conjugate **1** in 4 ml of CH_2Cl_2 and 4 mg of copper acetate were dissolved in 2 ml of CH_3OH. The reaction mixture was stirred under argon. The reaction's progress was monitored spectrophotometrically by recording the reaction's mixture absorbance spectrum every 5 min. The reaction was completed after 10 minutes. The mixture was transferred to a separating funnel with water and extracted with DCM (2×20 ml) to remove excess copper acetate. The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in the vacuum of a water-jet pump. The resulting product was dissolved in a minimum of DCM and purified by preparative TLC using DCM/methanol mixture (v/v 30:1). The purified conjugate was recrystallized from hexane. Yield: 22.25 mg. Electronic spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $M^{-1}cm^{-1}$): 388 (100), 502 (12), 638 (35). Mass spectrum (MALDI), *m/z*: 667.875 (M^+).

Pd complex of bacteriopheophorbide *a* methyl ester with cyclen (5). Twenty-five mg of bacteriopheophorbide a methyl ester conjugate with cyclen (**4**) and 17 mg of palladium acetate were dissolved in 4 ml of CH_2Cl_2 and mixed with a solution of 76 mg of 6-*O*-palmitoyl-L-ascorbic acid in 8 mL of CH_3OH. The reaction mixture was stirred under argon. The reaction's progress was monitored spectrophotometrically. The reaction was completed was completed after 20 minutes. The mixture was diluted with water and extracted with DCM (2×20 ml) to remove excess metalation agent. The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in the vacuum of a water-jet pump. The resulting product was dissolved in a minimum of DCM and purified by preparative TLC using DCM–methanol mixture (v/v 30:1). The purified conjugate was recrystallized from hexane. Yield: 21.25 mg. Electronic spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $M^{-1}cm^{-1}$): 351 (75), 515 (43), 750 (112). Mass spectrum (MALDI), *m/z*: 900.033 (M^+).

Cu complex of bacteriopheophorbide *a* methyl ester with cyclen (6). Twenty mg of conjugate **4** and 7 mg of copper acetate were dissolved in 4 ml of CH_2Cl_2 and mixed with a solution of 38 mg of 6-*O*-palmitoyl-L-ascorbic acid in 4 ml of CH_3OH. The reaction mixture was stirred under argon. The reaction's progress was monitored spectrophotometrically. The reaction was completed after 15 minutes. The mixture was transferred to a separating funnel with water and extracted with DCM (2×20 ml). A trace amount of water from the organic layer I was removed by sodium sulfate and the solvent was evaporated under a vacuum. The resulting product was dissolved in a minimal amount of DCM and purified by preparative TLC using DCM–methanol mixture (v/v 30:1). Conjugate **6** was recrystallized from hexane. Yield: 17.2 mg. Electronic spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $M^{-1}cm^{-1}$): 389 (100), 542 (75), 767 (245). Mass spectrum (MALDI), *m/z*: 858.529 (M^+).

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The authors declare no conflicts of interest.

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Relaxation and physicomechanical characteristics of polyethylenes with different molecular weights

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Objectives. *Determination of the influence of molecular weight on the modulus of elasticity, yield, strength, and retardation processes in polyethylene.*
Methods. *We used vane samples (thickness: 4 mm; length: 100 mm; width: 10 mm) made by injection molding at p = 60 MPa, T = 210 °C, τ = 15 s from the following polyethylenes: HDPE 277-73 (Stavrolen, Lukoil, Russia); BorSafe HE3490-IM (Borealis, Austria; black); CRP 100 Hostalen (Basell Polyolefins, Netherlands; black); Stavrolen PE4PP-25B (Stavrolen, Lukoil, Russia; black). The samples were in accordance with the defined standards for the AL 7000 LA-5 tensile testing machine. The study of relaxation characteristics was carried out in two modes: relaxation and retardation.*
Results. *We obtained stress-strain diagrams at various temperatures under isothermal conditions (T = const) and determined the influence of polyethylene molecular weights on the modulus of elasticity, yield, and strength of polyethylenes. We have shown that under isothermal conditions, when the stress equals the yield strength, the removal of the external action results in a two-stage response. The first stage is the stress relaxation. The second stage characterizes the elastic features of the studied materials under the external action ε = const.*
Conclusions. *We have established that temperature increase affects the physicomechanical characteristics of polyethylenes differently, depending on their molecular weights. The experiments have shown that when the stress exceeds the yield strength, at constant deformation, there is a complex response of the polyethylenes to external action. This response is characterized by two stress stages throughout the course of time. The first stage is characterized by asymptotic decrease in stress down to a constant value; the second stage is characterized by constant stress throughout the course of time. We have determined relaxation times for the relaxation stage (stage I) and calculated activation energy. We have also established that the activation energy depends on molecular weights of the polyethylenes. It has been shown that an increase in polyethylene molecular weight leads to a decrease in relaxation time and activation energy.*

Keywords: *relaxation, inelasticity, internal friction, modulus of elasticity, yield strength, polyethylene.*

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Релаксационные и физико-механические характеристики полиэтиленов с различной молекулярной массой

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Цель. *Определение влияния молекулярной массы полиэтиленов на модуль упругости, текучесть, прочность и процессы ретардации.*

Методы. *В качестве образцов были взяты лопатки (толщиной 4 мм, длиной 100 мм, шириной 10 мм), полученные методом литья под давлением p = 60 МПа при T = 210 °С, τ = 15 с, из полиэтилена следующих марок: ПЭВП 277-73 (Ставролен, Лукойл, Россия); BorSafe HE3490-IM (Borealis, Австрия; черный); CRP 100 Hostalen (Basell Polyolefins, Нидерланды; черный); Stavrolen PE4PP-25B (Ставролен, Лукойл, Россия; черный). Использованные образцы соответствовали стандартно-определенным образцам для исследования на разрывной машине AL 7000 LA-5. Исследование релаксационных характеристик проводилось в двух режимах: релаксационном и ретардационном.*

Результаты. *В результате проведения экспериментов были получены диаграммы «напряжение–деформация» при различных температурах в изотермических режимах (T = const) и определено влияние молекулярной массы на модуль упругости, текучесть и прочность полиэтиленов. Показано, что при напряжениях, равных пределу текучести, в изотермических условиях при снятии внешнего деформирующего воздействия наблюдаются две стадии отклика системы полиэтилена на это воздействие. Первый отклик – процесс релаксации напряжения и второй отклик – область, характеризующая упругие характеристики исследуемого материала при внешнем воздействии ε = const.*

Заключение. *Установлено, что повышение температуры неодинаково отражается на физико-механических характеристиках полиэтиленов различной молекулярной массы. Эксперименты показали, что при напряжениях выше предела текучести при постоянстве деформации наблюдается сложная реакция исследуемых полиэтиленов на внешнее воздействие. Эта реакция характеризуется двумя областями зависимости напряжений, возникших при деформации, от времени. Первая область характеризуется асимптотическим снижением напряжения до постоянного значения, а вторая область – постоянством напряжения во времени. Рассчитаны времена релаксации для релаксационной области (участок I), а также рассчитана величина энергии активации. Показано, что увеличение молекулярной массы полиэтиленов ведет к снижению времени релаксации и уменьшению энергии активации.*

Ключевые слова: *релаксация, неупругость, внутреннее трение, модуль упругости, предел текучести, полиэтилен.*

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Introduction

Amorphous-crystalline polyethylene (PE), despite the simple structure of its polymer chain, is characterized by multiplet relaxation behavior observed in solid state, from low temperatures and up to the melting temperature T_{melt} [1–3]. This can mostly be explained by the complex structure of crystalline polymers and their molecular motion, and this is why it is also challenging to establish all possible relaxation transitions in PE and determine their nature. Consequently, there is still no clear understanding of relaxation transitions in PE and how they are influenced by the molecular weight of the polymer. Research on local dissipative losses by a dynamics method [4] shows that the PE structure consists of four structural-kinetic subsystems that respond to external action quasi-independently; this happens when such deformation destabilizes mechanical and thermodynamic equilibria of all elements of these structural-kinetic subsystems. Theoretical analysis of these physicomechanical parameters allows us to determine the degree of relaxation microheterogeneity for elements of various structural-kinetic subsystems.

The aim of this work was to determine the influence of molecular weight on the modulus of elasticity, yield, strength, and retardation processes in polyethylene.

Materials and Methods

We used vane samples (thickness: 4 mm; length: 100 mm; width: 10 mm) made by injection molding at p = 60 MPa, T = 210 °C, τ = 15 s from the following polyethylenes: HDPE 277-73 (*Stavrolen, Lukoil,* Russia); BorSafe HE3490-IM (*Borealis*, Austria; black); CRP 100 Hostalen (*Basell Polyolefins*, Netherlands; black); Stavrolen PE4PP-25B (*Stavrolen, Lukoil,* Russia; black). Our samples were in accordance with the defined standards for the AL 7000 LA-5 tensile testing machine. The stretching was performed at the strain rate of $V_{\Delta l}$ = 100 mm/min. According to the preparation method, the sprue was placed toward the mold in such a way that it was co-oriented with the polymer molecules. After shrinkage, all PE samples with different molecular weights kept their shapes. We did not evaluate the influence of shrinkage on the macromolecule orientation.

The main physicochemical and physicomechanical characteristics of polyethylenes used in this study are shown in Table 1.

We performed the evaluation of relaxation characteristics in two modes:

1. The relaxation mode:
external action

$$\varepsilon(t) = \varepsilon_0 h(t) \begin{cases} 0 \text{ when } t < t_0 \\ \varepsilon_0 \text{ when } t \ge t_0 \end{cases} \tag{1}$$

response

$$\sigma(t) = \begin{cases} 0 \text{ when } t < t_0 \\ \sigma_0 = E\varepsilon_0 \text{ when } t \ge t_0 \text{ and } \sigma_0 \le \sigma_{pl} \\ \sigma_0 \Psi(t) \text{ when } t \ge t_0 \text{ and } \sigma_{pl} \le \sigma_0 \le \sigma_{el} \end{cases}, \tag{2}$$

where σ is a stress, MPa; ε is a strain, %; *E* is a modulus of elasticity, MPa; *t* is a time, s; t_0 is a moment of the external action removal; σ_{pl} is the proportionality limit (the limit of linear elasticity), MPa; σ_{el} is the elastic limit, MPa.

Table 1. Main characteristics of polyethylenes used in the study

№ п/п	PE type	HDPE 277-73	BorSafe HE3490-IM	CRP 100 Hostalen	Stavrolen PE4PP-25B
1	Molecular weight (MW), g/mol × 10^4	24	67	74	75
2	Molecular weight distribution (MWD)	Monomodal	Bimodal		Monomodal
3	Melt flow index, g per 10 min at 190 °C and 21.6 kgf at 190 °C and 5.0 kgf at 190 °C and 2.16 kgf	 17–25 – 5–7	 6.00 0.57 0.40	 5.50 0.52 0.38	 12–16 0.51 –
4	Melt stretching index, s	–	120	215	400
5	Density at 23 °C, g/cm³	0.957	0.962	0.960	0.952
6	Tensile yield strength, not below, MPa	25.5	24	–	16.7
7	Soot content, %	–	2	2	2
8	Melting temperature, °C	125–135	125–135	125–135	125–135
9	Type of soot distribution	–	I-II	I-II	I-II
10	ΔH, J/g	157.1	142.6	132.4	107.8
11	Degree of crystallinity, α, %	53.6	48.7	45.2	36.8

2. The retardation mode:
external action

$$\sigma(t) = \sigma_0 h(t) \rightarrow \begin{cases} 0 \text{ when } t < t_0 \\ \sigma_0 \text{ when } t \geq t_0 \end{cases} \quad (3)$$

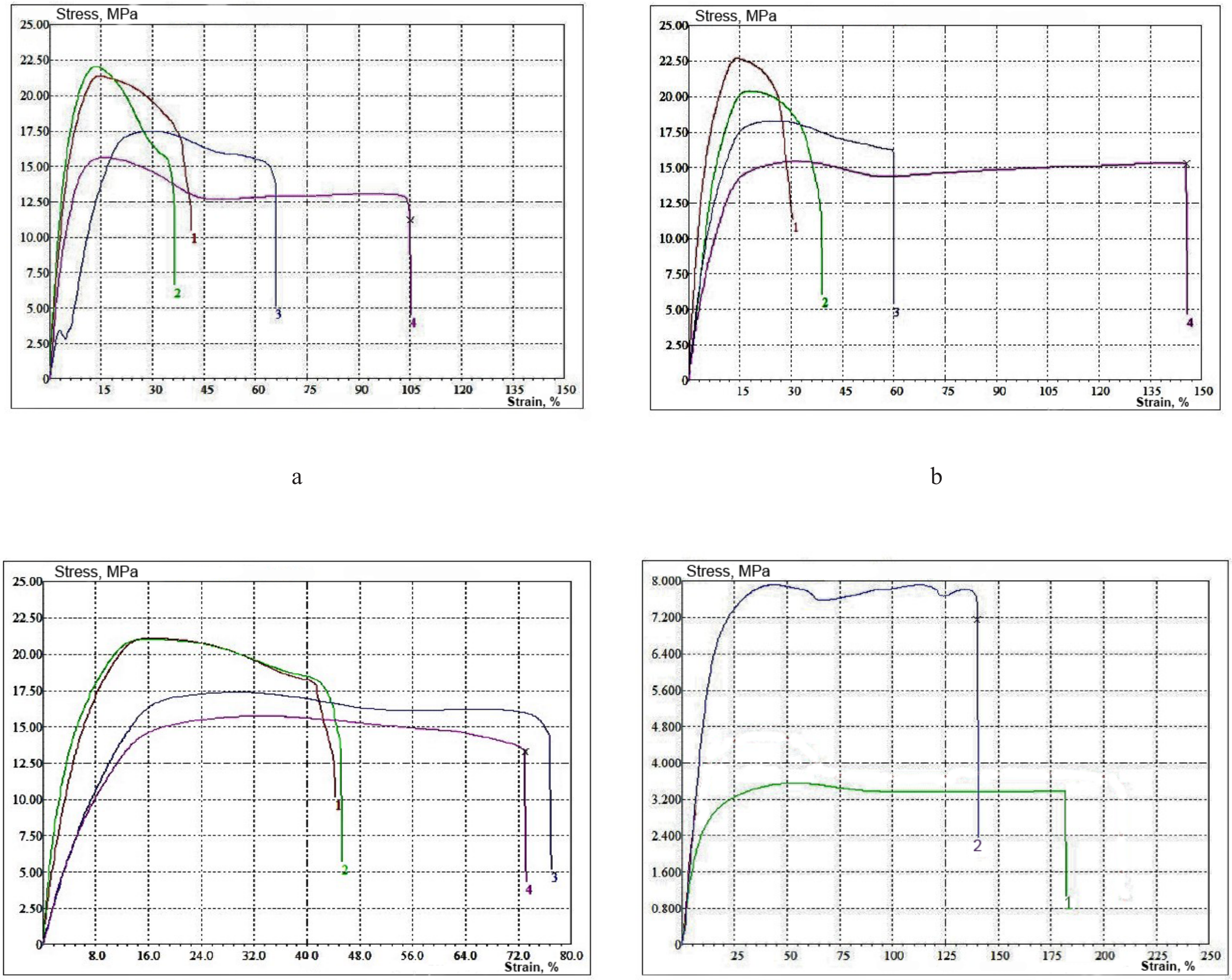
response

$$\varepsilon(t) = \begin{cases} 0 \text{ when } t < t_0 \\ \varepsilon_0 = \sigma_0 / E \text{ when } t \geq t_0 \text{ and } \sigma_0 \leq \sigma_{pl} \\ \varepsilon_0 I(t) \text{ when } t > t_0 \text{ and } \sigma_{pl} < \sigma_0 \leq \sigma_{el} \end{cases} . \quad (4)$$

This allowed us to evaluate the dependency of the modulus of elasticity and the yield strength on the molecular weight, using stress-strain diagrams. We were also able to determine creep modes and elastic aftereffect (retardation) modes. Knowing these parameters (and how they depend on molecular weights) allows us to evaluate the functions that describe the stage of inelastic response to an external action (equations 1–4), based on isothermal conditions of the hereditary theory of viscoelasticity.

Results and Discussion

We have obtained stress-strain diagrams at various temperatures under isothermal conditions (T = const) and these results are shown in Fig. 1.



a

b

c

d

Fig. 1. Stress–strain diagrams for BorSafe HE3490-IM (a), CRP 100 Hostalen (b), Stavrolen PE4PP-25B (c) polyethylenes at the following temperatures, °C:
1 – 21; *2* – 30; *3* – 40; *4* – 50; for HDPE 277-73 (curve 1) and Stavrolen PE4PP-25B (curve 2) polyethylenes at 100 °C (d).

We have determined the effect of molecular weight on the modulus of the elasticity, yield, and strength of polyethylene (Table 2).

Based on our experimental data, we have obtained temperature-dependency curves for the modulus of elasticity and the yield strength (Fig. 2), as well as curves showing the dependency of these parameters on the molecular weight (Fig. 3).

The experimental data show that temperature increase affects the physicomechanical characteristics of polyethylenes differently, depending on their molecular weights. In the case of HDPE 277-73, the PE with the lowest molecular weight (MW = 24×10^4 g/mol) (Table 1), we observe a gradual decrease in the modulus of elasticity (Fig. 2a) and the yield strength (Fig. 2b) upon temperature increase. In the case of PE with a higher molecular

Table 2. Physicomechanical characteristics of polyethylenes with different molecular weights (at $V_{\Delta l}$ = 100 mm/min)

Temperature of the experiment, °C	F_{max}*, kgf	Tensile strength at F_{max}, MPa	Strain at F_{max}, %	Yield strength, MPa	Strain of yield strength, %	Modulus of elasticity, MPa	Ultimate tensile strength, MPa	Strain at breakage point, %
HDPE 277-73								
21	88.65	21.71	13.18	21.71	12.35	891.74	12.4	–
30	84.50	20.67	13.83	20.67	12.73	837.26	12.73	–
40	74.36	18.21	14.42	18.21	13.60	742.89	13.6	–
50	59.85	14.67	16.14	14.67	15.47	563.77	15.47	–
BorSafe HE3490-IM								
21	87.25	21.39	14.65	21.38	14.01	731.37	10.99	41.44
30	89.83	22.02	13.62	22.02	13.15	714.99	12.43	36.47
40	71.35	17.49	30.00	17.48	28.37	169.92	13.78	65.89
50	63.86	15.66	15.97	15.66	15.75	231.77	11.18	105.2
CRP 100 Hostalen								
21	92.50	22.63	14.13	22.68	14.06	641.98	11.33	30.40
30	83.14	20.38	17.63	20.38	17.34	166.80	11.35	38.90
40	74.66	18.30	25.76	18.27	22.70	224.34	16.06	59.99
50	63.01	15.45	31.74	15.44	30.38	271.60	15.29	145.84
Stavrolen PE4PP-25B								
21	85.14	21.12	16.16	21.11	15.74	511.40	12.21	44.25
30	85.82	21.04	15.61	21.04	15.55	609.46	13.36	45.27
40	70.94	17.39	28.93	17.36	26.49	205.43	13.96	77.00
50	64.30	15.76	32.79	15.76	31.47	211.81	13.33	73.10
HDPE 277-73								
100	14.49	3.55	55.42	3.43	34.45	28.81	3.34	182.33
Stavrolen PE4PP-25B								
100	32.30	7.92	113.39	7.89	38.77	25.17	7.15	140.13

*F_{max} is the maximum stress during the tensile test.

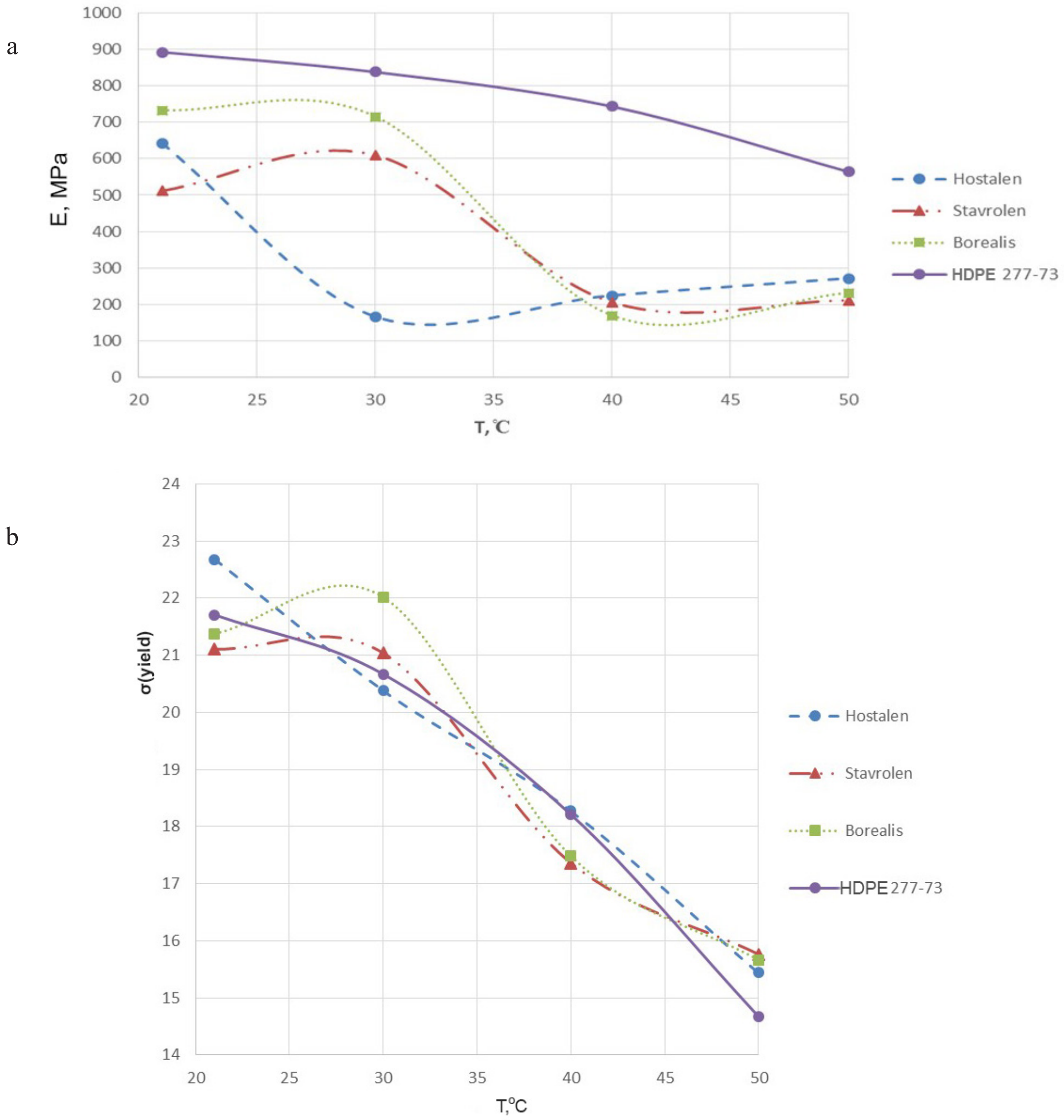


Fig. 2. Dependency of the modulus of elasticity (a) and the yield strength (b) for polyethylenes of different molecular weights on temperature.

weight, extreme changes in these parameters occur. For Stavrolen PE4PP-25B (MW = 75×10^4 g/mol) and BorSafe HE3490-IM (MW = 67×10^4 g/mol) polyethylenes (Table 1), we see that the parameters have a maximum at T = 30 °C, followed by a decrease and stabilization of the modulus of elasticity after 40 °C (Fig. 2a). Additionally, for the Hostalen polyethylene (MW = 74×10^4 g/mol) (Table 1), we observe an opposite tendency, where the modulus of elasticity decreases as the temperature increases to 30 °C, and afterwards it stabilizes, following a period of insignificant growth within the 40–50 °C range. At the same time, we observe abnormal behavior in the yield strength for Stavrolen PE4PP-25B and BorSafe HE3490-IM polyethylenes at T = 30 °C (Fig. 3b).

We have analyzed the inelasticity and stress relaxation of PEs using the same technique, at $\sigma_{el} < \sigma \approx \sigma_{yield}$ (σ_{yield} is the stress equaled the yield strength, MPa). A temperature of 100 ºC was chosen to speed up the experiment, because the increase in temperature leads to a decrease in the yield strength. Study of the dependence of relaxation times on molecular weight and temperature is a separate task and may be the object of future research. To perform these experiments, samples were subjected to a stress of $\sigma = \sigma_{yield}$ and strain of $\varepsilon = 42\%$ (Stavrolen PE4PP-25B) and $\varepsilon = 11\%$ (HDPE 277-73) (Fig. 4, stage I); after that, the external action was removed and the residual strain mode ε_{res} = const was observed (Fig. 4, stage II).

The strain that appears in the samples changes throughout the course of time, meaning that $\sigma = f(t)$. Area I in Fig. 5 – the upper part in the figure – describes the stress relaxation process, and area II describes the elastic nonrelaxing part of the stress in the PE.

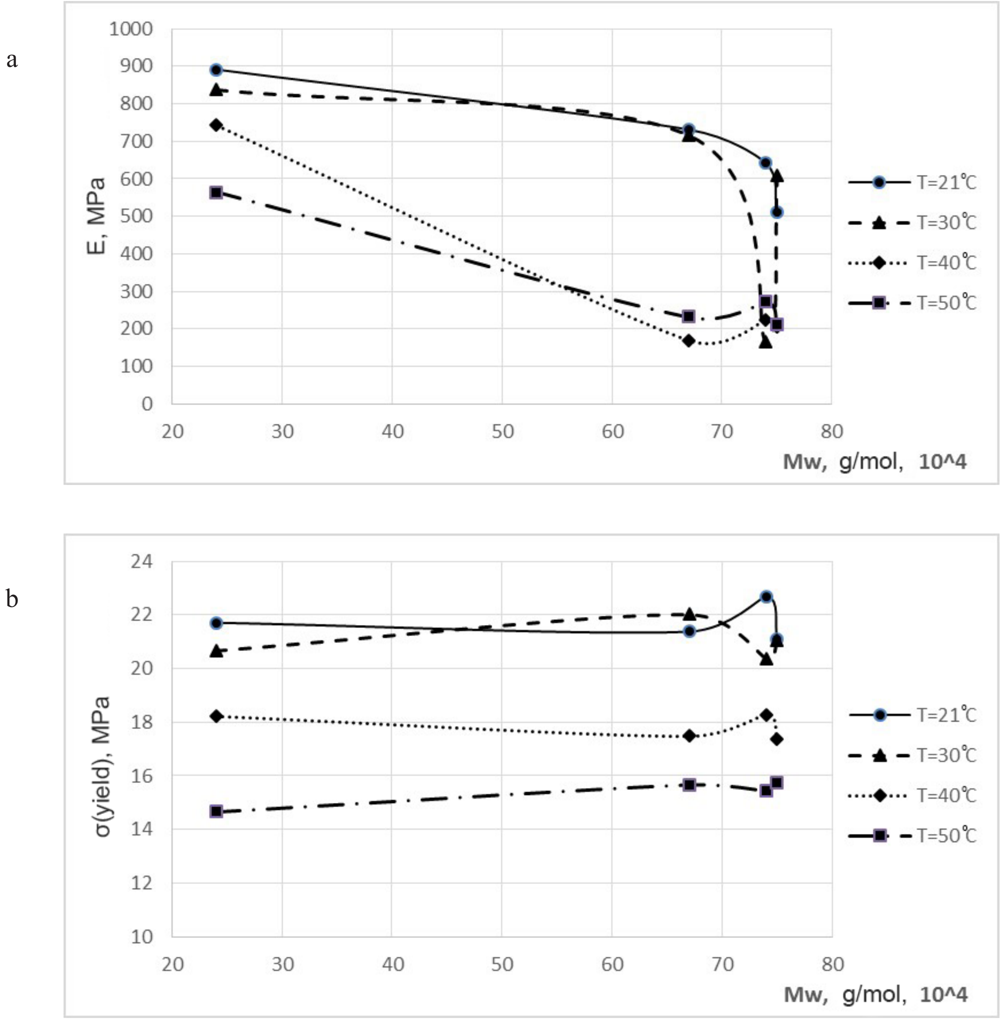


Fig. 3. Dependency of the modulus of elasticity (a) and the yield strength (b) on the molecular weight, for polyethylenes of different molecular weights; obtained under isothermal conditions.

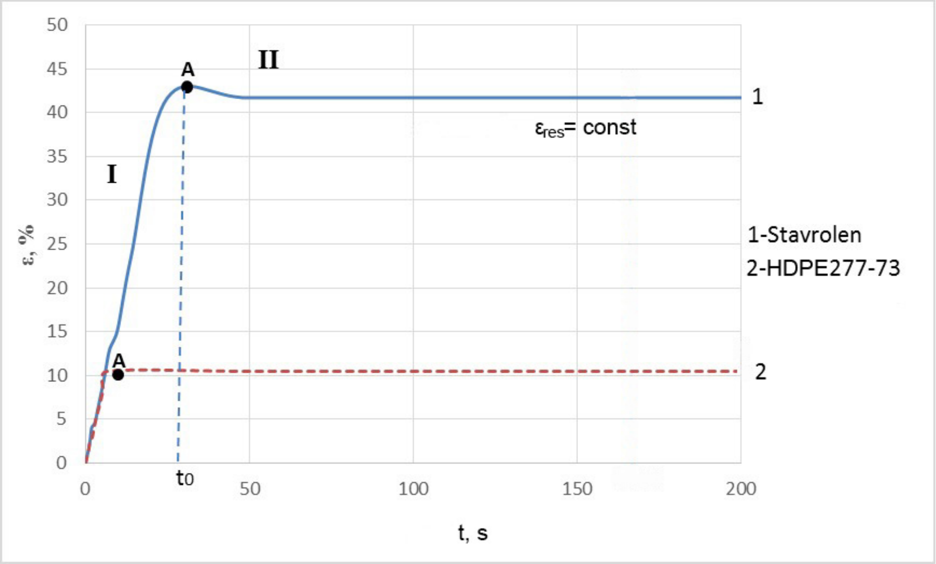


Fig. 4. Strain dependency on time, under isothermal conditions (T = 100 °C), for PEs with MW = 75×10^4 g/mol (curve 1) and MW = 24×10^4 g/mol (curve 2).

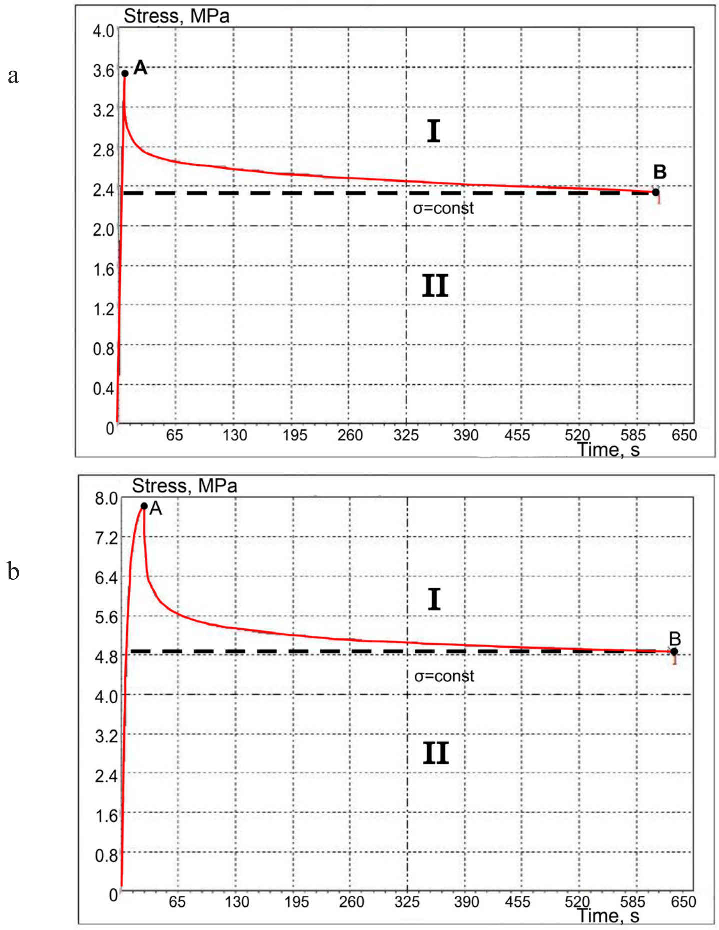


Fig. 5. Stress dependency on time for HDPE 277-73 (a) and Stavrolen PE4PP-25B (b).

Accordingly, for PEs with different molecular weights, the stress depends on time, which means that the stress does not change instantly with time, but rather stepwise, from point A to point B (Fig. 5a and 5b).

We have established that this stress asymptotically approaches a constant value σ = const (Fig. 5a and 5b). We have shown that when the stress equals the yield strength in isothermal conditions the removal of the external action results in a two-stage response. The first stage is the stress relaxation, and the second stage characterizes the elastic features of the studied materials under the external action ε = const.

In order to characterize the response of the PE during relaxation (the first stage response), we can use the Maxwell model:

$$\frac{d\sigma}{dt} + \frac{\sigma}{\tau} = E\frac{d\varepsilon}{dt}, \tag{5}$$

where σ is a stress, MPa; ε is a strain, %; *E* is a modulus of elasticity, MPa; *t* is the time, s; and τ is the relaxation time, s.

The solution of this differential equation is the equation that connects the stress relaxation curve with relaxation time:

$$\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right), \tag{6}$$

where σ(*t*) is the stress in the time moment *t*, MPa; and σ_0 is the stress in the time moment *t* = 0, MPa.

According to this equation, we can determine the relaxation function normalized to 1 (Fig. 6):

$$\varphi(t) = \frac{\sigma(t)}{\sigma_0}, \tag{7}$$

where φ(*t*) is the relaxation function.

Based on the analysis of the time-dependent relaxation function φ(*t*), the relaxation time τ can be determined using the φ(*t*) curve (Fig. 6) according to the formula:

$$\tau = \frac{1}{e}, \tag{8}$$

where *e* is the Euler number.

The τ values depend on the molecular weight of polyethylene. For HDPE 277-73 (MW = 24×10^4 g/mol) τ equals 10.1 s, and for Stavrolen PE4PP-25B (MW = 75×10^4 g/mol) τ equals 8.5 s.

The obtained values of relaxation time depend on the polyethylene molecular weight. In order to carefully characterize the function τ = *f*(MW), we have performed similar measurements for intermediate molecular weights.

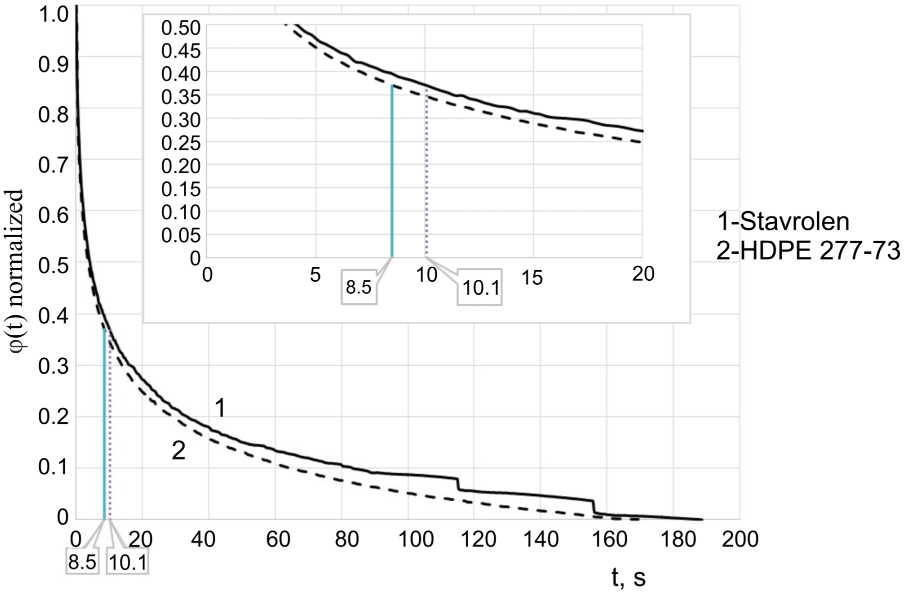


Fig. 6. Dependency of the normalized relaxation function on time, for PEs with MW = 75×10⁴ g/mol (curve 1) and MW = 24×10⁴ g/mol (curve 2).

Based on the Arrhenius equation for relaxation time

$$\tau_i = \tau_0 \exp \frac{U}{RT_i}, \tag{9}$$

and assuming that $\tau_0 = 1\times10^{-3}$ s for any polyethylene [5], we can calculate the activation energy of relaxation using the following formula:

$$U = RT_i \ln \frac{\tau_i}{\tau_0}, \tag{10}$$

where τ_i is the relaxation time, s, i.e. the time for transition of particles from one position to another with the overcoming of the potential barrier; U is the activation energy required to overcome the potential barrier, kJ/mol; τ_0 is the time of one attempt of a particle to pass through a barrier, s; R is the universal gas constant; and T_i is a temperature, K.

For example, for HDPE 277-73 (MW = 24×10⁴ g/mol) U equals 28.6 kJ/mol, and for Stavrolen PE4PP-25B (MW = 75×10⁴ g/mol) U equals 28.1 kJ/mol.

Our calculations show that the activation energy of relaxation does not depend greatly on the molecular weight. With the increase in the molecular weight of polyethylene, an insignificant decrease in activation energy occurs.

Conclusions

We have established that when the stress achieves $\sigma = \sigma_{pl}$ and ε_{res} = const, there are two response mechanisms in PE systems: mechanism I is the stage of stress relaxation (viscoelastic response); and mechanism II is the stage of elastic response that is characterized by constant stress σ = const. The value σ is a function of molecular weight. We have calculated relaxation times for the relaxation stage (stage I) and evaluated the activation energy, and established the connection $U = f(\mathrm{MW})$. We have established that an increase in the molecular weight of polyethylenes leads to a decrease in the values of relaxation time and activation energy.

The experiments have demonstrated that when the stress exceeds the yield strength, the constant deformation leads to complex responses of the PE to such external action. This mode is characterized by two stress stages developed throughout time. The first stage is characterized by the asymptotical decrease in stress to a constant value, and the second stage is characterized by constant stress throughout time.

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ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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Simultaneous determination of cationic surfactants in disinfectants

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Objectives. *Cationic surfactants are one of the classes of substances most commonly used in disinfectants. The trend in recent years has been the use of mixtures of several biocides, which poses new challenges for analytical chemistry. In this study, we describe a method for simultaneous determination in the disinfectants alkyldimethylbenzylammonium chloride (ADBAC), alkyldimethyl(ethylbenzyl)ammonium chloride (ADEBAC), chlorhexidine bigluconate (CHG), and polyhexamethylene biguanide hydrochloride (PHMB).*
Methods. *The proposed method is based on the use of reverse-phase and hydrophilic high-performance liquid chromatography with diode-array detection.*
Results. *The best separation of ADBAC, ADEBAC, and CHG was achieved using a column filled with modified spherical silica gel (5 μm, 4.6 × 250 mm) in gradient elution mode. Acetonitrile and acetate buffer with a pH of 5.4 were used as eluents at a flow rate of 1 ml/min. For the determination of PHMB in the presence of the substances under consideration, hydrophilic high performance liquid chromatography was used. The best separation was achieved on an amine phase column (5 μm, 4.6 × 250 mm) using the same eluents. To determine all the substances under consideration, a diode array detector was used. 3D chromatograms were recorded in the wavelength range from 190 to 400 nm.*
Conclusions. *We have shown that the result of the analysis does not depend on the ratio of cationic surfactants in disinfectants. There is also no influence of N,N-bis-(3-aminopropyl)-dodecylamine (Triamine, TA) and the components most commonly used for the manufacture of disinfectants, which was confirmed by testing the method for analyzing real objects. The linearity range for ADBAC was from 0.0062 to 0.97%, for ADEBAC from 0.000726 to 0.201%, for CHG from 0.0128 to 0.111%, and for PHMB from 0.00311 to 0.0205%. The calculated relative error for all determined substances was about 4%.*

Keywords: *alkyldimethylbenzylammonium chloride, alkyldimethyl(ethylbenzyl)ammonium chloride, chlorhexidine digluconate, polyhexamethylene biguanide hydrochloride, cationic surfactants, disinfectants, high performance liquid chromatography.*

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Определение катионных ПАВ в дезинфицирующих средствах при совместном присутствии

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Цели. *Катионные поверхностно-активные вещества являются одним из классов веществ, наиболее часто использующихся в качестве активнодействующих в дезинфицирующих средствах. Тенденцией последних лет является использование смесей нескольких биоцидов, что ставит новые задачи перед аналитической химией. В этой работе описан метод для определения при совместном присутствии в дезинфицирующих средствах алкилдиметилбензиламмоний хлорида (АДБАХ), алкилдиметил(этилбензил)аммоний хлорида (АДЭБАХ), хлоргексидина биглюконата (ХГБГ) и полигексаметиленбигуанид гидрохлорида (ПГМБ).*

Методы. *Предложенный метод основан на применении обращенно-фазовой и гидрофильной высокоэффективной жидкостной хроматографии с диодно-матричным детектированием.*

Результаты. *Наилучшее разделение АДБАХ, АДЭБАХ и ХГБГ было достигнуто при использовании колонки, заполненной модифицированным сферическим силикагелем (5 мкм, 4.6×250 мм) в режиме градиентного элюирования. В качестве элюентов использовали ацетонитрил и ацетатный буфер с pH 5.4 при скорости потока 1 мл/мин. Для определения ПГМБ в присутствии рассматриваемых веществ была использована гидрофильная высокоэффективная жидкостная хроматография. Наилучшее разделение было достигнуто на аминофазной колонке (5 мкм, 4.6 × 250 мм) при использовании тех же элюентов. Для определения всех рассматриваемых веществ использовали диодно-матричный детектор. 3D хроматограммы регистрировали в диапазоне длин волн от 190 до 400 нм.*

Выводы. *Проведенные исследования показали, что результат анализа не зависит от соотношения катионных поверхностно-активных веществ в дезинфицирующих средствах. Также отсутствует влияние N,N-бис(3-аминопропил)додециламина (Триамин, ТА) и наиболее часто используемых для изготовления дезинфицирующих средств компонентов, что было подтверждено при апробации метода для анализа реальных объектов. Диапазон линейности для АДБАХ составил от 0.0062 до 0.97 %, для АДЭБАХ – от 0.000726 до 0.201 %, для ХГБГ – от 0.0128 до 0.111 %, для ПГМБ – от 0.00311 до 0.0205 %. Рассчитанная относительная погрешность для всех определяемых веществ составила около 4 %.*

Ключевые слова: *алкилдиметилбензиламмоний хлорид, алкилдиметил(этилбензил)аммоний хлорид, хлоргексидина биглюконат, полигексаметиленбигуанид гидрохлорид, катионные ПАВ, дезинфицирующие средства, высокоэффективная жидкостная хроматография.*

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Introduction

Cationic surfactants are used as active components in disinfectants. They are represented by quaternary ammonium compounds (QACs), guanidine derivatives and tertiary amines. The most common cationic surfactants are alkyldimethylbenzylammonium chloride (ADBAC), didecyldimethylammonium chloride, polyhexamethylene guanidine hydrochloride, polyhexamethylene biguanide hydrochloride (PHMB), chlorhexidine bigluconate (CHG), and *N,N*-bis-(3-aminopropyl)-dodecylamine.

Disinfectants with surfactants are commonly used in medical organizations where compounds containing chlorine have been replaced for the purposes of prophylactic disinfection in the presence of patients [1]. A large spectrum of antimicrobial activity, as well as detergency, allow such compounds to be used in pre-sterilization cleaning. Cationic surfactants are less common in other types of disinfectants.

The substances mentioned above have different toxicological parameters that may change upon mixing with other compounds [2]. Thus, it is important to be able to quantify their concentrations, especially at the test stage prior to disinfectant registration; this is when efficacy and safety are evaluated.

Traditionally, quantification of quaternary ammonium compounds employs titrimetry methods based on formation of ion pairs with anionic surfactants. Various indicators, as well as ion-selective electrodes, are used to determine the titration endpoint. These methods do not require special equipment; however, they cannot be used for simultaneous quantification of several QACs. Analysis of CHG and PHMB may be performed by titrimetry [3–5] and chromatography [6–10]. However, these methods do not work for quantification of cationic surfactant mixtures. The results of the analyses may be affected by other active ingredients, such as *N,N*-bis-(3-aminopropyl)-dodecylamine and some functional components of disinfectants.

Several methods have been described where surfactant separation is achieved through high performance liquid chromatography (HPLC). Detection can be performed by mass spectrometry and spectrophotometry (UV). For mixtures of cationic and anionic surfactants, a charged aerosol detector (CAD) and evaporative light scattering detector (ELSD) have been suggested [11], whereas a diode array detector (DAD) can be used for quantification of ADBAC and trimethyltetradecylammonium chloride in disinfectants [12]. A large number of papers is dedicated to quantification of residual QAC mixtures in food [for example, see 13–15]. Capillary electrophoresis has been suggested for simultaneous quantification of PHMB and CHG [16]. A conductometric detector was used; separation was performed in a capillary filled with silica gel, with the length of 40 cm and inner diameter of 0.375 µm. The sensitivity of this method was 4 mg/L for PHMB and 0.4 mg/L for CHG.

HPLC with UV and DAD detection has been proposed for simultaneous quantification of ADBAC, CHG, and triclosan [17]. Component separation was performed on columns grafted with C8 and CN, with isocratic elution in the solvent mixture of acetonitrile–acetate buffer at pH 5.0. Better sensitivity was observed with C8 columns.

Studies [2–17] suggest quantification methods for individual surfactants as well as their mixtures. However, there are still no techniques for simultaneous determination of mixtures of several cationic surfactants in disinfectants, especially for ADBAC, didecyldimethylammonium chloride, polyhexamethylene guanidine hydrochloride, PHMB, CHG, *N,N*-bis-(3-aminopropyl)-dodecylamine. In the present work, we use HPLC with DAD to separate mixtures of the surfactants mentioned above.

Materials and Methods

Reagents

We used a 20% aqueous solution of chlorhexidine bigluconate (CHG); alkyldimethylbenzylammonium chloride (ADBAC; >95%); ammonium acetate for HPLC (*Sigma-Aldrich*, Germany); a 20% solution of polyhexamethylene biguanide hydrochloride (PHMB; *Vantocil TG, Lonza,* Switzerland); a 25% solution of alkyldimethyl(ethylbenzyl)ammonium chloride (ADEBAC; *Wuhan Dachu Hexing Technology Co., Ltd.,* China); a 30% solution of *N,N*-bis-(3-aminopropyl)-dodecylamine (*Lonza,* Switzerland); acetonitrile for HPLC (*Merck,* Germany); deionized water with resistivity not less than 18.2 MΩ×cm; distilled water according to GOST 6709-72. Other reagents were of *Pro Analysi* or higher grade. Commercial reagents were used without additional purification. Disinfectant samples were supplied by various Russian manufacturers.

Equipment

Chromatographic separation of the components was performed on the Thermo Ultimate 3000 HPLC system (*Thermo Scientific,* USA) with a built-in degasser, automatic sample injection, a column thermostat with the possibility of maintaining temperatures between 15 °C and 50 °C, and a diode array detector (DAD). Absorption spectra were registered in the wavelength range between 190 and 400 nm.

Chromatographic conditions for mixtures of ADBAC, ADEBAC, and CHG (method 1)

We achieved the best separation using the Thermo Acclaim Surfactant 5 µm column (4.6×250 mm) with the following eluents: acetonitrile (A) and a 0.1 M aqueous solution of ammonium acetate (B) (pH 5.4 with glacial acetic acid). Eluent ratios are shown in Table 1. The column thermostat was set at 30 °C. The flow rate was 1 mL/min. The sample volume was 10 µL. The chromatograms were recorded in the wavelength range between 190 and 400 nm. For calculations, we selected the wavelength of 264 nm.

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[1] MVI-2-2007-05-3. *Metodika vypolneniya izmerenii soderzhaniya khlorgeksidina biglyukonata v probakh dezinfitsiruyushchikh sredstv titrimetricheskim metodom* (MVI-2-2007-05-3. The method of quantification of chlorhexidine digluconate in samples of disinfectants by a titrimetric method) (in Russ.).

[2] The United States Pharmacopeia. USP 31. NF 26. 2008. 1732 p.

Table 1. Gradient elution for ADBAC, ADEBAC, and CHG separation

Time, min	Eluent A, %	Eluent B, %
0	0	100
8.0	0	100
18.0	80	20
24.0	30	70

Chromatographic conditions for PHMB (method 2)

We achieved the best separation using the Phenomenex Luna NH_2 5 µm column (4.6×250 mm) with the following eluents: acetonitrile (eluent A) and a 0.1 M aqueous solution of ammonium acetate (pH 5.4, eluent B). The gradients were the same as for ADBAC, ADEBAC, and CHG (Table 1). The chromatograms were recorded in the wavelength range between 190 and 400 nm. For calculations, we selected the wavelength of 240 nm. The column thermostat was set at 30 °C. The flow rate was 0.5 mL/min. The sample volume was 10 µL.

Data processing

Surfactants were identified according to their retention times and absorption spectra. After analysis of any five samples, we performed a run with pure acetonitrile to clean the column.

Calibration curves were based on six measurements. The linearity range was determined by peak area concentration graphs. We used the following criteria to determine the linearity range: linear regression with a correlation coefficient exceeding 0.99; deviation from the trendline not exceeding 15% for all points.

We collected and processed the chromatography data using Chromeleon 6 and Chromeleon 7 software (*Thermo Fischer Scientific Inc.*, USA). Statistical analysis was performed in accordance with RMG 61-2010, “Parameters of accuracy, correctness, and precision for methods of quantitative chemical analysis. Methods of assessment” and “Guideline I.C.H.H.T. Validation of analytical procedures: text and methodology Q2 (R1).” We used Excel 2016 (*Microsoft Inc.*, USA) and OriginPro (*OriginLab Corp.*, USA) software.

Results and Discussion

Alkyldimethylbenzylammonium chloride (ADBAC) and alkyldimethyl(ethylbenzyl)ammonium chloride (ADEBAC) consist of several homologs differing in the length of the alkyl chain. Due to the structural similarity of these substances, their chromatographic separation is challenging.

In attempting to find optimal conditions for chromatography, we took into account the resolution R_s whose value should be no lower than 1.5; and the peak asymmetry factor whose value should be between 0.8 and 1.5.

According to the specification sheet of the ADBAC used in our work, the substance consisted of two components: dodecyldimethylbenzylammonium chloride and tetradecyldimethylbenzylammonium chloride. Thus, the chromatogram of a 0.2% solution of ADBAC had two peaks at approximately 7.9 and 9.0 min. They are shown in Fig. 1 as C12 and C14, respectively.

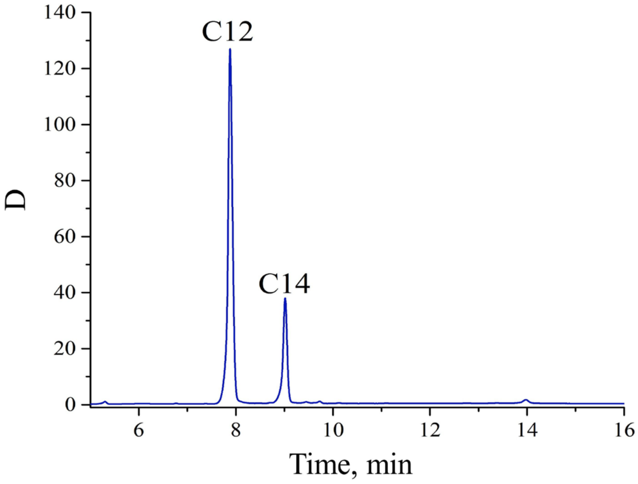

Fig. 1. Chromatogram of a 0.2% ADBAC solution in deionized water (method 1, Surfactant column).

For ADEBAC, we did not have information about the homologs comprising it. The chromatogram of a 0.2% ADEBAC solution in deionized water had four peaks, with retention times of approximately 8.4, 8.7, 9.5, and 9.7 min. We identified the components as dodecyldimethyl(ethylbenzyl)ammonium chloride, tetradecyldimethyl(ethylbenzyl)ammonium chloride, hexadecyldimethyl(ethylbenzyl)ammonium chloride, and octadecyldimethyl(ethylbenzyl)ammonium chloride. These peaks are shown in Fig. 2 as C12, C14, C16, and C18.

As expected, the mixture of ADBAC and ADEBAC had a chromatogram with 6 major peaks that, according to their retention times, corresponded to the peaks in the samples of ADBAC and ADEBAC (Fig. 3).

When we added CHG to the mixture of ADBAC and ADEBAC, it did not affect our analysis, since the retention time of CHG in our conditions was approximately 6.5 min (Table 2). Figure 4 shows that PHMB was not retained on the Surfactant column, whereas *N,N*-bis-(3-aminopropyl)-dodecylamine

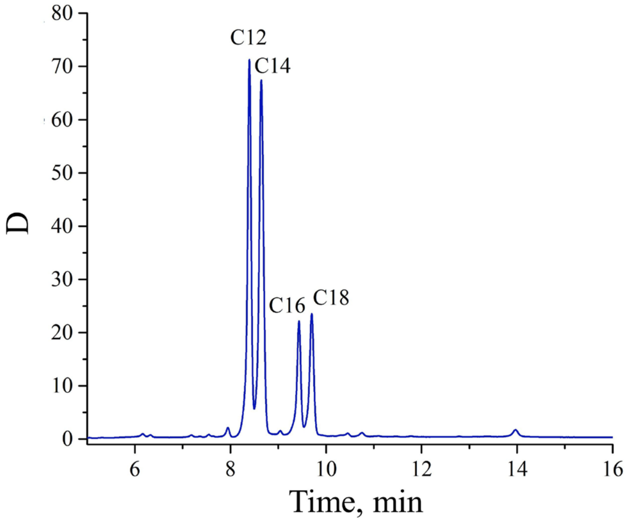

Fig. 2. Chromatogram of a 0.2% ADEBAC solution in deionized water (method 1, Surfactant column).

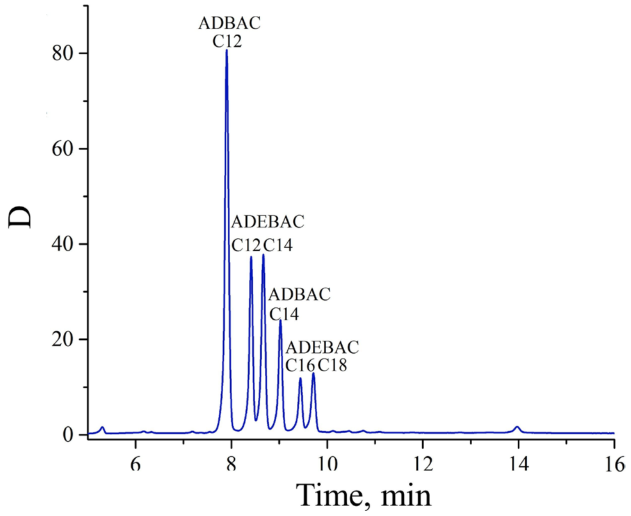

Fig. 3. Chromatogram of a mixture of ADBAC and ADEBAC in deionized water (method 1, Surfactant column).

(Triamine, TA) does not absorb light in the UV range of the spectrum, and so it also did not affect the analysis.

The peak asymmetry factors and the distances between the peaks were within the acceptable range (Table 2). Thus, our conditions are suitable for separation of CHG, ADBAC, and ADEBAC.

In our conditions (method 1, Surfactant column), the peak area concentration graph for ADBAC is linear in the range between 0.005 and 1.000%, for ADEBAC between 0.06 and 0.33%, and for CHG between 0.012 and 0.111%.

Table 2. Chromatography parameters (method 1, Surfactant column) for a mixture of ADBAC, ADEBAC, and CHG*

Substance		Retention time, min	R_s
CHG		6.5	2.96
ADBAC	C12	7.9	3.32
	C14	9.0	2.58
ADEBAC	C12	8.4	1.64
	C14	8.7	2.22
	C16	9.5	1.67
	C18	9.7	2.71

* *Note:* concentration of each component is 0.2%; average parameter value of five measurements is calculated.

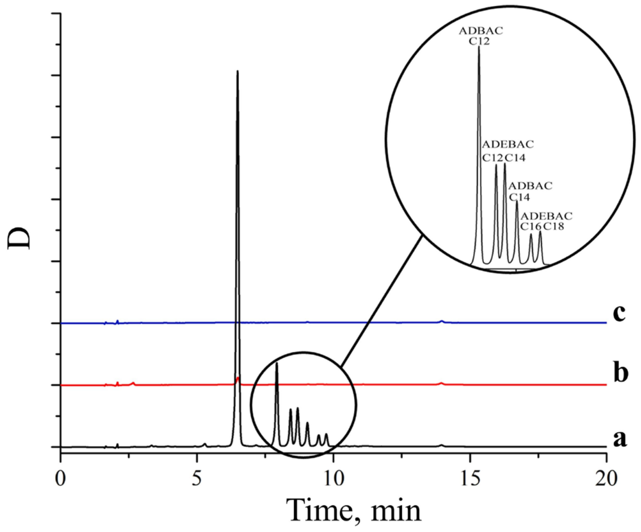

Fig. 4. Method 1, Surfactant column: **a** – chromatogram of a mixture of CHG, ADBAC, and ADEBAC; **b** – chromatogram of a 0.2% PHMB solution in deionized water; **c** – chromatogram of a 0.2% solution of *N,N*-bis-(3-aminopropyl)-dodecylamine in deionized water.

As we have shown, the Surfactant column is not suitable for PHMB quantification. Since this substance has an absorption peak at 240 nm, we could use HPLC with DAD. We were able to separate PHMB from other cationic surfactants only when we performed hydrophilic chromatography on a column with grafted amino groups. The retention time for PHMB in these conditions was approximately 6.5 min. The peak area–concentration graph for PHMB was linear in the range between 0.003 and 0.02%. The determination factor was 0.9961.

Quantification of PHMB in disinfectants may be affected only by ADBAC, ADEBAC, and CHG. When we performed chromatography of these substances and PHMB in deionized water, we determined that in these conditions the retention time for PHMB was approximately 6.5 min, for ADBAC approximately 9.2

min, for CHG approximately 9.8 min, and for ADEBAC approximately 11 min (Fig. 5). We could clearly identify only the peaks of dodecyldimethylbenzylammonium chloride and dodecyldimethyl(ethylbenzyl)ammonium chloride. The other homologs comprising ADBAC and ADEBAC also have peaks on the chromatogram, but they cannot be used for quantitative analysis. Thus, we did not see that these components could affect the analysis.

We used the methods described above for quantification of cationic surfactants in disinfectants. We then compared our results with those obtained by other methods, such as: two-phase titration of individual substances with methylene blue in alkaline conditions (for ADBAC)[3]; two-phase titration with bromophenol blue (for PHMB); and acid–base titration with hydrochloric acid in a water–ketone solution (for CHG)[4]. Model disinfectant formulations are presented in Table 3. A comparison of quantification methods for the cationic surfactants in these samples is shown in Table 4.

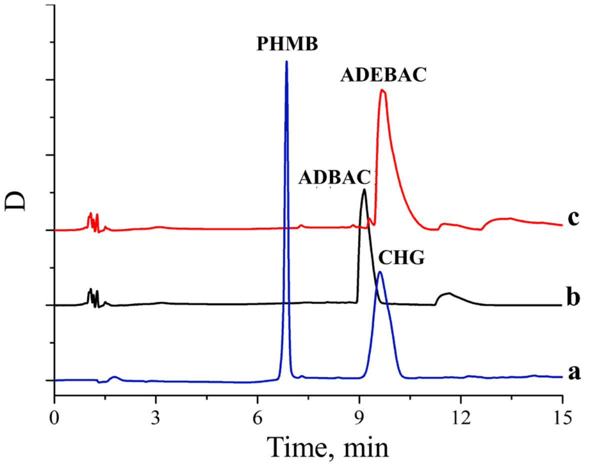

Fig. 5. Chromatography by method 2, Luna NH_2 column: **a** – chromatogram of a mixture of PHMB (0.02%) and CHG (0.05%) in deionized water; **b** – chromatogram of a 0.2% ADBAC solution in deionized water; and **c** – chromatogram of a 0.2% ADEBAC solution in deionized water.

Table 3. Model disinfectants formulations

Component	Contains, % (w/w)
Sample 1	
ADBAC	2.0
N,N-Bis-(3-aminopropyl)-dodecylamine	13.0
PHMB	0.4
Cocamidopropyl betaine	3.0
Nonoxynol AF 9-10	4.0
Potassium citrate	1.5
Water	To 100
Sample 2	
PHMB	0.25
CHG	0.25
2-Propanol	35.0
1-Propanol	30.0
Pentadecanol	0.3
Lactic acid	0.5
Citric acid	0.3
Water	To 100
Sample 3	
ADBAC	2.5
ADEBAC	2.5
N,N-Bis-(3-aminopropyl)-dodecylamine	10.0
Nonoxynol AF 9-10	5.0
Citric acid	0.8
Dye	0.001
Water	To 100

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[3] GOST R 57474-2017. *Dezinfektologiya i dezinfektsionnaya deyatel'nost'. Khimicheskie dezinfitsiruyushchie sredstva i antiseptiki. Metody opredeleniya chetvertichnykh ammonievykh soedinenii* (Disinfectology and disinfection activities. Chemical disinfectants and antiseptics. Methods for determination of quaternary ammonium compounds) (in Russ.).

[4] MVI 01.00282-2008 / 0184.23.12.13. *Opredelenie khlorgeksidina biglyukonata v vodnykh i vodno-spirtovykh rastvorakh* (Determination of chlorhexidine digluconate in aqueous and aqueous-alcoholic solutions) (in Russ.).

Table 4. Comparison of supposed and literature described methods for real disinfectants analysis

Surfactant	Amount introduced, %	Found by the proposed method, %	Found by titration method , %
Sample 1			
ADBAC	2.0	2.1±0.1	Separate quantification of the substances could not be performed*
PHMB	0.4	0.39±0.02	
Sample 2			
PHMB	0.25	0.24±0.01	0.22±0.02*
CHG	0.25	0.26±0.02	0.28±0.01**
Sample 3			
ADBAC	2.5	2.5±0.1	5.2±0.1* (sum of both QACs)
ADEBAC	2.5	2.4±0.1	

* Found by two-phase titration, %.
** Found by acid–base titration, %.

Table 5. Metrological parameters of the proposed methods*

Substance	S_r, %	S_R, %	r, %	R, %	±δ, %
ADBAC	1.21	1.69	3.98	5.57	3.94
ADEBAC	1.17	1.64	3.24	4.54	3.87
CHG	1.03	1.44	3.39	4,75	3.84
PHMB	1.23	1.73	4.07	5.70	3.68

* S_r – repeatability; S_R – reproducibility; r – repeatability limit; R – reproducibility limit; ±δ – relative error at P = 0.95.

In some cases, such as in Sample 2, titration methods can provide quantification of active compounds in disinfectants; however, they are often useless for a mixture of even two cationic surfactants, not to mention a greater number of analytes in a mixture. This statement is supported by our results for Samples 2 and 3. Additionally, the data shown in Table 3 suggest that chromatographic analysis is not affected by the presence of nonionic surfactants and other functional additives in disinfectants, thus making such chromatographic methods valuable.

The metrological characteristics of the proposed methods are shown in Table 5.

Conclusions

We have described the application of HPLC for quantification of cationic surfactants in disinfectants and have proposed methods for quantification of ADBAC, ADEBAC, PHMB, and CHG.

The proposed methods allow for the first time to quantify these four substances in disinfectants when they are present simultaneously. Titrimetry methods that are traditionally used for this purpose are not reliable, because their results may be affected by other components of disinfectants.

The proposed methods are quite simple and do not require complex equipment. This makes them highly desirable for quality control purposes and for tests prior to disinfectant registration. We have demonstrated the reliability of these chromatographic methods. They are not affected by other biologically active surfactants that may be found in disinfectants; additionally, we have successfully applied them for analysis of commercial disinfectants.

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