



ISSN 2518-718X (Print)  
ISSN 2663-4872 (Online)

# **BULLETIN** **OF THE KARAGANDA UNIVERSITY**

## **CHEMISTRY** Series

**№ 1(97)/2020**

ISSN 2518-718X (Print)  
ISSN 2663-4872 (Online)  
Индексі 74617  
Индекс 74617

**ҚАРАҒАНДЫ  
УНИВЕРСИТЕТІНІҢ  
ХАБАРШЫСЫ**

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**ВЕСТНИК**  
**КАРАГАНДИНСКОГО**  
**УНИВЕРСИТЕТА**

**BULLETIN**  
**OF THE KARAGANDA**  
**UNIVERSITY**

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**ХИМИЯ сериясы**

**Серия ХИМИЯ**

**CHEMISTRY Series**

**№ 1(97)/2020**

Қаңтар–ақпан–наурыз  
30 наурыз 2020 ж.

Январь–февраль–март  
30 марта 2020 г.

January–February–March  
March 30<sup>th</sup>, 2020

1996 жылдан бастап шығады  
Издается с 1996 года  
Founded in 1996

Жылына 4 рет шығады  
Выходит 4 раза в год  
Published 4 times a year

Қарағанды, 2020  
Караганда, 2020  
Karaganda, 2020

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**Қарағанды университетінің хабаршысы. Химия сериясы.**

**ISSN 2518-718X (Print). ISSN 2663-4872 (Online).**

Меншік иесі: «Академик Е.А. Бөкетов атындағы Қарағанды мемлекеттік университеті» РММ.

Қазақстан Республикасының Мәдениет және ақпарат министрлігімен тіркелген. 23.10.2012 ж. № 13110–Ж тіркеу куәлігі.

Басуға 28.03.2020 ж. қол қойылды. Пішімі 60×84 1/8. Қағазы офсеттік. Көлемі 15,75 б.т. Таралымы 200 дана. Бағасы келісім бойынша. Тапсырыс № 21.

Е.А. Бөкетов атындағы ҚарМУ баспасының баспаханасында басылып шықты.

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**Вестник Карагандинского университета. Серия «Химия».**

**ISSN 2518-718X (Print). ISSN 2663-4872 (Online).**

Собственник: РГП «Карагандинский государственный университет имени академика Е.А. Букетова».

Зарегистрирован Министерством культуры и информации Республики Казахстан. Регистрационное свидетельство № 13110–Ж от 23.10.2012 г.

Подписано в печать 28.03.2020 г. Формат 60×84 1/8. Бумага офсетная. Объем 15,75 п.л. Тираж 200 экз. Цена договорная. Заказ № 21.

Отпечатано в типографии издательства КарГУ им. Е.А. Букетова.

100012, Казахстан, г. Караганда, ул. Гоголя, 38, тел.: (7212) 51-38-20. E-mail: [izd\\_kargu@mail.ru](mailto:izd_kargu@mail.ru)

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**Bulletin of the Karaganda University. Chemistry series.**

**ISSN 2518-718X (Print). ISSN 2663-4872 (Online).**

Proprietary: RSE «Academician Ye.A. Buketov Karaganda State University».

Registered by the Ministry of Culture and Information of the Republic of Kazakhstan. Registration certificate No. 13110–Zh from 23.10.2012.

Signed in print 28.03.2020. Format 60×84 1/8. Offset paper. Volume 15,75 p.sh. Circulation 200 copies. Price upon request. Order № 21.

Printed in the Ye.A. Buketov Karaganda State University Publishing house.

38, Gogol Str., Karaganda, 100012, Kazakhstan. Tel.: (7212) 51-38-20. E-mail: [izd\\_kargu@mail.ru](mailto:izd_kargu@mail.ru)

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## Allantoin: synthesis and chemical properties

The availability and multifunctionality of allantoin makes it extremely attractive to unlock the synthetic potential on the basis thereof, especially for the needs of the pharmaceutical industry. Numerous publications on the allantoin chemistry are scarce, nonsystematic in nature and do not allow a deep understanding of the methods for its preparation and its chemical properties. In order to close this gap, the present review integrates the systematic data on the methods for the allantoin synthesis and the study of its chemical properties as well as the areas of allantoin practical application. In the present work, the methods most widely used in preparative practice to produce allantoin from the carbonyl compounds and urea are considered, and the ways of transformation of a number of nitrogen-containing heterocycles under the influence of various reagents leading to the target product are presented. The main chemical properties of allantoin are shown in hydrolysis reactions, complexation with organic and inorganic substrates, interactions with nucleophilic reagents, in chemoluminescence processes. In some cases, when the unconventional methods for the allantoin synthesis are given and allantoin transformations are considered, the mechanisms of the formation of final compounds are shown. A systematic material on the preparation methods and the chemical properties of allantoin can serve as a reliable navigator for those specialists who aim at manufacturing of allantoin-based practically important substances. Based on the integrated data it is pointed out that allantoin can be successfully used as a basic azaheterocycle to manufacture a wide range of new compounds, including bioactive ones.

**Keywords:** allantoin, urea, carbonyl compounds, azaheterocycles, complexes, luminescence, hydrolysis.

### Introduction

Allantoin belongs to the widely known azaheterocycles of the imidazolidinone series (in particular, hydantoins). Its useful biological properties have been the subject of several generalizing communications [1, 2]. However, at the same time, to date, there are no works in the literature that reflect the generalized chemistry of allantoin. Based on the aforesaid, this review aims to draw the attention of chemists and specialists in related fields to the methods for allantoin preparation as well as its chemical properties to expand the potential for application of allantoin-based compounds in organic synthesis and daily life.

#### 1. General information and application of allantoin

Allantoin (Fig. 1), also known as (2,5-dioxo-4-imidazolidinyl)urea, is a heterocyclic compound comprising a five-membered ring containing a urea substituent in the 4th position. Table 1 represents the main physical-chemical properties of allantoin.



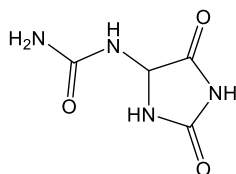


Figure 1. Allantoin structure

Table 1

**Physical-chemical properties of allantoin**

Parameter	Value
Appearance	White crystalline powder, odorless and tasteless
Melting point, °C	225 (with decomposition)
Solubility in water at 25 °C, g/l	5.7
Density, kg/m <sup>3</sup>	800
pH of 5 g/l solution at 25 °C	4.5–6
IR-spectrum, $\nu$ , cm <sup>-1</sup>	3436 (NH <sub>2</sub> ), 3068 (NH <sub>2</sub> ), 3192 (NH), 2947 (CH), 1780 (C=O), 1719 (C=O), 1667 (C=O)
IR-spectrum, $\delta$ , cm <sup>-1</sup>	1602 (NH <sub>2</sub> ), 1430 (NH)
NMR <sup>1</sup> H (DMSO-d <sub>6</sub> ), $\delta$ , ppm	8.05 (1H, s), 6.94 (1H, d), 5.83 (2H, s), 5.24 (1H, d)
NMR <sup>13</sup> C (DMSO-d <sub>6</sub> ), $\delta$ , ppm	173.79 (C=O), 157.70 (C=O), 157.06 (C=O), 62.61 (C-tert.)

Allantoin attracts the attention of researchers due to the fact that it is widely used as one of the active ingredients in skin care products, promotes the healing of scar tissue and scars that makes it the in-demand material for cosmetology and pharmaceutical practice. Currently, allantoin is included in more than 1300 various cosmetic products [1]. Thus, for instance, having a regenerating effect, allantoin helps to remove cicatrice tissues and scars [3]. As a part of creams, allantoin protects the skin from sunburns, chapping and cracking [4]. Allantoin also has a genotoxic effect [5] and restores normal skin moisture and elasticity [6]. The compound is able to reduce the genotoxic effect of ultraviolet radiation [7] and inhibit the development of a number of destructive processes caused by reactive oxygen species, i.e. exhibits antioxidant properties.

The main allantoin consumers are the cosmetics manufacturers as well as the pharmaceutical companies that use it as a feedstock to manufacture drugs intended for the treatment of various diseases [8]. Moreover, allantoin is used in agriculture as a plant growth regulator and is a component of fertilizers and veterinary disinfectants [9].

**2. Methods for allantoin preparation****2.1. Isolation from the cell structure of plants**

Allantoin was found in the callus of the *Coffea Arabica* plant [10]. To date, several methods are known for isolation of allantoin from the natural raw materials from the *Coffea Arabica* cell culture [10] and from the explants of leaves and apical shoots of the *Mertensia maritima* plant [11].

**2.2. Synthetic methods for allantoin preparation****2.2.1. Synthesis of allantoin from carbonyl compounds and urea**

The reactions of low molecular weight carbonyl compounds with urea are probably the most important in the allantoin synthesis since they represent the best conditions in terms of the availability of the reagents and the manufacturability of the process in general. Figure 2 illustrates the generalized methods for the allantoin preparation using carbonyl compounds with urea.

The principle of allantoin formation is exemplified by the use of mesoxalic acid or its monohydrate as the initial substrate in the reaction with urea at 110–115 °C.

One of the approaches to synthesize allantoin is the reaction in the presence of hydrogen peroxide as an oxidant, where glyoxal interaction with urea gives allantoin with a 58 % yield [12]. During the implementation of this process, the in situ transformation of glyoxal into glyoxalic acid under the action of the oxidant is postulated, and the acid is responsible for the final heterocyclization stage. Allantoin can be synthesized from various derivatives of acetic acid and urea, namely, from diethoxyacetic acid in the presence of HCl with a yield of 45 % [13], from dichloroacetate or dichloroacetic acid with a yield of 62 % [14].

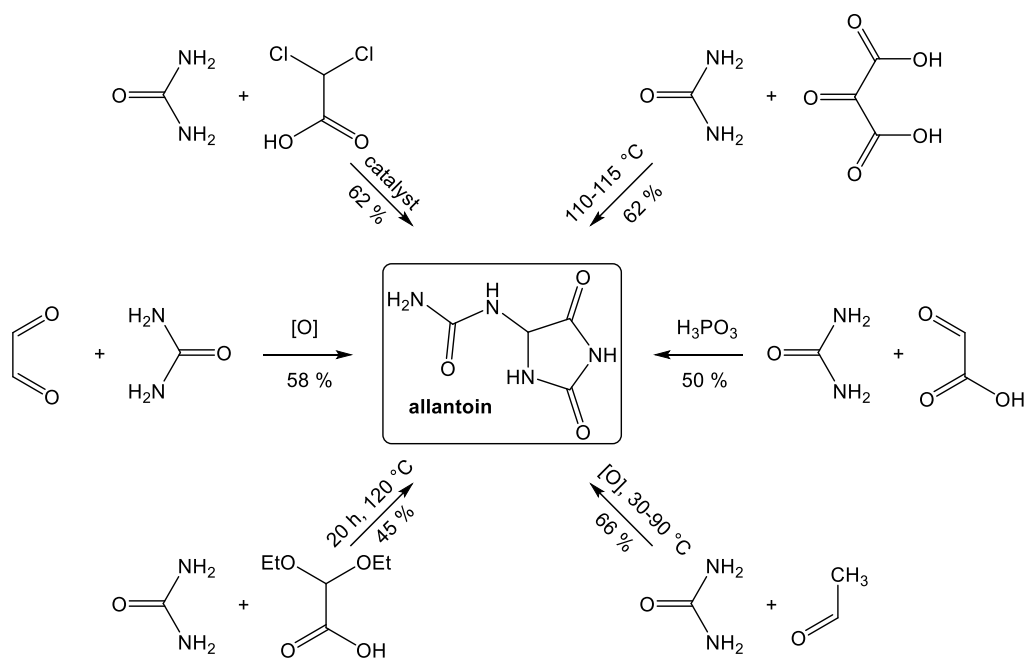


Figure 2. Synthesis of allantoin from carbonyl compounds and urea

The acetaldehyde-based allantoin synthesis involves the one-pot aldehyde oxidation with nitric acid followed by cyclization of the intermediate glyoxalic acid with urea, while the yield of the target product reaches 66 % [15].

Currently, the industrial allantoin production is based on the condensation of glyoxalic acid and urea in the presence of various catalysts: mineral acids [16], cation exchange resins [17], solid acids [18], ionic liquids [19], supported catalysts and zeolites [20, 21].

#### 2.2.2. Synthesis from azaheterocycles

Figure 3 represents the most successful methods for allantoin production that utilize the chemical methods of transformation of various nitrogen-containing heterocycles.

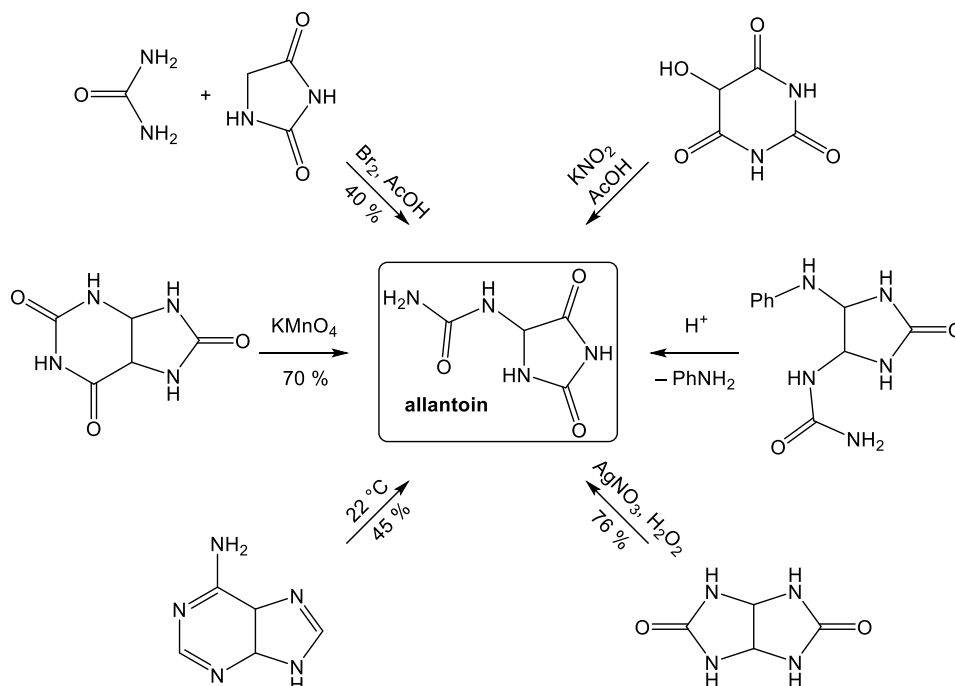


Figure 3. Allantoin synthesis from azaheterocycles

The oxidation of uric acid with potassium permanganate in an aqueous solution was found to lead to the allantoin formation with a yield of 70 %. The use of other oxidants results in a non-selective reaction performance since along with the target allantoin, various by-products are formed: acyclic amides, hydantoin, oxonic acid, 4-imidazolidine carboxamide, oxalic acid, etc.

The electrolysis of an adenine aqueous solution in a phosphate buffer at room temperature is accompanied by the oxidative degradation [22] to a number of nitrogen-containing heterocycles, where allantoin is the main product (45 %).

The interaction of hydantoin and urea in the presence of bromine and acetic acid [23] allows synthesizing allantoin with a relatively low yield (40 %). The allantoin formation implies an intermediate C-bromination process followed by N-alkylation of urea with brominated hydantoin.

The practical result affected the alloxan by  $\text{KNO}_2$  and acetic acid is that in this case it is preferable to narrow the pyrimidine trion cycle to the allantoin one, and the urea molecule, a product of the complete destruction of alloxan, is involved in the allantoin formation.

Ref. [24] shows that under the action of  $\text{H}_2\text{O}_2$  in the presence of  $\text{AgNO}_3$  at 65 °C, glycoluril transforms with the opening of one of the imidazolinone rings leading to allantoin with a high yield (76 %).

An example is given for the selective hydrolysis of the phenylamino derivative of allantoin in the presence of mineral acids [25] yielding allantoin.

### 3. Chemical properties of allantoin

Already at the beginning of the last century, a communication appeared [26] postulating the phenomenon of reversible isomerism (keto-enol tautomerism) for the allantoin molecule, and Figure 4 represents the tautomeric equilibrium established.

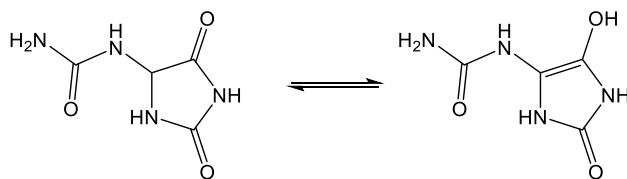


Figure 4. Allantoin tautomeric equilibrium

Allantoin is known to exist as a racemic mixture of (R) and (S) stereoisomers. A number of studies [27, 28] considers the accumulation of (R)-allantoin and (S)-allantoin during the non-enzymatic and enzymatic oxidative urate decomposition into allantoin during the purine catabolism in many organisms. The non-enzymatic racemization of allantoin was found to result in the accumulation of (R)-allantoin, since the enzymes that convert allantoin to allantoate are specific for the (S)-isomer. The allantoin racemase enzyme catalyzes the reversible conversion between the two allantoin enantiomers, thereby ensuring the overall efficiency of the catabolic pathway and preventing the allantoin accumulation. Figure 5 shows the racemic mixture of allantoin.

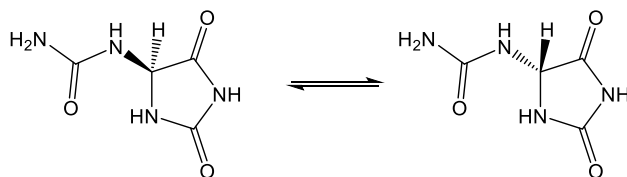


Figure 5. Allantoin racemization

To explain the spatial orientation paths in the allantoin stereochemistry, a mechanism was proposed [29] for the mutual transition of allantoin stereoisomers into a racemic mixture under the action of urate oxidase (Fig. 6).

Further studies [30] of allantoin diastereomers showed that the allantoin molecule had two optical centers and two stereoisomers that are not the mirror images of each other and confirmed the transition of one stereoisomer into another one (Fig. 7).

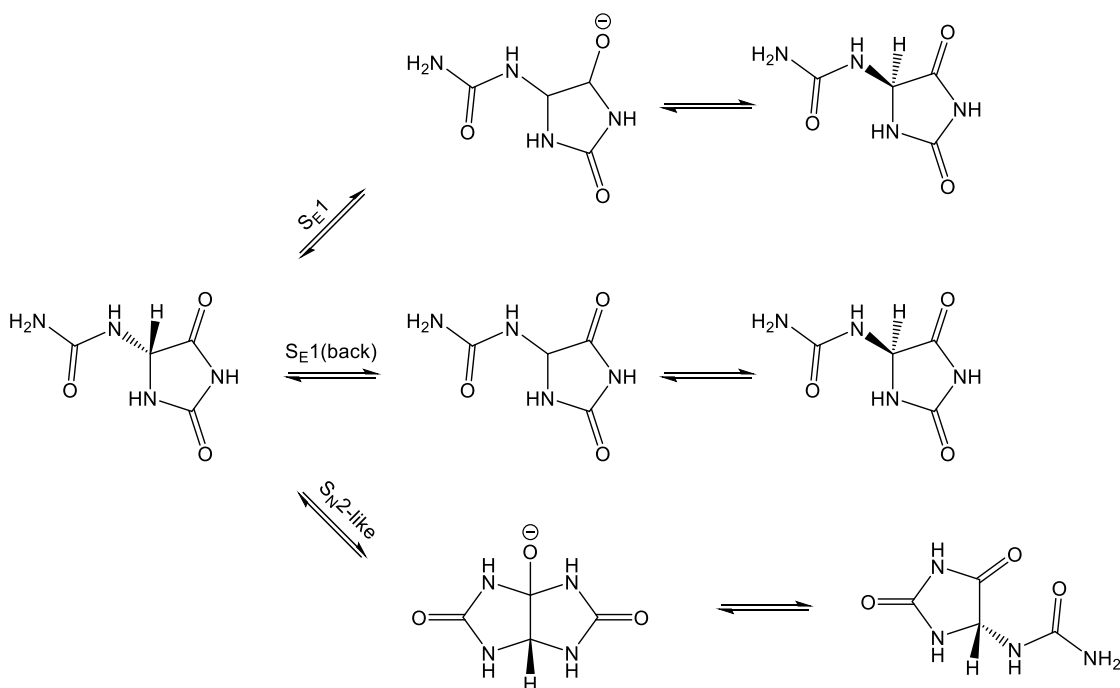


Figure 6. The mechanism of formation of allantoin stereoisomers

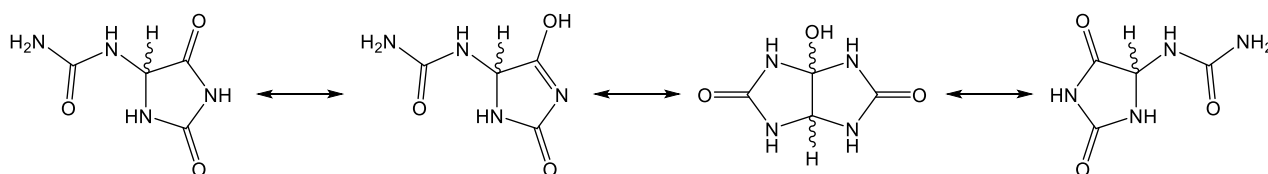


Figure 7. Transition of allantoin stereoisomers

### 3.1. Complexation reactions

Currently, numerous studies are devoted to the methods to prepare various organic and organometallic complexes of allantoin by changing the nature of the ligand, including the use of the mechanochemical synthesis. Thus, the synthesis of the allantoin organic complexes with pantoic [31], polygalacturonic [32], ascorbic [33], and urocanic [34] acids as well as glycine [35], was carried out. Figure 8 shows several examples.

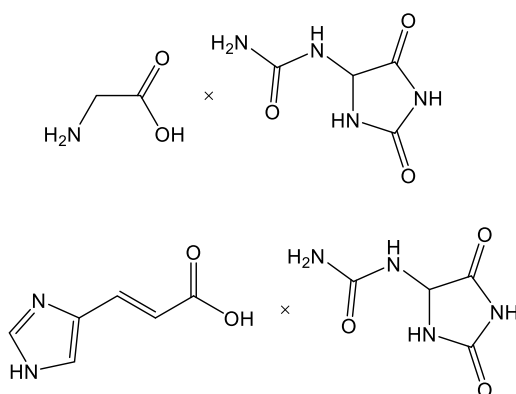


Figure 8. Allantoin complexes with organic acids

The synthesized allantoin-aluminum and allantoin-chlorohydroxyaluminum complexes with various organic acids [36] have found application in cosmetology as a part of deodorants, astringent lotions, aftershave, and other personal hygiene products (Fig. 9) [37, 38].

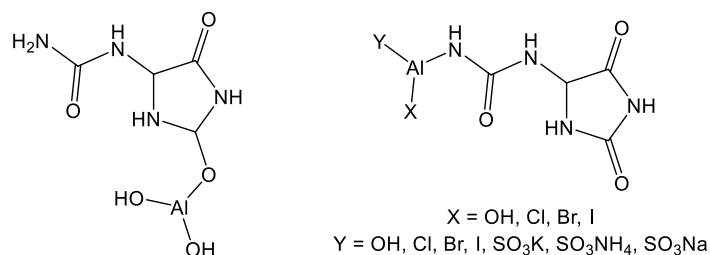


Figure 9. Allantoin-aluminum complexes

There is no doubt that the abovementioned examples of the preparation of allantoin complexes with organic ligands do not exhaust all the opportunities to create such compounds.

Figure 10 represents certain successes achieved in the synthesis of allantoin complexes and the composition of the allantoin-chlorohydroxyaluminium complex with ascorbic acid with the participation of the imide atom of the allantoin heterocyclic fragment [33].

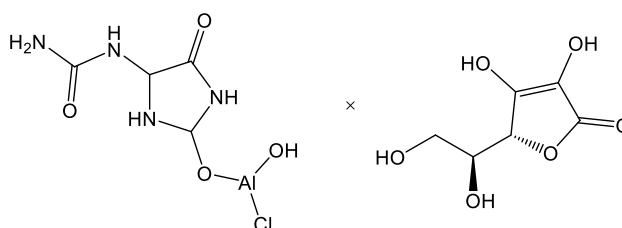


Figure 10. Allantoin-aluminum complexes

Figure 11 shows the same type of complex, where the total composition of the allantoin-aluminum complexes with various organic acids is presented [37, 38], however, the terminal amino group of the urea substituent is involved.

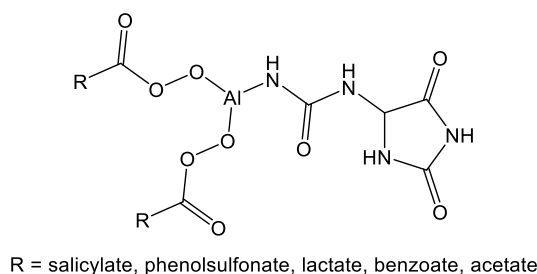


Figure 11. Allantoin-aluminum complexes

The intensive development was the study of allantoin complexes with silver, zinc and organic acids due to their manifestation of the wound healing, bactericidal [39, 40] and antithrombotic properties [41]. Figure 12 illustrates the overall composition of allantoin-zinc-silver complexes.

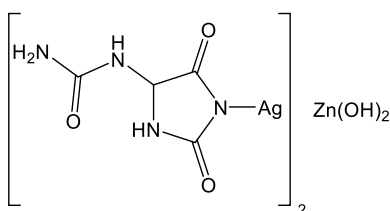


Figure 12. Complexes of allantoin with silver and zinc

### 3.2. Hydrolysis reactions

Allantoin is prone to chemical and enzymatic hydrolysis reactions, including those in living organisms [42] leading to allantoic acid (Fig. 13).

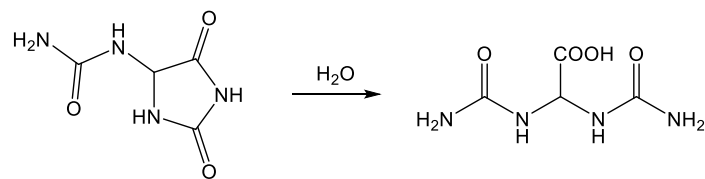


Figure 13. Hydrolysis of allantoin

By changing the depth of the allantoin hydrolysis it was found [43] that 5-aminohydantoin and fulminic or carbamic acid are the products of this reaction (Fig. 14).

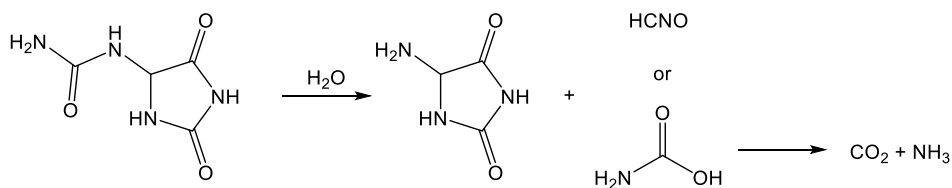


Figure 14. Hydrolysis of allantoin

### 3.3. Chemo- and electrochemoluminescence

Saqib et al. [44] found the allantoin ability for intensive chemoluminescence with lucigenin. To explain the results, a reaction mechanism was proposed (Fig. 15) suggesting that allantoin can decompose and release a cyanide radical in an alkaline medium to react with lucigenin.

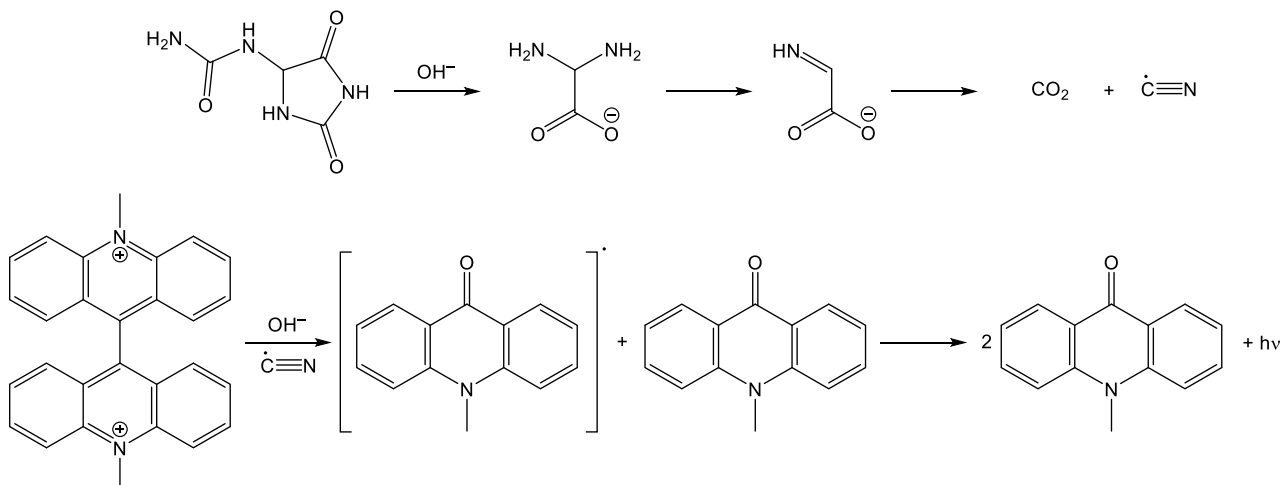


Figure 15. The mechanism of allantoin chemoluminescence

In the experiment described in Ref. [45], the electrochemiluminescence based on allantoin and tris(2,2'-bipyridine) ruthenium  $[\text{Ru}(\text{bPy})_3]^{2+}$  in an alkaline buffer solution at  $\text{pH} = 11.0$  was studied. Given the specific nature of the established effect, the reaction mechanism (Fig. 16) suggests that allantoin in an alkaline medium turns into a radical anion involved in further stages of electrochemiluminescence.

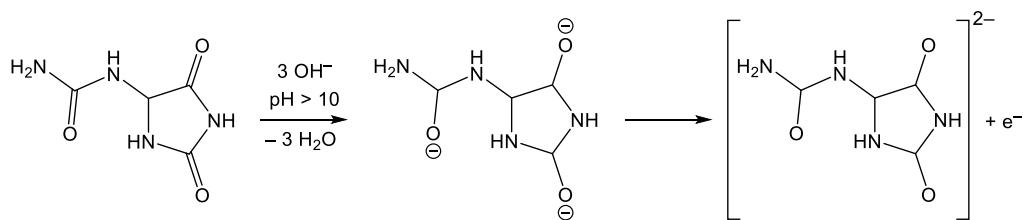


Figure 16. Allantoin-based electrochemiluminescence

### 3.4. Interaction with phenol

A method based on the reaction of allantoin and phenol [20] in the presence of heterogeneous catalysts comprising mineral acids supported on solid zeolite supports allows producing the ortho/para-hydroxyphenyl-hydantoins (Fig. 17).

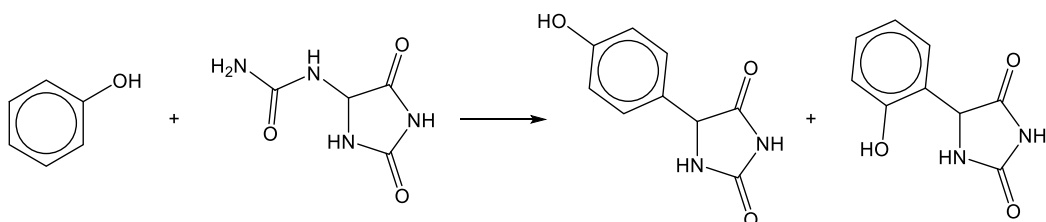


Figure 17. Reaction of allantoin and phenol

### 3.5. Nitrogen Substitution Reactions

For the first time, the N-alkylation of allantoin was carried out at the beginning of the 20th century [46]. In the proposed method, the silver-substituted allantoin was initially prepared followed by the Ag replacement by methyl group under the influence of methyl iodide. Figure 18 shows the process for producing of 1-(1-methyl-2,5-dioxoimidazolidin-4-yl)urea and 1-(3-methyl-2,5-dioxoimidazolidin-4-yl)urea using these reactions.

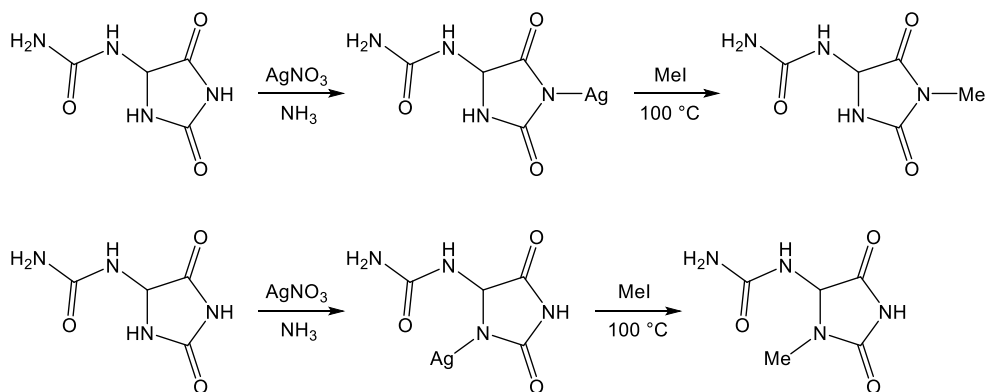


Figure 18. N-methylation of allantoin

In Ref. [47], a comprehensive silylation of allantoin was carried out by heating the latter with bistrimethylsilylacetamide (BSA) in pyridine (Fig. 19).

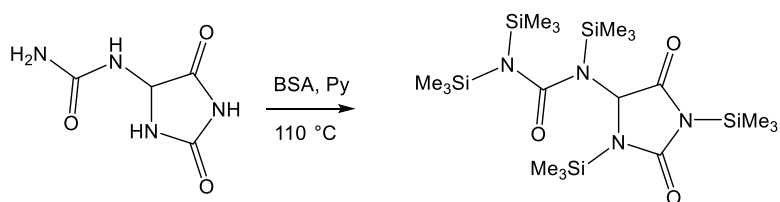


Figure 19. N-silylation of allantoin

### 3.6. Reactions with aldehydes

There is a noticeable amount of bactericidal substances that are synthesized by the interaction of allantoin with glutaraldehyde [48] and formaldehyde [49]. Figure 20 shows an example of the allantoin condensation reaction with glutaraldehyde.

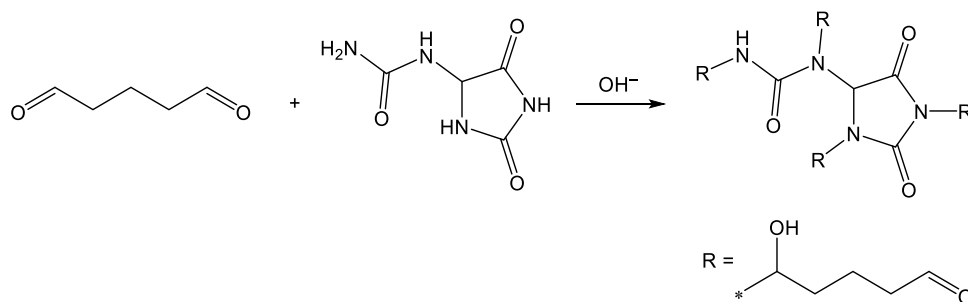


Figure 20. Allantoin condensation with glutaraldehyde

The most studied are the allantoin condensation reactions with formaldehyde (Fig. 21).

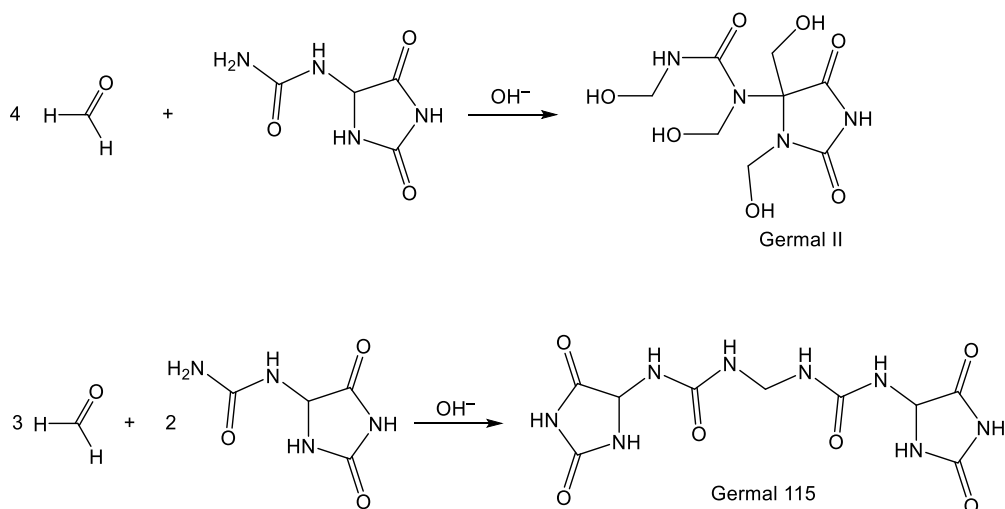


Figure 21. Allantoin condensation with formaldehyde

Diazolidinyl urea (Germal II) and imidazolidinyl urea (Germal 115) are the well-known methylol derivatives of allantoin widely used in various fields of human activity. Diazolidinyl urea (Germal II) is a heterocyclic compound comprising methyl-substituted allantoin derivative. Currently, the location of substituted methylol groups in this compound is a matter of discussion, and two main configurations are assumed. According to the published data [49], diazolidinyl urea is a tetra-N-methylol derivative of allantoin, however, recent studies [50] have shown that the product of the allantoin condensation with formaldehyde is a compound where one of the four methylol groups is bonded to the tertiary carbon atom of the hydantoin cycle. Table 2 represents the physical-chemical properties of Germal II and Germal 115.

Table 2

Physical-chemical properties of diazolidinyl urea and imidazolidinyl urea

Parameter	Value	
	Diazolidinyl urea [51]	Imidazolidinyl urea [52]
Appearance	White crystalline powder with a slight characteristic odor	White crystalline powder with a slight characteristic odor
Solubility	Easily soluble in water, propylene glycol	Soluble in water, ethylene glycol, propylene glycol, glycerin, slightly soluble in methanol, insoluble in ethanol



Diazolidinyl urea is one of the most commonly used preservatives in cosmetics [53–55] releasing formaldehyde as a result of decomposition. The concentrations of the released formaldehyde in the cosmetic products and the factors affecting the release of formaldehyde during the decomposition of diazolidinyl urea have been previously studied [56, 57]. However, to date, there is not much data on its decomposition, and analytical methods to determine the diazolidinyl urea have been developed during the last 15 years [53, 58]. It was previously reported that (4-hydroxymethyl-2,5-dioxo-imidazolidin-4-yl)urea (HU compound in Figure 22) is the only decomposition product of diazolidinyl urea [53]. The scheme 21 shows a possible decomposition path for diazolidinyl urea. Doi et al. [59] proved that diazolidinyl urea (compound 1) releases formaldehyde to form the HU (compound 8) and six other decomposition intermediates (compounds 2–7).

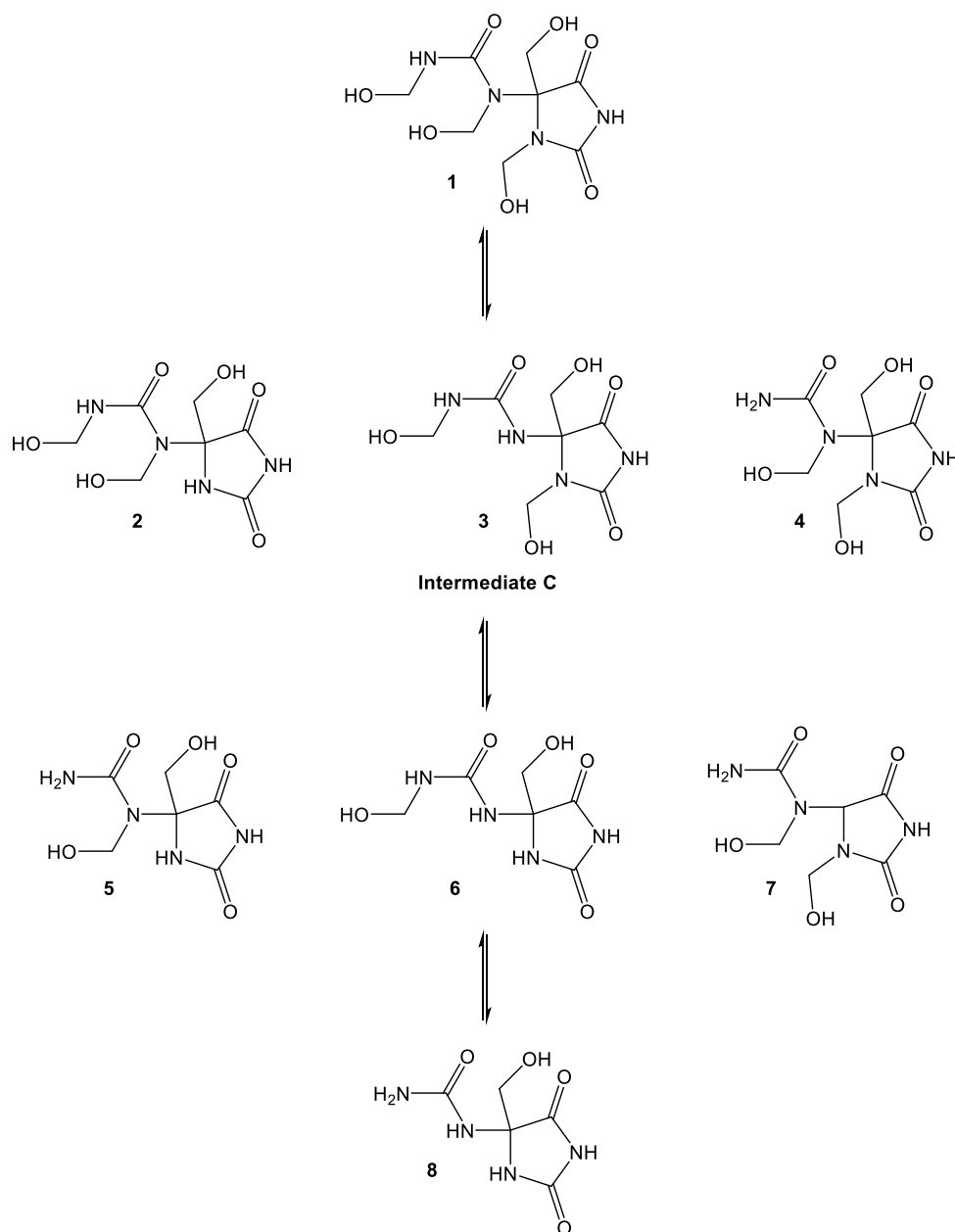


Figure 22. Decomposition products of diazolidinyl urea

The Germal II and Germal 115 are bactericidal components that are mainly used as preservatives in cosmetic products, protect them from bacteria, yeast, and mold. These substances are a part of various shampoos, hair conditioners, shaving gels. Being active against both gram-negative and gram-positive bacteria, these compounds have antimicrobial activity, can be used individually [50] and in a combination with para-

hydroxybenzoic acid esters (parabens), are also synergistic with a number of other preservatives. Imidazolidinyl urea has the same positive effects as diazolidinyl urea, but it has no antifungal effect [60].

Both compounds can cause irritation to the eyes and skin, and are also capable of causing the contact dermatitis, since they release free formaldehyde, however, the amount of this formaldehyde is much lower than the recommended limits [61]. The use of diazolidinyl urea as a part of the personal care products is allowed in concentrations of up to 0.5 wt.% [51].

### Conclusions

Thus, this work summarizes the information on the methods for producing allantoin from various substrates and considers its inherent chemical properties. An analysis of the literature on the chemical properties of allantoin shows that it is most characteristic for the complexation reactions that allow obtaining new biologically active compounds. In some cases, the work is focused on the methods to prepare and use allantoin under industrial conditions.

### Acknowledgement

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the Federal Target Program «Investigation and Developments on Priority Directions of Development of the Scientific Technological Complex of Russia for 2014–2020», Agreement No. 05.604.21.0251, unique identifier of project RFMEFI60419X0251.

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### Аллантоин: синтезі және химиялық қасиеттері

Аллантоиннің қол жетімділігі мен көп функционалдылығы оның негізінде синтетикалық заттар алуда, соның ішінде фармацевтикалық өндіріс қажеттіліктері үшін үлкен қызығушылық туғызуда. Аллантоин химиясы туралы көптеген әдеби көздер толық емес, жүйесіз және бұл мәліметтер оның алыну әдістері мен химиялық қасиеттерін толық түсінуге мүмкіндік бермейді. Осы мақалада аллантоинді синтездеу және химиялық қасиеттерін зерттеу әдістері, оның практикалық қолданылуы туралы жүйеленген мәліметтер келтірілген. Бұл жұмыста аллантоиннің карбонилді қосылыстар мен мочевинадан алудың препаративтік тәжірибеде кеңінен қолданылатын әдістері қарастырылған және азотқұрамды гетероциклдердің әртүрлі реагенттер әсерінен негізгі өнімге әкелетін трансформациялық айналулар жолдары көрсетілген. Аллантоиннің негізгі химиялық қасиеттері гидролиз реакцияларында, органикалық және бейорганикалық субстраттармен комплекстүзде, нуклеофильді реактивтермен әрекеттесуде, хеомлюминесценция процестерінде көрсетілген. Аллантоин синтезінің стандартты емес әдістері мен оның химиялық өзгерістерге ұшырауы берілген жерлерінде соңғы өнімдердің түзілу механизмдері көрсетілген. Аллантоиннің синтезі мен химиялық қасиеттері туралы жүйелі материал аллантоин негізінде маңызды заттарды синтездеп алуға бағытталған мамандар үшін қажетті құрал бола алады. Жалпыланған мәліметтер негізінде аллантоинді азатероцикл ретінде жаңа биологиялық белсенді және басқа да қосылыстардың кең спектрін алу үшін қолдануға болатындығы айтылған.

*Кілт сөздер:* аллантоин, мочевина, карбонилді қосылыстар, азатероциклдер, комплекстер, люминесценция, гидролиз.

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### Аллантоин: синтез и химические свойства

Доступность и полифункциональность аллантоина делают его крайне привлекательным для реализации синтетического потенциала на его основе, особенно для нужд фармацевтической промышленности. Многочисленные литературные сведения по химии аллантоина носят отрывочный, несистемный характер, и они не позволяют иметь полноценное представление о методах его получения и его химических свойствах. С целью устранения данного пробела в представленной обзорной статье приведены систематизированные данные по методам синтеза аллантоина и изучению его химических свойств, а также затронуты области практического применения аллантоина. Рассмотрены наиболее распространенные в препаративной практике методы получения аллантоина из карбонильных соединений и мочевины, а также приведены пути трансформации ряда азотсодержащих гетероциклов под действием различных реагентов, приводящие к целевому продукту. Основные химические свойства аллантоина представлены в реакциях гидролиза, комплексообразования с органическими и неорганическими субстратами, взаимодействия с нуклеофильными реагентами, в процессах хеомлюминесценции. В отдельных случаях, когда приводятся нетиповые методы синтеза аллантоина и рассматриваются его превращения, показаны механизмы образования конечных соединений. Систематизированный материал по методам синтеза и химическим свойствам аллантоина может служить надежным навигатором для тех специалистов,

которые нацелены получать практически важные вещества на основе аллантиина. На основании обобщенных данных отмечено, что аллантиин может быть успешно использован в качестве базового азаетероцикла для получения широкого круга новых биологически активных и других соединений.

**Ключевые слова:** аллантиин, мочевины, карбонильные соединения, азаетероциклы, комплексы, люминесценция, гидролиз.

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## **Interpolymer complex of biopolymers as a soil structure-forming agent**

An interpolymer complex based on biopolymers — chitosan (CS) and sodium alginate (AlNa) was synthesized. The chitosan-sodium alginate interpolymer complex was prepared by mixing equimolar solutions of polymers in a given proportion. Chitosan solution in citric acid and aqueous solution of sodium alginate were used. The composition of the interpolymer complex is determined by the methods of gravimetry, turbidimetry and dynamic laser light scattering and is  $[CS]:[AlNa] = 2:3$ . Interpolymer complex is formed as a result of ion-ion interaction between cationic polyelectrolyte chitosan and anionic polyelectrolyte sodium alginate. Agrochemical parameters of soil were determined without and with treatment of certain biopolymers and interpolymer complex. Soil treatment by the individual biopolymers and the prepared interpolymer complex has not been appreciably affected in its basic agrochemical parameters. As a result of laboratory experiments, it is shown that the prepared interpolymer complex is more effective means of protecting the soil from water erosion in comparison with individual biopolymers. Vegetation experiments in the laboratory revealed that soil treatment interpolymer complex has a positive effect on the growth and development of cucumber. Consequently, the synthesized interpolymer complex can be used as an effective environmentally sound structure-forming agent for the soil.

**Keywords:** interpolymer complex, biopolymers, chitosan, sodium alginate, composition, soil, structure-forming agent.

### *Introduction*

Desertification and degradation of agricultural soils is one of the global problems of our time [1]. Currently, the main reasons for the deterioration of soil quality are water and wind erosion, irrational use of land. As a result, part of the fertile land is useless for arable land every year. This leads to genetic changes in the soil and leads to the process of degradation. The structure and water-physical properties of the soil are changing under the influence of anthropogenic factors, which leads to a decrease in its fertility.

Restoration of fertility and erosion control are clearly impossible without improvement of soil water-physical properties. Therefore, optimization of water-physical properties and stabilization of soil structure is one of the most important tasks in the field of soil ecology. One of the optimal ways to improve the structural and aggregate state of soils is the treatment of the top layer of soil by interpolymer complexes (IPCs) [2].

Surface treatment of soil IPC allows to achieve soil consolidation for 3–5 years, can prevent water and wind erosion and the associated spread of various contaminants [3], marked air and water permeability of coatings IPC [2, 4–6]. Ecologically safe biopolymers and IPC based on them are promising structure-forming agents [7–8].

The goal of research is the preparation of IPC based on the biopolymers — chitosan (CS) and sodium alginate (AL), to study the structure-forming properties of IPC and the effect on the growth and development of vegetable crops.

### *Experimental*

High molecular weight chitosan with a molecular weight of 190 kDa, degree of deacetylation 85 %, Sigma-Aldrich (Germany).  $10^{-2}$  M solution of chitosan in 3 % citric acid were used. Sodium alginate with a molecular weight of 440 kDa manufactured by Sigma-Aldrich (China), used  $10^{-2}$  M aqueous alginate solution [9–10]. The composition of IPC was determined by the following methods: gravimetry, turbidimetry and dynamic laser light scattering.

For study the formation of IPC by gravimetric method, a series of solutions with different volume ratios of equimolar solutions ( $10^{-2}$  mol/l) of CS and AL were prepared according to Table 1.

Table 1

Ratio of components to preparation IPC

Ratio	The volume of solution, ml	
	CS	AL
[100]:[0]	10	0
[90]:[10]	9	1
[80]:[20]	8	2
[70]:[30]	7	3
[60]:[40]	6	4
[50]:[50]	5	5
[40]:[60]	4	6
[30]:[70]	3	7
[20]:[80]	2	8
[10]:[90]	1	9
[0]:[100]	0	10

The resulting solutions were mixed in a rotator for 6 hours, then centrifuged for 15 minutes at a rotation speed of 3500 rpm, then drained the liquid and weighed the wet precipitation.

For study the formation of IPC by turbidimetric method, after mixing the obtained solutions in accordance with Table 1, the optical density of each solution was measured on the spectrophotometer Specord 210 plus (Analytik Jena, Germany) at a wavelength of 400 nm. Based on the received data, a graph of the dependence on the composition of the optical density solution was drawn.

The measurements of  $\zeta$ -potential (macromolecule recharge) carried out by dynamic laser light scattering method on the device Zetasizer Nano ZS90 (Malvern, UK).

Samples of dark chestnut soil of the dry steppe zone of the East Kazakhstan region were selected in 5 km from the Vodnyi village near Semey town. The study of the main agrochemical parameters of the soil, such as: field humidity, acidity, moisture capacity, water resistance, nutrient content (phosphorus, nitrogen), organic matter and humus content was carried out according to the generally accepted methods.

To study the soil resistance to water erosion, glass Petri dishes were used in the model experiment. In each dish is introduced 50 g of the sample in dark-chestnut soil, sifted through a sieve  $d = 0.25$  mm. the Soil in the first Cup of dry (control, polymers and IPC not included), the soil in 2-dish handled IPC [CS]:[AL] = 2:3, the soil in the 3-dish was administered 12.5 ml of  $10^{-3}$  M of chitosan dissolved in 3 % citric acid, 4-dish was administered 12.5 ml of  $10^{-3}$  M aqueous solution of sodium alginate. All cups were dried for 5 days at  $t = 20$  °C. The dried soil samples were then tilted  $15^\circ$  and 100 ml of distilled water was sprayed. Washing water was collected in glass flasks.

Vegetation experiments were carried out in the laboratory at a temperature of 20 °C. Wagner vessels measuring  $1.7 \text{ dm}^3$  and a surface area of  $1.68 \cdot 10^{-2} \text{ m}^2$  were used as soil containers. Before the experiment, the vessels were cleaned of mechanical impurities, the dishes were rinsed with running water, and then with distilled water. The average soil sample was taken. To ensure the moisture content of the lower soil layer at a depth of 2 cm from the bottom with the compaction of the first layer, glass tubes were placed. The vessels were filled with soil 10 cm high from the bottom of the vessel, leaving 2.5 cm from the upper edge of the vessel. Each vessel is signed in accordance with the experience option.

For vegetation experiments as a vegetable culture cucumber (*Cucumis*) «Kustovoy» was selected, which is cultivated in many regions of the Kazakhstan.

Harvesting of plant seeds. Seeds of cucumbers of the «Kustovoy» variety were placed in glass Petri dishes and germinated between the filter paper moistened with pre-distilled water in the dark. From the seeds laid for the vegetation experiment, intact seeds with well-developed roots were selected. Planting of plant seeds. Soil treatment with biopolymers and IPC by two-solution method was carried out according to the following scheme:

1. Control experience — not included biopolymers and IPC.
2. Treatment by CS ( $8.05 \cdot 10^{-3}$  g/vessel).
3. Treatment by AL ( $5 \cdot 10^{-2}$  g/vessel).
4. Treatment by IPC [CS]:[AL] = 2:3 ( $6.44 \cdot 10^{-3}$  g/vessel :  $6 \cdot 10^{-2}$  g/vessel).



5. Introduction of dry mixed fertilizer «Vyrastaika»  $(\text{NH}_4)_2\text{SO}_4 - \{\text{NH}_4\text{H}_2\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4\} - \text{KH}_2\text{PO}_4 = 12-14-16$  (0.84 g/vessel).

6. Treatment by IPC and dry mixed fertilizers.

After tillage, cucumber seeds were planted, the distance between them was kept from 2 cm to 4 rows in each. Planting depth 1 cm. Top layer of soil is moistened with purified water from a spray bottle, resulting in a restoration of a polymer film in the surface of soil. Watering of the soil was carried out once in 2 days, keeping 60 percent of the full moisture capacity. Every day the vessels were moved in randomized mode to avoid the impact of external factors on the development of the plant. The emergence of the first shoots and the appearance of mass shoots were observed, daily evaluation of biometric parameters of the organs of terrestrial growth was conducted as well.

### Results and Discussion

The results of gravimetric and turbidimetric studies of complexation and measurements of  $\zeta$ -potential (macromolecule recharge) showed that the composition of IPC is formed  $[\text{CS}]:[\text{AL}] = 4:6$  or  $2:3$  (Figs. 1–3).

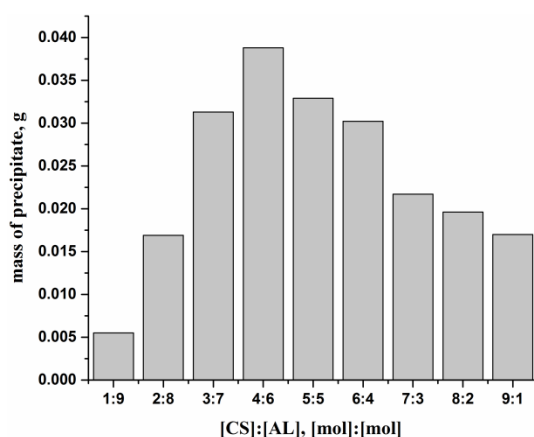


Figure 1. Chart based on weight of solids, the ratio  $[\text{CS}]:[\text{AL}]$

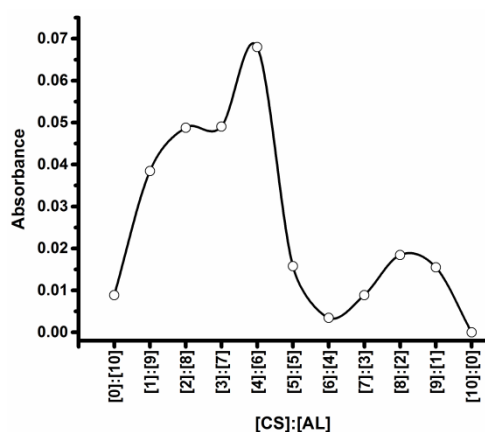


Figure 2. The dependence of the light absorption ratio  $[\text{CS}]:[\text{AL}]$

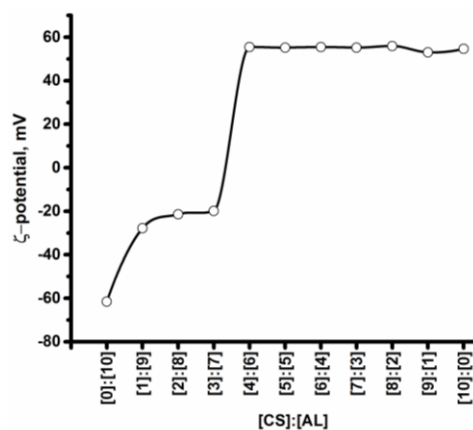


Figure 3. The dependence of the  $\zeta$ -potential on the composition IPC

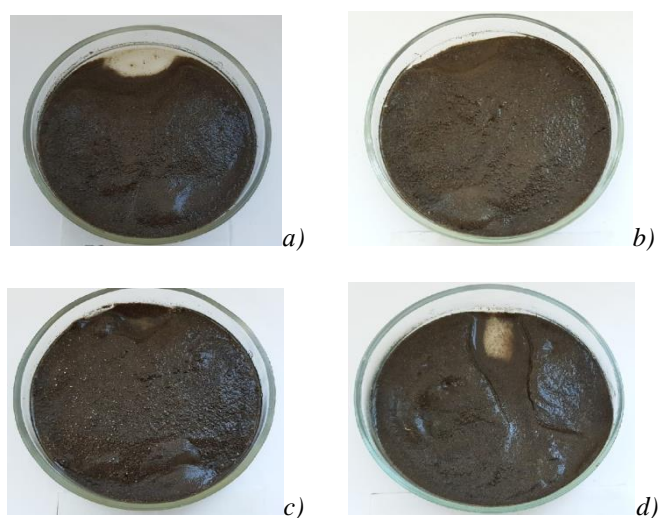
Previously, we have prepared a IPC structure  $[\text{CS}]:[\text{AL}] = 1:4$  [11]. However, in that work chitosan was dissolved in hydrochloric acid, in this work chitosan is dissolved in citric acid. Thus, the nature of the solvent affects the composition of the prepared IPC. Agrochemical parameters of soil without treatment and after treatment of separate biopolymers and IPC are determined. Table 2 shows that biopolymers and IPC do not change the pH of the aqueous extract and increase the pH of the salt extract. There was no noticeable effect on other soil parameters.

Table 2

## Agrochemical parameters of soil

Structurant	Agrochemical parameters			
	pH <sub>water</sub>	pH <sub>salt</sub>	NH <sub>4</sub> <sup>+</sup> , mg/g soil	P <sub>2</sub> O <sub>5</sub> , mg/g soil
Before making	6.909	7.207	0.61	2.25
CS	6.917	7.560	0.62	2.25
AL	6.921	7.581	0.61	2.,23
IPC	6.926	7.552	0.67	2.27

Figure 4 shows the results of a study of soil resistance to water erosion. There is soil erosion in the control experiment and in the dish treated with individual polymers. The washout is not observed only in the dish treated with IPC.



*a* — control; *b* — soil treated with IPC; *c* — soil treated with chitosan; *d* — soil treated with sodium alginate

Figure 4. Soil after spraying with distilled water

Each experiment was repeated three times. The washing water of the soil treated by IPC is the most transparent in comparison with other washing waters. Then the soil samples were dried for another 5 days at  $t = 20\text{ }^{\circ}\text{C}$  and weighed. According to the results of calculations, a diagram of soil resistance to water erosion was designed (Fig. 5).

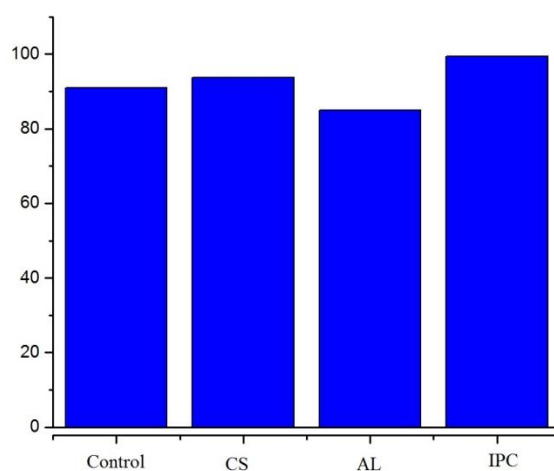


Figure 5. Diagram of soil resistance to water erosion, %

Thus, it was shown that the IPC of [CS]:[AL] = 2:3, is the most effective means to protect the soil from water erosion.

The results of vegetation experiments for 32 days are shown in Figures 6–8.

The period from sowing before the appearance of initial seedlings was 8 days and before mass seedlings — 12 days. In this case, the initial and mass germination in the experiment with IPC and IPC + fertilizer was 8–10 % higher than the control. Cucumber varieties «Kustovoy» refers to bee pollinated and 30–40 days after the emergence of seedlings, it is advisable to transplant the seedlings into open ground.

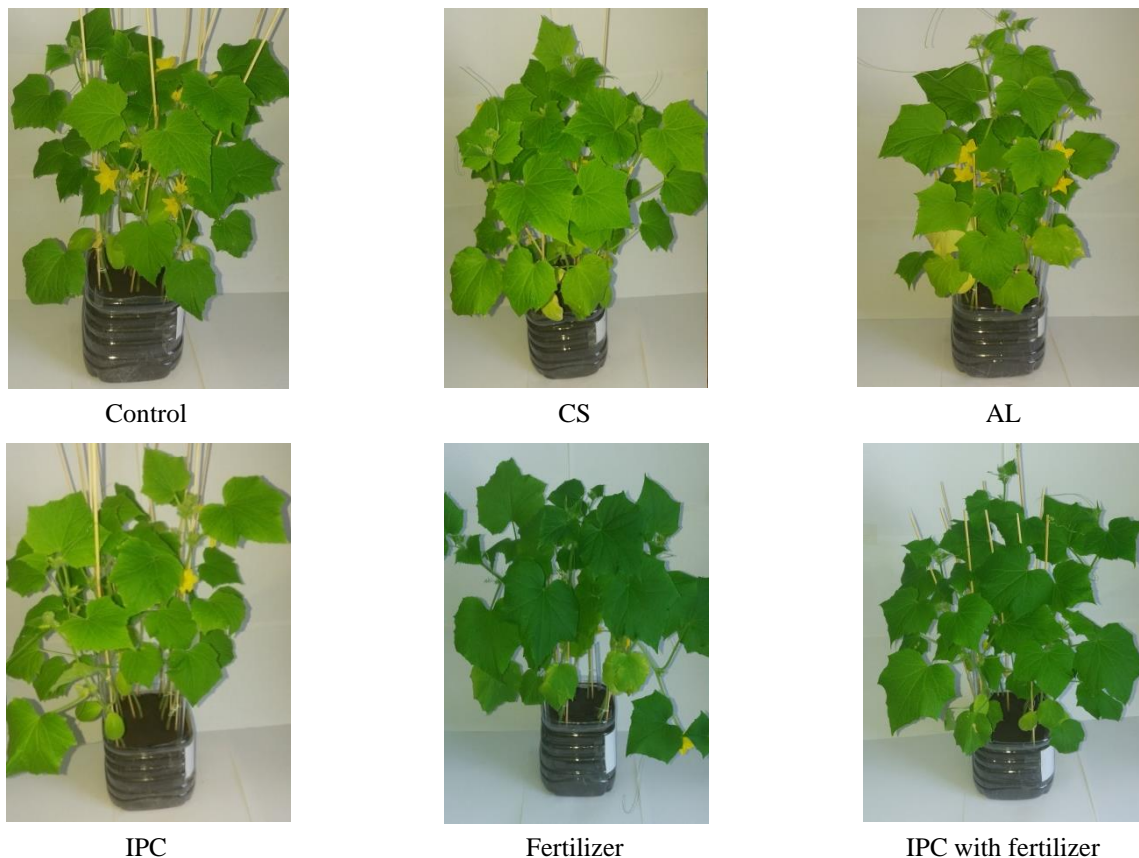


Figure 6. Growing experience in the vessels of Wagner

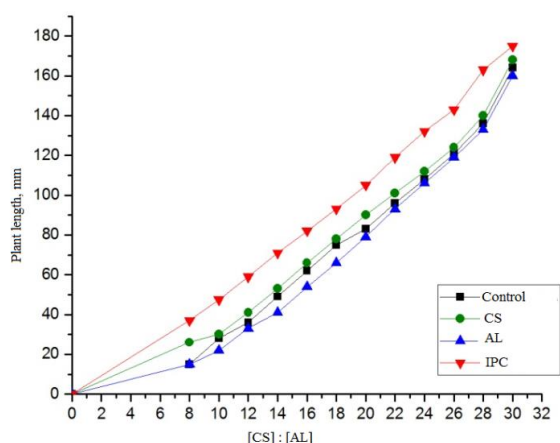


Figure 7. Dynamics of growth of cucumber during the technology of processing of soil biopolymers and IPC based on them

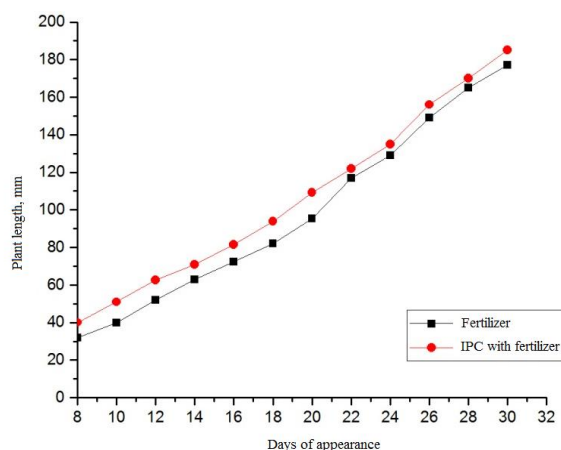


Figure 8. Dynamics of cucumber growth in soil treatment technology IPC with fertilizer

According to the results of biometric observation at the end of the growing season, the height of the main stem of the cucumber in the experimental variants was 47.2 cm (with CS), 40.5 cm (with AL), 49.7 cm (with IPC), 61.2 cm (with fertilizer), 71 cm (with IPC and fertilizer), and 39.5 cm in the control variant (Fig. 7, 8). The greatest development of the root system was registered for the experimental variants with IPC (biomass was 0.41 g, length of the main root 7.3 cm) and with IPC + fertilizer (0.40–0.45 g and 8.8–10.0 cm). We also recorded the stimulating effect of IPC and fertilizer on the development of parameters such as leaf length (9.7–10.5 cm), while there was no difference between the options in the number of leaves (7–8 pcs) and flowers (1–2 pcs) for one plant.

Therefore, it was found that IPC has a positive effect on the growth and development of cucumber.

### Conclusion

IPC on the basis of biopolymers of chitosan and sodium alginate was prepared. The composition of the IPC determined by the gravimetric, turbidimetric and dynamic laser light scattering methods and is [CS]:[AL] = 2:3. Soil treatment by the individual biopolymers and the resulting IPC is not appreciably affected in its main agrochemical properties, however, processing IPC has greatly improved the resistance of soil to water erosion. Vegetation experiments in the laboratory revealed that soil treatment IPC has a positive effect on the growth and development of cucumber. Thus, it can be concluded that the IPC of the composition [CS]:[AL] = 2:3 can be used as an effective, environmentally compatible soil structure-forming agent.

*The study was carried out with the financial support of the Ministry of education and science of the Republic of Kazakhstan, grant AP 05134681.*

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### Биополимерлердің интерполимерлі комплексі топырақ құрылымтүзушісі ретінде

Хитозан (ХТЗ) және натрий альгинаты (АлНа) биополимерлері әрекеттесуі арқылы интерполимерлі комплекс (ИПК) синтезделді. Хитозан — натрий альгинаты интерполимерлі комплексі полимерлердің эквиволярлық ерітінділерін әр түрлі пропорцияда араластыру әдісімен алынды. ИПК синтездеу үшін хитозанның лимон қышқылындағы ерітіндісі мен натрий альгинатының сулы ерітіндісі пайдаланылған. Түзілген интерполимерлі комплекс құрамы гравиметрия, турбидиметрия және динамикалық лазерлік жарық шашырау әдістерімен анықталған және  $[ХТЗ]:[АлНа] = 2:3$  тең. ИПК катионды полиэлектролит хитозан мен анионды полиэлектролит натрий альгинаты арасындағы ион-иондық әрекеттесу нәтижесінде түзіледі. Топырақ үлгілерінің агрохимиялық көрсеткіштерін жеке биополимерлерді ИПК енгізбестен және енгізгеннен кейін анықтаған. Топырақты жеке биополимерлермен және алынған ИПК-мен өңдеу оның негізгі агрохимиялық көрсеткіштеріне айтарлықтай әсер еткен жоқ. Жеке биополимерлермен, яғни комплекс компоненттерімен және синтезделген ИПК-мен жүргізілген зертханалық тәжірибе нәтижесінде жеке биополимерлермен, яғни комплекс компоненттерімен салыстырғанда алынған интерполимерлі комплекс топырақты су эрозиясынан қорғаудың тиімді құралы болып табылатыны көрсетілген. Зертханалық жағдайда жүргізілген вегетациялық тәжірибе нәтижесінде топырақты ИПК-мен өңдеу көкөністің — қиярдың өсуі мен дамуына оң әсер ететіні анықталды. Демек, биополимерлерден синтезделген ИПК тиімді экологиялық қауіпсіз топырақ құрылымтүзушісі ретінде пайдаланылуы мүмкін деп қорытындылауға болады.

*Кілт сөздер:* интерполимерлі комплекс, биополимер, хитозан, натрий альгинаты, құрам, топырақ, құрылымтүзуші.

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### Интерполимерный комплекс биополимеров как структурообразователь почвы

Синтезирован интерполимерный комплекс (ИПК) на основе биополимеров хитозана (ХТЗ) и альгината натрия (АлНа). Интерполимерный комплекс хитозан–альгинат натрия был получен методом смешения эквиволярных растворов полимеров в заданной пропорции. Для синтеза ИПК использованы раствор хитозана в лимонной кислоте и водный раствор альгината натрия. Состав ИПК определен методами гравиметрии, турбидиметрии и динамического лазерного светорассеяния и равен  $[ХТЗ]:[АлНа] = 2:3$ . Интерполимерный комплекс образован в результате ион-ионного взаимодействия между катионным полиэлектролитом — хитозаном и анионным полиэлектролитом — альгинатом натрия. Определены агрохимические показатели образцов почвы без и после внесения отдельных биополимеров и ИПК. Обработка почвы отдельными биополимерами и полученным интерполимерным комплексом заметно не повлияла на ее основные агрохимические показатели. В результате лабораторных опытов с отдельными биополимерами и синтезированным ИПК показано, что полученный интерполимерный комплекс является более эффективным средством защиты почвы от водной эрозии по сравнению с отдельными биополимерами — компонентами комплекса. Полученные результаты вегетационных опытов в лабораторных условиях выявили, что обработка почвы ИПК положительно влияет на рост и развитие овощной культуры — огурца. Следовательно, можно заключить, что синтезированный из биополимеров ИПК может быть использован как эффективный экологически безопасный структурообразователь почвы.

*Ключевые слова:* интерполимерный комплекс, биополимер, хитозан, альгинат натрия, состав, почва, структурообразователь.

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## Reaction between guaiacol and glyoxalic acid under microwave irradiation

In this paper, we considered the opportunity to use microwave irradiation as an alternative to the convection heating method during the guaiacol condensation reaction with glyoxalic acid in an aqueous solution in the presence of sodium hydroxide in order to preparatively obtain the 4-hydroxy-3-methoxymindic acid, an intermediate of the vanillin synthesis. The experiments under the influence of the microwave irradiation were carried out using the «Speedwave four» microwave system that allowed varying the irradiation power in the range from 0 to 1450 W. The condensation reaction was carried out at the irradiation power of 290, 580, 870, and 1160 W. The effects of time, temperature and microwave radiation power on the desired product yield of the condensation reaction was established by varying the reaction conditions during the experiments. Using this method, the experimental conditions of highest product yield were determined when temperature of the reaction mixture, the irradiation power and synthesis time were 70 °C, 870 W, and 30 minutes respectively. A comparison of the results of the synthesis of 4-hydroxy-3-methoxymindic acid under the microwave activation and for the conventional procedure was performed. The use of the microwave irradiation was found to significantly reduce (up to 20 times) the synthesis time, however, the maximum product yield achieved by this method turned out to be lower compared to the one obtained by conventional procedure. The 4-hydroxy-3-methoxymindic acid synthesized samples structure was confirmed using IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Keywords:** vanillylmandelic acid, guaiacol, glyoxalic acid, condensation, microwave irradiation.

### 1 Introduction

4-Hydroxy-3-methoxymindic acid (2) (vanillylmandelic acid, VMA) is an important intermediate in the vanillin synthesis (3) using the guaiacol method [1–4] (Fig. 1). This method is more ecofriendly than the one used to produce vanillin from the lignin-containing raw materials and allows obtaining the desired product (2) of high quality with lower cost as compared with the natural vanillin and the one obtained from the natural raw materials.

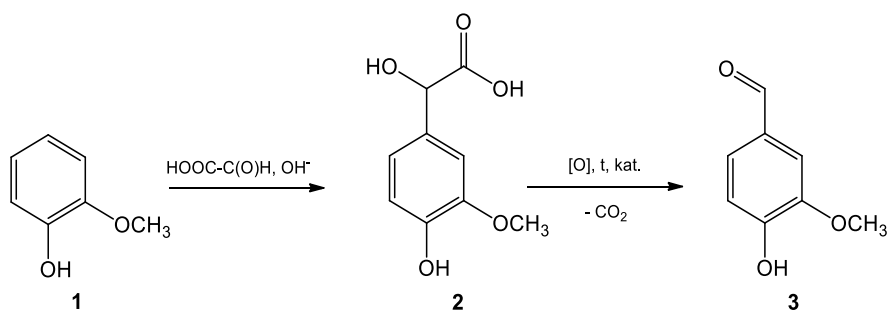


Figure 1. Vanillin synthesis using guaiacol method

It is noteworthy that the key disadvantage of the abovementioned method of vanillin preparation is the significant duration of the guaiacolate condensation with glyoxylate that can exceed a day [2].

The condensation time can be reduced by increasing the temperature, however, the prolonged heating of the reaction mixture in the case of guaiacol and glyoxalic acid decreases the yield of the desired product due to the acceleration of the side reactions [5] as well as due to the instability of glyoxalic acid upon heating [2]. The use of the special catalysts [6–8] can also reduce the duration of the condensation stage, but this approach significantly increases the costs of vanillin production (3).

One of the methods to increase the rate of many organic reactions is to use the microwave radiation. The advantages of this approach include the uniformity and the absence of delayed heating of the reaction mixture, the opportunity for rapid temperature control and the instant energy supply cut as well as a number of other

parameters [9]. Although the mechanism of the effect of microwave irradiation on the behavior of the chemical processes is still poorly understood, many studies have been published confirming the advantages of using of microwave activation to prepare various organic compounds [10–13].

At the moment, the use of the microwave activation in the vanillin (3) synthesis is described only for its production by curcumin oxidation [14], and the use of such an approach to the guaiacol (1) condensation with glyoxalic acid has not been found in the available literature.

## 2 Experimental

### 2.1 Materials and methods

Commercially available guaiacol (99 %, Aldrich Organics) and an aqueous solution of glyoxalic acid (50 %, Aldrich) were used as reagents. A solution of sodium hydroxide (30 %) was obtained by dissolving a portion of sodium hydroxide (chemically pure, Vecton).

The experiments using microwave irradiation were carried out using the «Speedwave four» microwave sample preparation system (Berghof Products + Instruments GmbH) with a maximum power of 1450 W and a magnetron frequency of 2450 MHz that allowed varying the temperature in the range of 50–230°C.

To control the progress of the reactions, a reverse phase HPLC method was used on a Shimadzu LC-20 Prominence liquid chromatograph equipped with a PDA-20A UV detector.

### 2.2 Synthesis using microwave irradiation

A portion of 0.94 g (0.0075 mol) of guaiacol was mixed with 11.5 ml of water and 1.1 g of a 30 % sodium hydroxide solution with vigorous stirring. 0.7 g (0.0047 mol) of a 50 % glyoxalic acid solution and 5.0 ml of water were mixed separately. The resulting solutions were combined, placed in a fluoroplastic autoclave of the microwave system and kept for 10, 20 and 30 minutes at different temperatures and irradiation powers.

### 2.3 Synthesis by the conventional procedure

9.3 g of guaiacol and 115.0 ml of water were placed in a round bottom flask. 10.6 g of a 30 % sodium hydroxide solution were added to the reaction mixture with a vigorous stirring. Then a mixture of 7.4 g of a 50 % solution of glyoxalic acid and 50.0 g of water was added to the resulting sodium guaiacolate solution. The reaction mixture was kept at a temperature of 30 °C from 5 to 25 hours.

### 2.4 Synthesis by the conventional procedure

To isolate the desired product (2), the reaction mixture was acidified up to a pH level of 4–5 by the addition of hydrochloric acid and the excess of guaiacol was separated by extraction with benzene. The aqueous phase was acidified up to pH = 1 and the desired product was extracted with the ethyl acetate. The extract was evaporated to dryness and the bottom residue was recrystallized from a minimum amount of ethyl acetate. The product (2) was obtained with the MP = 131–133 °C (132–133 °C in Ref. [3]). The IR spectrum:  $\nu$ ,  $\text{cm}^{-1}$ : 3336 (OH), 2971 ( $\text{CH}_3$ ), 2932 ( $\text{CH}_3$ ), 1744 ( $\text{C}=\text{O}$ ), 1713 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum:  $\delta$ , ppm ( $\text{DMSO}-d_6$ ): s.w. 12.47, s. 8.96, d. 6.96, d. 6.78, d. 6.72, s.w. 5.68, s. 4.89, s. 3.75.

## 3 Results and discussion

In the present work we studied the opportunity to synthesize vanillylmandelic acid (2) by the guaiacol (1) condensation with glyoxalic acid under the effect of the microwave irradiation as compared with the traditional synthesis method. With that, we conducted a series of experiments to determine the optimal synthesis conditions. The reaction mixture was subjected to the microwave irradiation with a power of 290, 580, 870, and 1160 W.

While conducting the experiments with varying the irradiation power without the additional heating (Table 1), no increase in the reaction rate is observed compared to the conventional synthesis procedure. The maximum yield achieved in 1 hour of the experiment for the product (2) (34 %) is comparable with the one obtained without the irradiation for the same synthesis time.

An increase in the heating of the reaction mixture contributed to an increase in the VMA yield. The best results were obtained when carrying out the reaction at a temperature of 70 °C (Table 1). The maximum VMA yield was achieved by irradiating the reaction mixture at a power of 870 W for 30 minutes. Further exposure of the reaction mixture is not feasible, since the yield of the desired product is gradually reduced that is probably due to the progressing side processes.



Table 1

VMA yield (2) dependence on the experimental conditions

Seq. No.	Irradiation rate, W	Temperature, °C	Time, min			
			10	20	30	60
			VMA yield, %			
1	290	No heating	8	10	13	–
2	580	No heating	9	11	15	–
3	870	No heating	12	17	30	33
4	1160	No heating	11	14	19	34
5	290	70	62	63	66	–
6	580	70	65	66	68	–
7	870	70	65	68	71	67
8	1160	70	66	67	66	65

Under the conditions of the conventional synthesis procedure, the VMA (2) yield of about 70 % can be achieved only after 10 hours (Fig. 2), that is, the synthesis time under the microwave activation is reduced by 20 times. However, the maximum yield of the desired product (2) is higher as compared with the irradiation-less process. This is due to the acceleration of the side process of the formation of 4-hydroxy-5-methoxy-1,3-benzene-diglyoxalic acid during the reaction at elevated temperatures. The results of the HPLC analysis of the reaction mixtures show that during the synthesis under the microwave irradiation, the content of this impurity in the reaction mixture is 2.5 times higher than in the synthesis without irradiation.

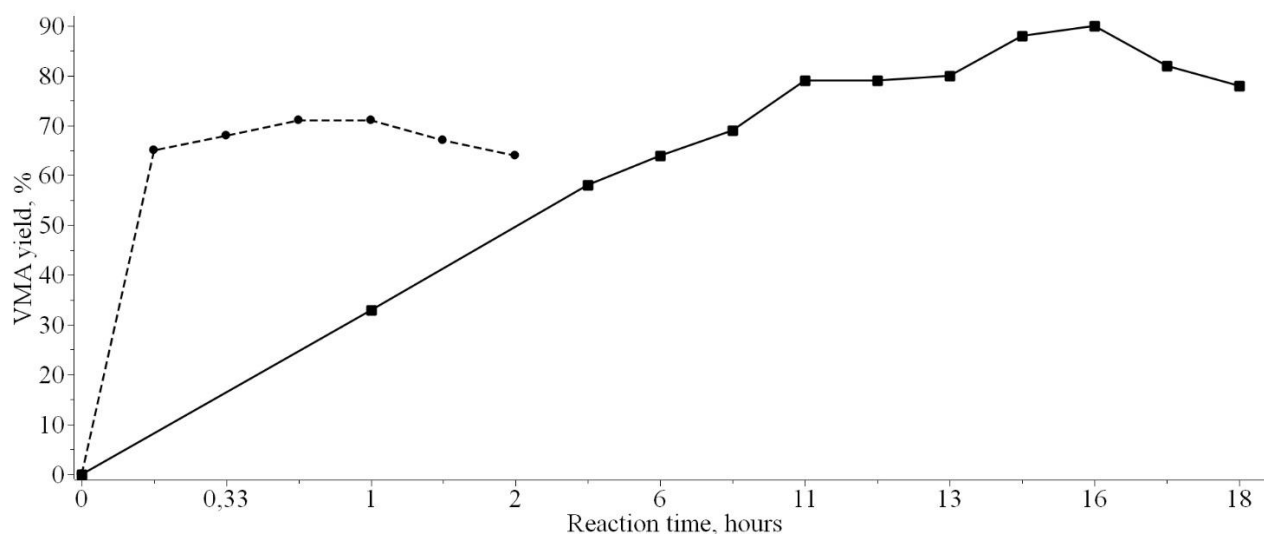


Figure 2. Dependence of VMA yield on the reaction time

### Conclusions

Thus, for the first time, the synthesis of vanillylmandelic acid using the microwave irradiation was carried out and allowed us to reduce the synthesis duration by 20 times in comparison with the traditional methods. The best results were achieved when carrying out the reaction at 70 °C and the irradiation power of 870 W.

### Acknowledgement

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the Federal Target Program «Investigation and Developments on Priority Directions of Development of the Scientific Technological Complex of Russia for 2014–2020», Agreement No. 14.575.21.0170, unique identifier of project RFMEFI57517X0170.

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### Микротолкынды сәулелену кезіндегі гваякол мен глиоксаль қышқылының реакциясы

Мақалада ванилин синтезінің жартылай өнімі болып табылатын 4-гидрокси-3-метоксиминдаль қышқылын препаративтік әдіспен алу мақсатында конвекциялық қыздыру әдісіне балама ретінде микротолкынды сәулелену әдісін пайдалану арқылы натрий гидроксиді қатысында сулы ерітіндідегі гваякол мен глиоксаль қышқылының конденсация реакциясы қарастырылған. Тәжірибелер сәулелену қуатын 0-ден 1450 Вт-қа дейінгі интервалда тәжірибе жүргізуге болатын «Speedwavefour» микротолкынды жүйесі көмегімен жүргізілген. Конденсация реакциясы 290, 580, 870 және 1160 Вт сәулелену қуаты жағдайында жүрді. Реакция жағдайларын өзгерте отырып, тәжірибелерді жүргізу барысында конденсация реакциясының негізгі өнімінің түзілуіне уақыт, температура және микротолкынды қуаттың әсері анықталған. Өнімнің ең жоғары шығымын алуға мүмкіндік беретін эксперимент шарттары анықталған: реакция қоспасының температурасы 70 °C және сәулелендіру қуаты 870 Вт. Синтездеу уақыты 30 мин құрады. Микротолкынды активтендіру және дәстүрлі әдісті қолданып реакцияны жүргізу жағдайындағы 4-гидрокси-3-метоксиметин қышқылы синтезінің нәтижелеріне салыстыру жасалған. Микротолкынды сәулеленуді қолдану синтездеу уақытын едәуір қысқартады (20 есе), алайда бұл әдіс нәтижесінде алынған өнімнің шығымы дәстүрлі әдіске қарағанда төмен болып шықты. Синтезделіп алынған 4-гидрокси-3-метоксиминдаль қышқылының туындыларының құрылысы ИҚ-, <sup>1</sup>H және <sup>13</sup>C ЯМР-спектроскопия әдістерінің нәтижелерін талдау арқылы дәлелденген.

*Кілт сөздер:* ванилминдаль қышқылы, гваякол, глиоксаль қышқылы, конденсация, микротолкынды сәулелену.

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### Реакция гваякола и глиоксалевой кислоты в условиях микроволнового облучения

В статье рассмотрена возможность применения микроволнового облучения в качестве альтернативы конвекционному способу нагрева при проведении реакции конденсации гваякола и глиоксалевой кислоты в водном растворе в присутствии гидроксида натрия с целью препаративного получения 4-гидрокси-3-метоксиминдальной кислоты, являющейся полупродуктом синтеза ванилина. Эксперименты под воздействием микроволнового облучения были проведены с использованием микроволновой системы «Speedwavefour», позволяющей варьировать мощность облучения в интервале от 0 до 1450 Вт. Реакцию конденсации проводили при мощности облучения 290, 580, 870 и 1160 Вт. В ходе проведенных экспериментов путем варьирования условий реакций установлено влияние времени, температуры и мощности микроволнового облучения на выход целевого продукта реакции конденсации. Определены условия проведения эксперимента, позволяющие получить наибольший выход продукта данным методом, а именно: температура реакционной смеси 70 °С и мощность облучения 870 Вт. При этом время синтеза составило 30 мин. Проведено сравнение результатов синтеза 4-гидрокси-3-метоксиминдальной кислоты в условиях микроволновой активации и традиционным методом. Установлено, что использование микроволнового облучения позволяет значительно (до 20 раз) сократить время синтеза, однако максимальный достигнутый данным методом выход продукта оказался ниже по сравнению с традиционным методом. Строение синтезированных образцов 4-гидрокси-3-метоксиминдальной кислоты подтверждено результатами анализа методами ИК-,  $^1\text{H}$  и  $^{13}\text{C}$  ЯМР-спектроскопии.

*Ключевые слова:* ванилилминдальная кислота, гваякол, глиоксалева кислота, конденсация, микроволновое облучение.

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## Antiradical activity and bioprediction of *o*- and *p*-hydroxybenzoic acid hydrazide derivatives

This article provides results of evaluation of synthesized biologically active substances 1–4 antiradical activity according to their ability to interact with the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH<sup>•</sup>). It was found that all synthesized compounds 1–4 have antiradical activity. Pronounced antiradical activity was shown by N-ethyl-2-(2-hydroxybenzoyl)hydrazine-carbothioamide (1) (IC<sub>50</sub>(DPPH) = 12.5 μM) and N-ethyl-2-(4-hydroxybenzoyl)hydrazine-carbothioamide (2) (IC<sub>50</sub>(DPPH) = 16.7 μM) samples under the conditions of this test system. Activity of N-ethyl-2-(2-hydroxybenzoyl)hydrazinecarbothioamide (1) and N-ethyl-2-(4-hydroxybenzoyl)hydrazinecarbothioamide (2) samples are comparable to activity of known antioxidants. Studied substances 1 and 2 are promising for further advanced research of their antioxidant properties and other types of biological activity. Results of PASS computer system applicability estimation for prediction of biological activity using structural formula as a part of pre-experimental screening are provided. Expected activity of chemical compounds combines physiological activity of initial hydrazides of *o*- and *p*-hydroxybenzoic acids as well as components of structural molecule. According to bioprediction data analysis, all compounds can act as inhibitors with a high degree of probability.

**Keywords:** antioxidant, antiradical activity, free radical, thiosemicarbazide, 1,2,4-triazole, DPPH, bioprediction, PASS.

### Introduction

Antioxidants have found widespread practical application in chemistry, chemical engineering, food industry and pharmacy. Multiple contributions are provided on research of various natural compounds [1–4], their synthetic analogues [5–12] and botanicals extracts [13–15] antioxidative activity. Antioxidative therapy is a way of treating various diseases which develop significantly through free-radical processes [16, 17]. Antioxidants are implemented in therapy of various pathologies including inflammatory processes [18–20] and cardiovascular diseases [21, 22]. They are used as adaptogens in stress conditions [23] and for treatment of neurodegenerative disorders, such as Alzheimer's and Parkinson disease as well as cognitive dysfunction.

In recent years there has been search and streamlined synthesis of new multifunctional phenol type antioxidants superior in their efficiency to existing analogues considering peculiarities of structure and antioxidative activity interrelation. A promising area of highly effective antioxidants creation is synthesis of «hybrid molecules» combining several functional groups reacting independently or synergistically to substrates oxidation process in lipidic or water phase.

The purpose of this paper is to research the anti-radical activity of synthetic compounds 1–4 in reference to 2,2-diphenyl-1-picrylhydrazyl (DPPH), and expand the synthetic antioxidants based on hydrazides of *o*- and *p*-hydroxybenzoic acids.

### Experimental

For studied samples 1–4 antiradical activity estimation in test with DPPH radical methanol solution of DPPH (100 μM) was used. For selection of substances with pronounced antiradical activity 2 ml of 100 μM DPPH methanol solution was mixed with 20 ml of researched substance dissolved in methanol in 5 mM concentration. This way, the final concentration of test sample in reaction mixture was 50 μM. Optical density reduction at 515 nm was measured 10 minutes after adding test sample to DPPH solution. Interaction with the DPPH radical was carried out at final concentrations of 50, 25, 20, 15, 10, 5 and 2.5 μM for studied substances

that can reduce the optical density more than 50 %. Then, the test sample concentration that can reduce the optical density by 50 % ( $IC_{50}(DPPH)$ ) was determined.

Computer prediction of biological activity was carried out using PASS software which predicts 4000 types of biological activity based on training array analysis containing structural formulas and biological activity data of more than 300,000 chemical compounds. Structural formulas of studied compounds are entered into system as files of Mol or SDF format. Prediction results are calculated as compound probability of displaying certain biological activity (Pa) and probability of not displaying such activity (Pi). PASS system is thoroughly described in works [24–26] <http://www.way2drug.com/passonline> website provides resource allowing to predict more than 4000 types of biological activity.

### Results and Discussion

Previously we have synthesized hydrazide derivatives of *o*- and *n*-hydrobenzoic acids (1–4) [27–29] which contain thioamide group, ethyl unit and 1,2,4-triazole groups. 1–4 compounds antiradical properties estimation for the purpose of revealing active antioxidants was carried out for the first time.

Several series of experiments were carried out to define antiradical properties according to technique [30]. DPPH radical and test sample solution optical density are shown in Table 1.

Table 1

**Optical density of 100  $\mu$ M DPPH radical with 50  $\mu$ M examined substance solution after 10 minute incubation period**

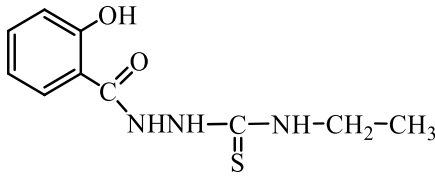
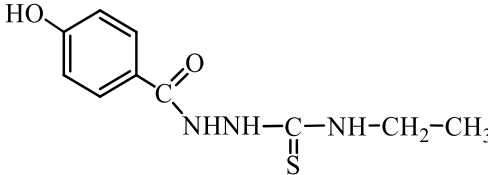
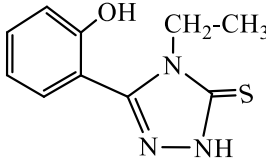
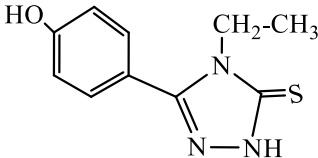
No.	Structural formula and substance name	Optical density, rel. unit
1	 N-ethyl-2-(2-hydroxybenzoyl)hydrazine-carbothioamide (1)	0.112
2	 N-ethyl-2-(4-hydroxybenzoyl)hydrazine-carbothioamide (2)	0.127
3	 3-(2-hydroxyphenyl)-4-ethyl-1H-1,2,4-triazol-5(4H)-thione (3)	0.587
4	 3-(4-hydroxyphenyl)-4-ethyl-1H-1,2,4-triazol-5(4H)-thione (4)	0.418
5	Control (DPPH solution without test sample)	0.852

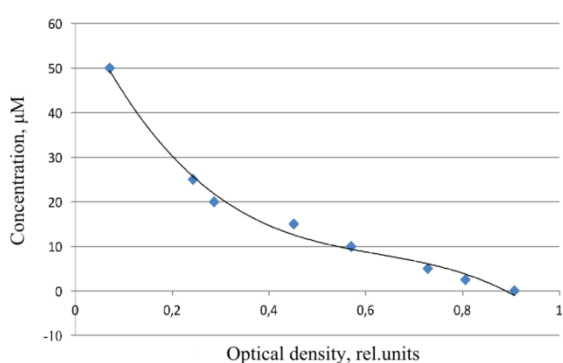
Table 1 shows that all 1–4 compounds are capable of antiradical activity, compounds 3 and 4 are able to reduce optical density below 50 %, so from all compounds 1–4 only compounds 1 and 2 are promising for further research.

Second series of experiment was carried out to study ability of compounds 1 and 2 to interact with DPPH radical at various concentrations (from 2.5 to 50  $\mu$ M) (Table 2, Fig. 1).

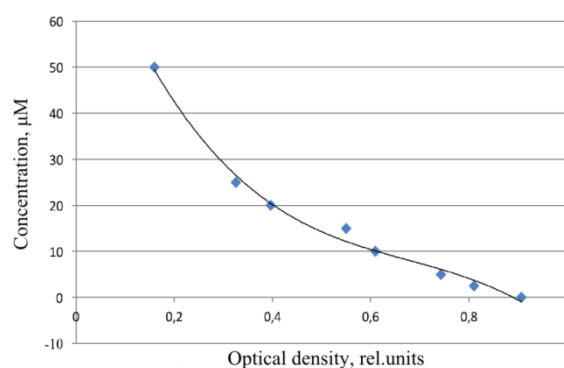
Table 2

**Optical density of DPPH radical 100  $\mu\text{M}$  with test sample 1 and 2 solution at final concentrations 50, 25, 20, 15, 10, 5 and 2.5  $\mu\text{M}$  after 10 minute incubation**

No.	Final concentration of substances 1 and 2 in the reaction mixture, $\mu\text{M}$	Optical density, rel. unit	
		reaction mixture of compound 1	reaction mixture of compound 2
1	50	0.071	0.159
2	25	0.243	0.325
3	20	0.287	0.396
4	15	0.451	0.55
5	10	0.57	0.609
6	5	0.728	0.743
7	2.5	0.806	0.810
	Control (DPPH solution without test sample)	0.907	0.907



a)



b)

Figure 1. Dependence of optical density of the reaction mixture compound 1 (a) and compound 2 (b) on the concentration

Using created calibration curves (Fig. 1) concentrations of N-ethyl-2-(2-hydroxybenzoyl)-hydrazinecarbothioamide (1) and N-ethyl-2-(4-hydroxybenzoyl)hydrazinecarbothioamide (2) were determined. Estimation of 1–4 compounds antiradical activity towards DPPH radical showed that in conditions of given test system samples 1 and 2 displayed the most pronounced antiradical activity. The concentration of samples 1 and 2 to be able to reduce optical density of DPPH radical 100  $\mu\text{M}$  solution by 50 % was found.  $\text{IC}_{50}(\text{DPPH})$  for compound 1 is 12.5  $\mu\text{M}$ ,  $\text{IC}_{50}(\text{DPPH})$  for compound 2 is 16.7  $\mu\text{M}$ .

Referring to the data, the  $\text{IC}_{50}(\text{DPPH})$  for the standard ascorbic acid sample is 19.9  $\mu\text{M}$ . 1 and 2 samples activity is competitive with ascorbic acid reference sample.

According to reference data [31, 32]  $\text{IC}_{50}(\text{DPPH})$  ( $\mu\text{M}$ ) for known antioxidants is the following: glutathione — 49, hydroquinone — 27, trolox — 28,  $\alpha$ -tocopherol — 28, quercetin — 8. This way, antiradical activity of samples 1 and 2 is comparable to that of known antioxidants. Studied substances 1 and 2 are promising for further research of their antioxidative properties. Experimentally received results allow for the conclusion about practicability of further research in order to search for prospective antioxidant compounds among derivatives of *o*- and *p*-hydroxybenzoic acids are reasonable.

According to Chemical Abstract Service data, nowadays there are more than 65 million known chemical compound structures, while amount of those virtually generated *in silico* but not synthesized yet exceeded 165 billion [33, 34]. Despite widespread use of high performance screening methods, it is not possible to experimentally test millions of compounds to define their biological activity. This is one of fundamental issues of contemporary chemistry — research of «structure-activity» correlations of physiologically active compounds [35, 36]. Due to this, a very important component of modern approaches to research and development of new bioactive substances are information technologies which allow reducing amount of substances researched in biological experiments and streamline patterns of their research. One of the ways of using information technologies for searching bioactive substances is computer-assisted bioactivity prediction through chemical structure.

In order to define compounds 1–4 expected biological activity we have carried out bioprediction using one of the most effective contemporary software — PASS (Prediction of Activity Spectra for Substances) (Table 3), which is used to define «structure-activity» correlations. Result of expected activity for compounds 1–4 is shown in Table 3.

Table 3

**Results of a computer bioprediction of the expected type of biological activity of compounds 1–4**

Comp. No.	Probability	Ranging	Activity type names
1	0.846	0.003	Gonadotropin antagonist
	0.815	0.004	HMGCS2 expression enhancer
	0.814	0.011	Taurine dehydrogenase inhibitor
	0.802	0.002	PfA-M1 aminopeptidase inhibitor
	0.769	0.004	Catechol oxidase inhibitor
	0.760	0.004	Antituberculosic
	0.727	0.005	Antimycobacterial
	0.725	0.005	Ovulation inhibitor
2	0.857	0.005	Taurine dehydrogenase inhibitor
	0.847	0.003	Gonadotropin antagonist
	0.819	0.004	HMGCS2 expression enhancer
	0.792	0.003	PfA-M1 aminopeptidase inhibitor
	0.739	0.003	Trimethylamine dehydrogenase inhibitor
	0.725	0.004	Antituberculosic
	0.744	0.038	Mucomembranous protector
3	0.839	0.007	Arylacetonitrilase inhibitor
	0.827	0.004	Histidine kinase inhibitor
	0.772	0.005	Gamma-guanidinobutyraldehyde dehydrogenase inhibitor
	0.751	0.009	Proteasome ATPase inhibitor
	0.748	0.012	Glutathione thiolesterase inhibitor
	0.725	0.005	Aminobutyraldehyde dehydrogenase inhibitor
	0.718	0.003	Alkaline phosphatase inhibitor
4	0.881	0.005	Arylacetonitrilase inhibitor
	0.824	0.005	Glutathione thiolesterase inhibitor
	0.812	0.004	Gamma-guanidinobutyraldehyde dehydrogenase inhibitor
	0.799	0.005	Proteasome ATPase inhibitor
	0.797	0.008	Muramoyltetrapeptide carboxypeptidase inhibitor
	0.782	0.004	Sulfite reductase inhibitor
	0.755	0.007	Peroxidase inhibitor
	0.751	0.011	NADPH-cytochrome-c2 reductase inhibitor
	0.740	0.004	Aminobutyraldehyde dehydrogenase inhibitor
	0.715	0.013	2-Hydroxyquinoline 8-monooxygenase inhibitor
	0.747	0.049	Aspulvinone dimethylallyltransferase inhibitor
	0.715	0.018	Ribulose-phosphate 3-epimerase inhibitor
	0.712	0.015	UDP-N-acetylglucosamine 4-epimerase inhibitor
	0.701	0.012	Fatty-acyl-CoA synthase inhibitor

Compounds 1–4 bioprediction data analysis suggests that the compounds can display inhibitive, antimicrobial and antitubercular activity with a high degree of probability. PASS system provides comparable antitubercular activity probability for compounds 1 and 2 ( $P_a = 0.760$  and  $P_a = 0.725$ ), compound 2 can display antimicrobial activity ( $P_a = 0.727$ ). Compounds 1–4 can act as various inhibitors with probability ( $P_a > 0.7$ ). Compounds 3 and 4 are highly likely to be enzyme inhibitors.

Data of computer-assisted biological activity prediction from PASS online computer system require further experimental research and validation but provide opportunity for dedicated research of specific biological activity types which have quite high probability of experimental displaying. This way, prediction data can be taken to plan further experimental studies in test systems of *in vitro* and *in vivo*.

### Conclusions

1. All synthesized compounds have anti-radical activity, but compounds 1 and 2 have pronounced anti-radical activity. The activity of samples 1 and 2 is not inferior to the reference sample of ascorbic acid. The  $IC_{50}$ (DPPH) for ascorbic acid is 19.9  $\mu$ M. The  $IC_{50}$ (DPPH) for N-ethyl-2-(2-hydroxybenzoyl)hydrazinecarbothioamide (1) is 12.5  $\mu$ M, and  $IC_{50}$ (DPPH) for N-ethyl-2-(4-hydroxybenzoyl)hydrazinecarbothioamide (2) is 16.7  $\mu$ M. The researched substances of 1 and 2 are perspective for an in-depth study of their antioxidant properties.
2. The prediction data can be taken to plan further experimental studies in test systems of *in vitro* and *in vivo*.

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### ***o*- және *n*-гидроксibenзой қышқылының гидразид туындыларының радикалға қарсы белсенділігі мен биоболжамы**

Мақалада биологиялық белсенді заттардың 2,2-дифенил-1-пикрилгидразил (ДФПГ, DPPH) радикалымен әрекеттесу қабілеті бойынша радикалға қарсы белсенділікті бағалау нәтижелері келтірілген. Осы тест-жүйе жағдайында *N*-этил-2-(2-гидрокси-бензоил)гидразинкарботиоамид (1) және *N*-этил-2-(4-гидроксibenзоил)гидразинкарботиоамид (2) үлгілері радикалға қарсы белсенділікті көрсеткені және олардың біріншісі  $IC_{50}(DPPH) = 12.5 \mu M$ , екіншісі  $IC_{50}(DPPH) = 16.7 \mu M$ -ға тең екендігі айқындалды. Зерттелген 1–4 қосылыстардың ішінде тек 1 мен 2 қосылыстарының оксидантқа қарсы қасиеті мен биоактивтіліктің басқа түрлерін одан әрі терең зерттеуге перспективалы болып табылады. PASS компьютерлік бағдарламаны қолдана отырып, тәжірибелік алдын-ала скрининг кезеңі ретінде құрылымдық формула бойынша биологиялық белсенділікті болжау үшін пайдалану мүмкіндігінің бағалау нәтижелері келтірілген. Химиялық қосылыстардың күтілетін белсенділігі *o*- және *n*-гидроксibenзой қышқылдарының бастапқы гидразидтерінің физиологиялық белсенділігі мен құрылымдық молекуланың құрамдас бөліктерін біріктіреді. Биоболжамның талданған мәліметтерінен, барлық қосылыстардың ингибитор ретінде болу мүмкіндігі үлесі жоғары.

*Кілт сөздер:* антиоксидант, радикалға қарсы белсенділік, бос радикал, тиосемикарбазид, 1,2,4-триазол, ДФПГ, биоболжам, PASS.

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## Антирадикальная активность и биопрогноз производных гидразидов *o*- и *p*-гидроксibenзойных кислот

В статье приведены результаты оценки антирадикальной активности синтезированных биологически активных веществ 1–4 по способности взаимодействовать с радикалом — 2,2-дифенил-1-пикрилгидразилом (ДФПГ, DPPH<sup>\*</sup>). Установлено, что все синтезированные соединения обладают антирадикальной активностью, но в условиях данной тест-системы выраженную антирадикальную активность проявили образцы N-этил-2-(2-гидроксibenзоил)гидразинкарботиоамида (1) IC<sub>50</sub>(DPPH) = 12,5 мМ, для N-этил-2-(4-гидроксibenзоил)гидразинкарботиоамида (2) IC<sub>50</sub>(DPPH) оказалось равной 16,7 мМ. Активность образцов N-этил-2-(2-гидроксibenзоил)гидразинкарботиоамида (1) и N-этил-2-(4-гидроксibenзоил)гидразинкарботиоамида (2) сопоставима с активностью известных антиоксидантов. Поэтому из синтезированных соединений 1–4 соединения 1 и 2 перспективны для дальнейшего углубленного изучения их антиоксидантных свойств и других видов биоактивности. Приведены результаты оценки возможности использования компьютерной системы PASS для прогнозирования биологической активности по структурной формуле как этапа доэкспериментального скрининга. Предполагаемая активность химических соединений комбинирует как физиологическую активность исходных гидразидов *o*- и *p*-гидроксibenзойных кислот, так и составляющих компонентов структурной молекулы. Из анализа данных биопрогнозирования все соединения с высокой степенью вероятности могут выступать в качестве ингибиторов.

*Ключевые слова:* антиоксидант, антирадикальная активность, свободный радикал, тиосемикарбазид, 1,2,4-триазол, ДФПГ, биопрогноз, PASS.

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## **Investigation of isophorone diisocyanate oligoisocyanurate effect on water dispersible polyurethane properties**

Oligoisocyanurates (OIC) are the products of various diisocyanates cyclotrimerization reaction, with their functionality being more than three (potential crosslinking agents). They are applicable in chemical polymer industry as an additive to diisocyanates for polyurethane coatings obtaining with various properties, as well as an isocyanate-containing component on its own for polyurethane synthesis. The OIC-based polymers possess a number of unique properties, e.g. improved thermal stability, fire resistance, UV resistance, also they are not expected to undergo hydrolysis. We studied the effect of isophorone diisocyanate oligoisocyanurate content on hydrodynamic, thermo-mechanical and thermal properties of resulting water dispersible polyurethanes. Samples of water dispersible polyurethanes containing isophorone diisocyanate (IPDI), poly (butylene adipate) (PBA) and 2,2-dimethylolpropionic acid (DMPA) were prepared following acetone method for this purpose, with IPDI OIC amount being 10–30 wt.% per pure IPDI. IPDI OIC was partially blocked with morpholine to exclude crosslinking in WDPU synthesis. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and dynamic light scattering (DLS) were used to characterize the polymers obtained. It was established that oligoisocyanurates improve the characteristics of both water dispersible polyurethanes and their polymer films. Moreover, oligoisocyanurates prevent polyurethane coatings crystallization due to its branched structure, which without a doubt will affect their performance positively.

**Keywords:** polyurethane, water dispersible polyurethane, isophorone diisocyanate, 2,2-bis(hydroxymethyl)propionic acid, poly(butylene adipate), isophorone diisocyanate oligoisocyanurate, dynamic light scattering, dynamic mechanical analysis

### *Introduction*

Polyurethane is one of the most demanded polymers in many industries nowadays. It stands out by a sufficiently large operating temperature range and high strength characteristics. The application of polyurethanes varies from sheets for making surfaces of spindles, rollers, wheels to base for paints, varnishes and binders for important composites.

Water-based polyurethane dispersions, namely one- (1K) and two-component (2K) waterborne polyurethane compositions are reported to be a relatively new eco-friendly type of polyurethane coating compounds. Their application tends to increase in the painting of wood, plastic, metals and other materials [1–3]. Despite the high quality, unique durability and environmental benefits of 2K waterborne polyurethanes, they have significant disadvantages related to the limited viability and relative toxicity of the isocyanate component. 1K waterborne polyurethane based on prepolymers of physical drying or self-crosslinking film forming agents appeared to be much more technologically advanced and safe.

The preparation of a prepolymer is the main stage in the synthesis of 1K water dispersible polyurethanes (WDPU). Bifunctional isocyanates, e.g. isophorone diisocyanate (IPDI) [4], hexamethylene diisocyanate (HDI) [5], toluene diisocyanate (TDI) [6] etc., polyols of various molecular weight [7], as well as hydroxyl- or amino-terminated low molecular weight bifunctional chain extenders [8] are used for that purpose. It is also necessary to reach the water dispersibility for the resulting prepolymer — to that end, a hydrophilic agent is introduced into the composition. Salt of 2,2-bis(hydroxymethyl)propionic acid (DMPA) is one of the most commonly used hydrophilic agents [9, 10].

Oligoisocyanurates (OIC), which are the products of the cyclotrimerization reaction of various diisocyanates [11, 12], are possible to use in the synthesis of WDPU. OIC found application in chemical industry as an additive to diisocyanates in order to obtain polyurethane coatings with refined properties [13], as well as an isocyanate-containing component on its own in the synthesis of polyurethane and hybrid composites [14, 15], and aerogels. It was reported [16, 17] that polyurethanes obtained using OIC had high thermal resistance and fireproof, also resistance to UV and hydrolysis. Furthermore, OIC can be modified with various low molecular

weight compounds containing groups reactive to isocyanate ones. The above-mentioned fact also allows vary WDPUs properties over a wide range.

After having reviewed the available sources, a limited number of works dedicated to WDPUs synthesis using HDI- [13, 18–20] and IPDI-based [3, 15] OIC were found. Moreover, the effect of the HDI OIC content on WDPUs properties was studied thoroughly in the first articles, while only basic opportunity to obtain WDPUs was shown in the latter ones.

In our opinion, the use of IPDI-based OIC in the WDPUs synthesis seems preferable due to IPDI containing aliphatic and cycloaliphatic isocyanate groups of different reactivity. The reactivity of isocyanate groups can vary widely [21, 22] depending on the synthesis conditions. This provides the ability to control the pre-polymer structure and hence the properties of the final product. Furthermore, IPDI-based OIC are completely soluble even at NCO conversion of ~73 % as noted in the [3]. In contrast, the critical gelation conversion of HDI cyclotrimerization reaction products is only 50 %. This experimental fact allows changing WDPUs properties to a larger extent due to the various degree of OIC modification.

There is no doubt that 1K WDPUs properties with IPDI-based OIC depend on the isocyanurate content in the system, the degree of modification and the IPDI NCO groups conversion in OIC.

The objective of this study thereby is to investigate the effect of IPDI-based OIC content in WDPUs on hydrodynamic, thermal and thermo-mechanical properties of resulting products.

### *Experimental*

#### *Materials and instruments*

IPDI (98 %) was purchased from Sigma-Aldrich and then purified by vacuum distillation at  $T = 90\text{ }^{\circ}\text{C}$  (10 mmHg);  $T_b = 158\text{--}159\text{ }^{\circ}\text{C}$ ;  $d_{25}^{25} = 1,049\text{ g/cm}^3$ ;  $n_D^{20} = 1,4840$ .

2,2-bis(hydroxymethyl)propionic acid (98 %) (DMPA) was purchased from Sigma-Aldrich, 1,2-diaminopropane (99 %) (DAP) and N,N,N-triethylamine (99 %) (TEA) were purchased from Acros Organics. These chemicals were used without further purification.

Poly(butylene adipate) (PBA) was purchased from Aldrich; the content of hydroxyl groups is 1.7 wt.% ( $M_n \sim 2000$ ), determined by chemical method.

Acetone, morpholine (99 %) and 1,4-butanediol (99 %) (BD) were purchased from Sigma-Aldrich. These chemicals were purified by standard method [23].

Catalysts: 1,4-diazobicyclo[2.2.2]octane (98 %) (DABCO), propylene oxide (98 %) (PO) and dibutyltin dilaurate (95 %) (DBTDL) were purchased from Aldrich and were used without further purification.

#### *Synthesis of isophorone diisocyanate oligoisocyanurates*

Polycyclotrimerization of IPDI was carried out in the mass in presence of DABCO (0.4 wt.%) + PO (2 wt.%) catalytic system,  $T = 60\text{ }^{\circ}\text{C}$ . The reaction was controlled by FTIR spectroscopy using ALPHA spectrometer (Bruker, Germany) using NaCl cuvettes by a decrease in absorption line intensity ( $\nu = 2270\text{ cm}^{-1}$ ) which corresponds to NCO asymmetric stretching vibrations.

IPDI-based OIC with NCO conversion of 20 % for the WDPUs synthesis was partially blocked with morpholine, 0.31 g of morpholine per 1 g of IPDI OIC. The content of aliphatic and cycloaliphatic NCO groups in the IPDI OIC determined by the method described in [24] was 33 % and 67 %, respectively.

#### *Synthesis of waterborne polyurethanes*

Synthesis of WDPUs-10 containing 10 wt.% of IPDI OIC (per pure IPDI) went as it follows. DMPA (1.20 g) and TEA (0.90 g) were put into a 250 mL flask with ground glass neck. A sample of PBA (14.89 g) and BD (0.58 g) were added to the flask and were dissolved with constant stirring and  $T = 55\text{ }^{\circ}\text{C}$  after the obtained DMPA salt was dissolved in acetone (32 g), pre-drained on molecular sieves. Then, IPDI (10.00 g) and DBTDL (0.06 g) were added to the flask. The reaction of urethane formation was carried out for 3 hours with constant stirring and  $T = 55\text{ }^{\circ}\text{C}$  and was controlled by carrying out the titrimetric analysis [25]. After the reaction being done, partially blocked IPDI OIC (1.31 g) dissolved in acetone (5 g) was added into the flask. The reaction was carried out for 30 minutes.

After the first stage, the reaction mass was allowed to cool to the room temperature. Then, a chain extension was performed, with PDA sample (1.78 g) dissolved in 93 g of distilled water added to the flask with intense stirring ( $[\text{NH}_2]/[\text{NCO}] = 1$ ). The excess acetone was removed in vacuum. The solid content in the final product was 25 %.

WDPU-20, WDPU-30 and OIC-free WDPU-0 were prepared by the described technique. The precise formulation of WDPUs obtained is reflected in Table 1. DMPA content in every sample was 4 wt.%, first stage of synthesis was characterized with the reactive groups ratio  $[NCO]/[OH] = 2.0$ .

Table 1

Composition of water dispersible polyurethanes

Sample	DMPA, g	TEA, g	PBA, g	BD, g	IPDI, g	IPDI OIC, g	Blocking agent, g	PDA, g	PBA, wt. %
WDPU-0	1.16	0.87	14.89	0.58	10.00	0	0	1.80	50.8
WDPU-10	1.20	0.90	14.89	0.58	10.00	1.0	0.31	1.78	48.6
WDPU-20	1.25	0.94	14.89	0.58	10.00	2.0	0.62	1.75	46.5
WDPU-30	1.30	0.98	14.89	0.58	10.00	3.0	0.93	1.72	44.6

#### Researching methods

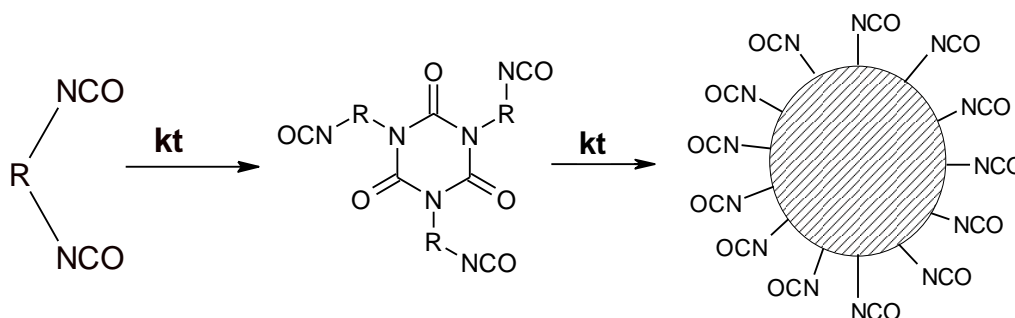
The viscoelastic properties of WDPU samples were investigated by dynamic mechanical analysis (DMA) using a DMA 242 C device (Netzsch-Gerätebau GmbH, Germany): uniaxial tension on film samples, working length of 10 mm, width of 3 mm, thickness of ~0.2–0.3 mm, continuous scanning,  $T = -170 \div +170$  °C, a speed of 2°/min, helium atmosphere. A sinusoidal oscillating force was applied to the samples, allowing one to develop strain amplitude of up to 30  $\mu$ m at fixed frequency of 1 Hz. The temperatures of relaxation transitions were determined by the inflection points on the curves of the safe modulus ( $E'$ ).

Thermal analysis of WDPU samples was carried out using a METTLER TOLEDO DSC822e differential scanning calorimeter with a heating rate of 20°/min.

The particle size distribution in WDPU dispersions was determined by dynamic light scattering at 25 and 60 °C using a Photocor Compact.

#### Results and Discussion

As shown in [3], polycyclotrimerization can be presented as follows:



Trifunctional cycles are formed at the first stage during cyclotrimerization of diisocyanates. They form  $n$ -mers and then a crosslinked polymer at subsequent reaction stages. As previously mentioned, the critical gelation conversion (CGC) in IPDI polycycloaddition is able to reach 73 %. However, using IPDI OIC in WDPU synthesis with NCO conversion not having yet reached CGC will result in obtaining crosslinked polymers highly likely. This deals with the obvious fact that different compounds that contain more than three functional groups, act as possible crosslinking agents. The part of polyfunctional compounds will obviously increase with the conversion of isocyanate groups. It is necessary to block partially the NCO groups of OIC to eliminate possible crosslinked structures formation during the WDPU synthesis. We determined [3] the critical gelation conversion in reaction between IPDI OIC and bifunctional compounds at different NCO group conversion values to define the minimum of NCO groups ( $\omega_{NCO}^{blocked}$ ) that are to be blocked. So,  $\omega_{NCO}^{blocked}$  vs. NCO group conversion of IPDI OIC graph was obtained based on the data mentioned above (Fig. 1).

The minimum required value of  $\omega_{NCO}^{blocked}$  increases with increasing of isocyanate groups conversion of IPDI OIC as expected.

However, polymer crosslinking and, accordingly, coating hardening after application means an open road to damp- and heat-proof coatings. Attention therefore should be paid to hydroxyl- and amine-terminated components with other functional groups as IPDI OIC blocking agents, e.g. double bonds (allyl alcohol, allylamine etc.). Self-crosslinking 1K WDPU can be obtained using that kind of IPDI OIC blocking agent. The degree of

crosslinking for WDPU-based coatings will obviously be determined by functional groups content in the composition. Thus, there are two ways to control crosslinking. The first one is selecting highly converted IPDI OIC, and the second way is varying the IPDI OIC content in WDPU synthesis. We have investigated the second way in the context of this work.

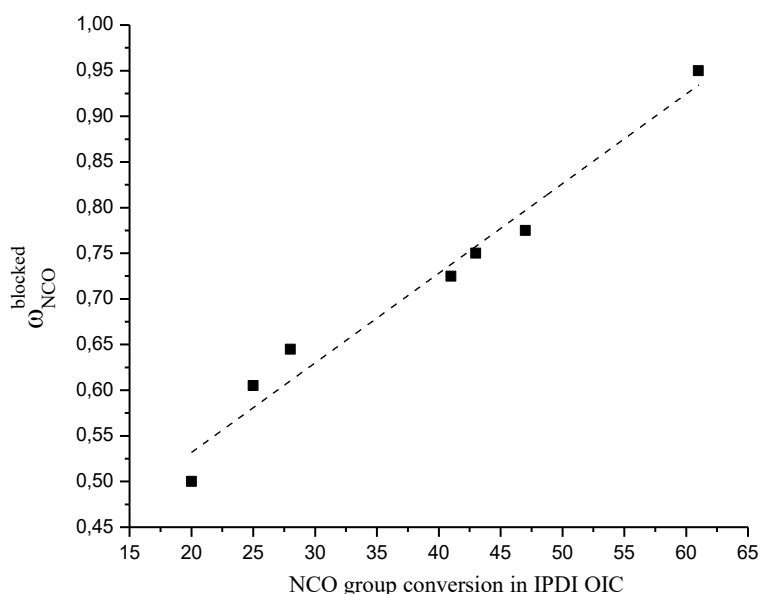


Figure 1.  $\omega_{\text{NCO}}^{\text{blocked}}$  vs. NCO group conversion in IPDI OIC graph

To determine how IPDI OIC content influences waterborne polyurethanes, we prepared 3 samples containing IPDI OIC by weight (per free IPDI): 10 % (WDPU-10), 20 % (WDPU-20) and 30 % (WDPU-30) (Table 1). OIC-free WDPU-0 obtained under similar conditions was used as a reference sample.

The size of dispersed particles and their distribution in dispersion medium is one of the main characteristics of any colloidal solution. Dynamic light scattering of all obtained dispersions was carried out to establish the IPDI OIC content impact in WDPU on their hydrodynamic characteristics. Table 2 and Figure 2 show results of the analysis.

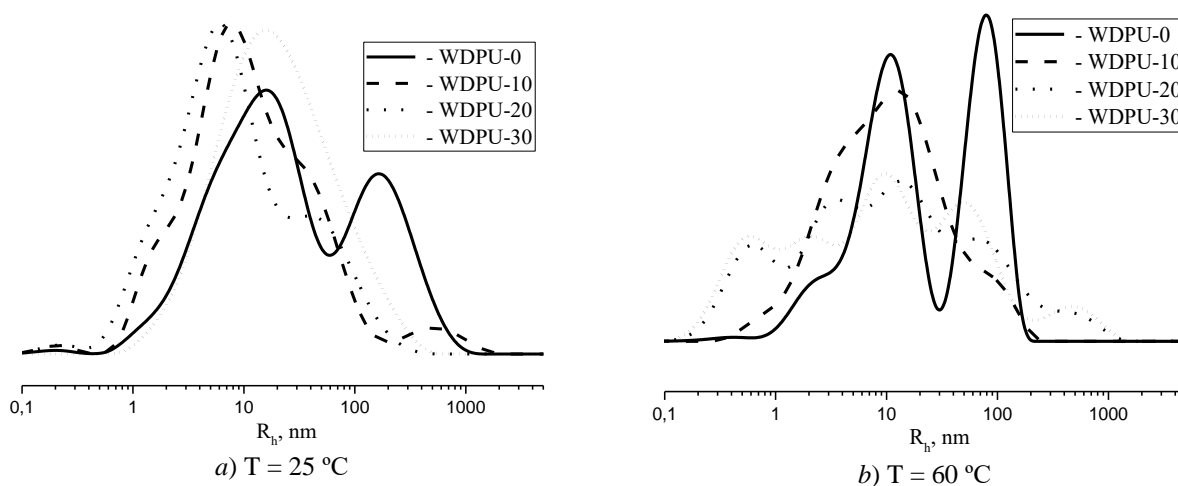


Figure 2. Particles size distribution

The trend that is observed for WDPU-0 and WDPU-10 samples (Table 2) is worth mentioning, where a decrease in average hydrodynamic radius ( $R_h^N$ ) and the diminishing of particle size distribution (Fig. 2) with the increase in temperature can be seen. This observed pattern is apparently the result of aggregates destruction. It should be noted that distribution narrowing occurs due to the destruction of the aggregates of dispersion

particles larger than 100 nm. In contrast, the distribution broadens with increasing temperature for WDPU-20 and WDPU-30 samples. This may indicate their lower resistance to the temperature increase.

Table 2

### Hydrodynamic characteristics of WDPU

Sample	$R_h^N$ , nm	
	T = 25 °C	T = 60 °C
WDPU-0	78.7 (16,0; 201.2)*	38.9 (9.6; 78.5)*
WDPU-10	40.8	20.0
WDPU-20	20.4	49.1
WDPU-30	36.0	50.5

Note. \* —  $R_h^N$  was determined for every peak.

It can be seen from the Table 2 that IPDI OIC-containing WDPU are characterized by a lower value of  $R_h^N$  and by a narrower particle size distribution in comparison to WDPU-0 at room temperature. Thus we can conclude that IPDI OIC introduction (from 10 wt.% to 30 wt.% per pure IPDI) in to WDPU positively affects on their hydrodynamic characteristics.

The analysis of IPDI OIC content influence on WDPU thermo-mechanical properties using the DMA method was the next step.

Table 3 shows the transition temperatures measured by inflection points on dynamic elastic modulus ( $E'$ ) vs. temperature graph and by maxima on dynamic loss modulus ( $E''$ ) vs. temperature graph. There are also elastic modulus values for sample temperature 30 °C higher than glass transition temperature.

Table 3

### Thermo-mechanical and thermal properties of WDPU

Sample	DMA					DSC		
	$E'_{T_g+30\text{ °C}}$ , MPa	$T_1$ , °C (by $E''$ )	$T_2$ , °C (by $E''$ )	$T_3$ , °C (by $E'$ )	$T_4$ , °C (by $E'$ )	$T_g$ , °C	$T_m$	$\Delta H_m$ , kJ/g
WDPU-0	1194	-148	-56	37	115	-52	119	-22.6
WDPU-10	1250	-148	-55	37	112	-53	116	-11.1
WDPU-20	1297	-148	-53	37	102	-54	107	-13.1
WDPU-30	1360	-149	-53	37	99	-52	106	-9.61

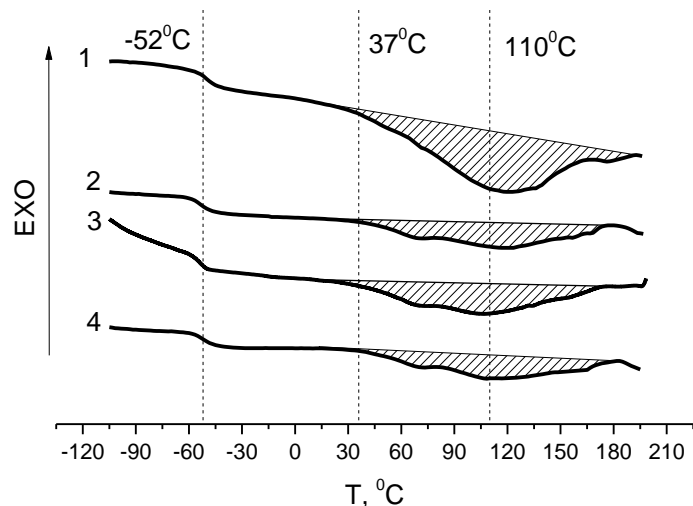
It is well known from the kinetic theory of elasticity [26] that the molar mass of interstitial polymer chains is inversely proportional to the dynamic elastic modulus for sample temperature 30 °C higher than glass transition temperature ( $E'_{T_g+30\text{ °C}}$ ). Therefore, we can suggest relying on the modulus variation data (Table 3), that the molecular weight of polyurethane interstitial chains decreases when the IPDI OIC percentage in WDPU composition increases, with the assumption of constant density of WDPU-0 — WDPU-30 polymer samples. This is most likely due to the fact that, following its high branching and polarity, IPDI OIC enhances the polyurethane mesh formation possibility mainly by reason of hydrogen bonds.

All four samples revealed qualitatively equal results for temperature transitions. The first transition ( $T_1$ ) is most likely a  $\beta$ -transition. The second peak on the loss modulus ( $E''$ ) vs. temperature graph resulted by the 'thawing' of polyester block segmental mobility. Thereby  $T_2$  is the glass transition temperature ( $T_g$ ). It can be seen from the Table 3 that  $T_g$  for studied polyurethanes there hardly depends on the IPDI OIC content. Temperature transitions  $T_3$  and  $T_4$  are most likely associated with initial melting of WDPU samples crystalline phase (first), as well as with their transition to a viscous flow state (second).

The nature of observed temperature transitions was confirmed by DSC analysis (Fig. 3, Table 3).

Degree of crystallinity is an important characteristic of polymer films. It can be estimated indirectly by melting enthalpy ( $\Delta H_m$ ) magnitude due to close chemical nature of prepared WDPU. So, Table 3 indicates more than double decrease in  $\Delta H_m$  value with an increasing in IPDI OIC content in WDPU. The obtained experimental fact can be apparently explained by the branched structure of OIC, limiting the polyester block 'packing'. It should be expected that a further increase in IPDI OIC content in WDPU can lead to a completely amorphous polymer yielding.





1 — WDPU-0; 2 — WDPU-10; 3 — WDPU-20; 4 — WDPU-30

Figure 3. DSC thermograms

### Conclusions

We have investigated the effect of isophorone diisocyanate oligoisocyanurate content in water-dispersible polyurethane compositions on their hydrodynamic, thermo-mechanical, and thermal properties in this work. According to the obtained results it was found that the OIC introduction improves properties of both aqueous polyurethane dispersions and their polymer films. This is indicated, in particular, by decreasing of dispersed particle average size. Furthermore, isophorone diisocyanate oligoisocyanurates block the crystallization of coatings they involved in due to its branching. It will undoubtedly positively affect the performance of these coatings when used at reduced temperatures. Along with this, oligoisocyanurate introduction to water dispersible polyurethane compositions has no significant effect on decreasing of glass transition temperatures. It should provide high performance characteristics at low operating temperatures.

### Acknowledgments

This work was performed in accordance with the state task, state registration No. AAAA-A19-119041090087-4 using the equipment of the Multi-User Analytical Center of IPCP RAS.

We also wish to express our appreciation to Senior Research, Bubnova M.L., for performing DMA analysis and helping with results explanation.

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## Изофорондиизоцианат олигоизоцианураттарының судисперсиялық полиуретандардың қасиеттеріне әсерін зерттеу

Олигоизоцианураттар (ОИЦ) — түрлі диизоцианаттарды циклотримеризациялау реакциясы, функционалдылығы үшін көп (әлеуетті байланыстырушы агенттер). Олар химиялық полимерлік өнеркәсіпте түрлі қасиеттері бар полиуретанды жабындарды алу үшін диизоцианаттарға қоспа ретінде, сондай-ақ тікелей полиуретандар синтезіне арналған изоцианаты бар компонент ретінде қолданыс тапты. ОИЦ негізінде синтезделген полимерлер бірқатар бірегей қасиеттерге ие, атап айтқанда, жоғары термо-отқа, сондай-ақ, УК-сәулеленуге және гидролизге төзімді. Мақалада алынған өнімдердің гидродинамикалық,

термомеханикалық және жылу физикалық қасиеттеріне судисперсиялық полиуретандар құрамындағы изофорондиизоцианат (ИФДИ ОИЦ) олигоизоцианурат құрамының әсері зерттелген. Осы мақсатта ацетондық әдіспен изофорондиизоцианат (ИФДИ), полибутиленадипинат (ПБА) және еркін ИФДИ салыстырмалы түрде 10–30 % салмақ ОИЦ ИФДИ, полибутиленадипинат (ПБА) және 2,2-бис(гидроксиметил)пропион қышқылы (ДМПА) негізіндегі судисперсиялық полиуретандардың үлгілері синтезделді. NCO-ифди ОИЦ тобының ВДПУ синтезі кезінде тігілген құрылымдардың пайда болуын болдырмау үшін морфолинмен қоршалған. Алынған дисперсиялар мен олардың негізіндегі жабындар динамикалық механикалық талдау (ДМА), дифференциалды сканерлеу калориметрия (ДСК) және жарықтың динамикалық шашырауы (ДРС) әдістерін пайдалана отырып сипатталған. Олигоизоцианураттар полиуретандардың су дисперсияларының, сондай-ақ олардың негізіндегі полимерлік пленкалардың сипаттамаларын жақсартатыны анықталды. Сонымен қатар, олигоизоцианураттар олардың негізіндегі жабындардың кристалдануына кедергі келтіреді, бұл олардың пайдалану сипаттамаларына оң әсер етеді.

*Кілт сөздер:* полиуретан, полиуретандардың су дисперсиясы, изофорондиизоцианат, 2,2-бис(гидроксиметил)пропион қышқылы, полибутиленадипинат, олигоизоцианурат изофорондиизоцианата, динамикалық жарық шашырауы, динамикалық механикалық талдау.

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## Исследование влияния олигоизоциануратов изофорондиизоцианата на свойства вододисперсионных полиуретанов

Олигоизоцианураты (ОИЦ) — продукты реакции циклотримеризации различных диизоцианатов с функциональностью больше трех (потенциальные сшивающие агенты). Они нашли применение в химической полимерной промышленности в качестве добавки к диизоцианатам для получения полиуретановых покрытий с различными свойствами, а также непосредственно в качестве изоцианатсодержащего компонента для синтеза полиуретанов. Полимеры, синтезированные на основе ОИЦ, обладают рядом уникальных свойств, а именно: повышенной термо-, огнестойкостью, а также устойчивостью к УФ-излучению и гидролизу. В статье исследовано влияние содержания олигоизоциануратов изофорондиизоцианата (ОИЦ ИФДИ) в составе вододисперсионных полиуретанов на гидродинамические, термомеханические и теплофизические свойства получаемых продуктов. С этой целью ацетоновым методом были синтезированы образцы вододисперсионных полиуретанов на основе изофорондиизоцианата (ИФДИ), полибутиленадипината (ПБА) и 2,2-бис(гидроксиметил)пропионовой кислоты (ДМПА), содержащие 10–30 % весовых ОИЦ ИФДИ относительно свободного ИФДИ. Для исключения образования сшитых структур при синтезе ВДПУ NCO-группы ОИЦ ИФДИ частично блокировали морфолином. Полученные дисперсии и покрытия на их основе были охарактеризованы с использованием методов динамического механического анализа (ДМА), дифференциальной сканирующей калориметрии (ДСК) и динамического рассеяния света (ДРС). Установлено, что олигоизоцианураты улучшают характеристики как водных дисперсий полиуретанов, так и полимерных пленок на их основе. Кроме того, ввиду своей разветвленности, олигоизоцианураты препятствуют кристаллизации покрытий на их основе, что, несомненно, положительно скажется на их эксплуатационных характеристиках.

*Ключевые слова:* полиуретан, водная дисперсия полиуретанов, изофорондиизоцианат, 2,2-бис(гидроксиметил)пропионовая кислота, полибутиленадипинат, олигоизоцианурат изофорондиизоцианата, динамическое светорассеяние, динамический механический анализ.

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## **Production of cyclodextrin nanocomplexes based on N'-((5-nitrofur-2-yl)methylene)isonicotinohydrazide and research of their structure by physical and chemical methods**

In the present work, the supramolecular complexes of N'-((5-nitrofur-2-yl)methylene)isonicotinohydrazide with  $\beta$ -cyclodextrin ( $\beta$ -CD) and 2-hydroxypropyl- $\beta$ -cyclodextrin (2-HP- $\beta$ -CD) were first obtained and studied. The NMR methods of one-dimensional  $^1\text{H}$ ,  $^{13}\text{C}$  spectroscopy confirmed the structure of the obtained inclusion complexes. The structure of the compounds was also studied by two-dimensional NMR spectroscopy COSY ( $^1\text{H}$ - $^1\text{H}$ ) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature. Comparison of the integral intensities of the  $^1\text{H}$  NMR signals of the initial substrate and  $\beta$ - and 2-HP- $\beta$ -CD in supramolecular complexes showed that in both cases complexes of the composition of one substrate molecule per one receptor molecule are formed. It was found that the interaction of N'-((5-nitrofur-2-yl)methylene)isonicotinohydrazide with the studied  $\beta$ -cyclodextrins forms inclusion complexes with the penetration of the substrate molecule into the internal cavity of the receptor by the pyridine fragment in the case of using  $\beta$ -CD and the furanose cycle in the case of 2-HP- $\beta$ -CD. The resulting supramolecular complexes can dissolve in water or form stable aqueous dispersions.

**Keywords:** hydrazones, N'-((5-nitrofur-2-yl)methylene)isonicotinohydrazide,  $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, inclusion complexes, NMR spectroscopy, supramolecular complexes, COSY ( $^1\text{H}$ - $^1\text{H}$ ), HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ).

### *Introduction*

Hydrazones obtained on the basis of the well-known isonicotinic acid hydrazide are used as antibacterial and anti-tuberculosis drugs, analytical reagents and dyes [1]. However, some of them have low solubility in water. At present, various ways have been developed and are used to increase the solubility of drugs in water: the use of special excipients, including the inclusion of drugs in the structure of water-soluble polymers [2].

A possible solution to the problem of water solubility of hydrophobic substances is the use of complexation technology with cyclodextrins. Using the complexation method to obtain biologically active substance clathrates with cyclodextrins will increase the water solubility of hydrophobic and slightly soluble substances, their bioavailability and chemical stability [3]. This will extend the half-life of the active component and, therefore, reduce the dose of the drug used.

Cyclodextrins (CDs) belong to the group of water-soluble compounds, but do not have high solubility at normal temperature due to the relatively strong intramolecular hydrogen bonds in the crystal lattice [3, 4]. The lowest solubility among all natural cyclodextrins has  $\beta$ -cyclodextrin. Being in a dry crystalline state, cyclodextrins do not have high hygroscopicity [5]. However, in the process of crystallization of cyclodextrins from aqueous solutions, water molecules are actively included in the torus cavity, and are also present in the crystal structure of the substance, binding to the outer surface of the molecules.

The structure of the cyclodextrin crystals is stabilized by intermolecular hydrogen bonds. In the crystalline hydrate state, the aggregates of cyclodextrin molecules have a tubular or network shape, and, due to different orientations, form particles resembling needle-like or prism-like agglomerates in appearance (Fig. 1).

The crystal shape of the cyclodextrin molecules depends on the degree of hydration. With the removal of water, the crystals become amorphous [6]. During the formation of inclusion complexes, water molecules are displaced from the cavities of the cyclodextrin torus as a result of incorporation of the corresponding «guest» substance into the torus cavity.

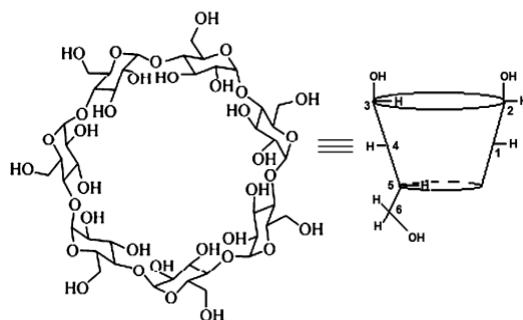


Figure 1. The structure of the cyclodextrin crystals

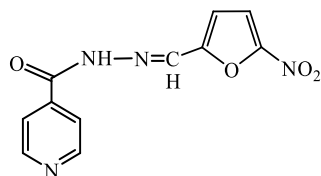
Cyclodextrins are insoluble in most organic solvents, but are also able to dissolve in some polar aprotic solvents [7]. The temperature dependence of the solubility of cyclodextrin may vary as a result of the complexation process with the molecule of the «guest» substance. Inclusion complexes may have greater solubility in water than intact cyclodextrins, provided that the molecules of the «guest» substance are readily soluble in water. And, on the contrary, during the formation of inclusion complexes with hydrophobic molecules of the «guest» substance, the solubility of cyclodextrins in water may decrease [6]. Despite the decrease in the solubility of cyclodextrin molecules («matrix» molecules), the solubility of a hydrophobic compound in aqueous systems in the inclusion complex may increase [8].

The stability of the formed complexes is due to the formation of various non-covalent forces of interaction between the cyclodextrin and «guest» molecules: van der Waals, hydrophobic, etc. Cyclodextrin in the complex protects the «guest» molecule from damage by various reactive molecules and thereby reduces the oxidation rate of steric rearrangements, hydrolysis, racemization and enzymatic destruction [3].

In this regard, the use of cyclic oligosaccharides,  $\beta$ -cyclodextrins (receptor), as a component of the supramolecular system for obtaining a water-soluble complex with hydrazone (substrate) is promising. The possibility of inclusion of the active substance in the capsule of  $\beta$ -cyclodextrin is due to hydrophobic interactions between the BAC and the complexing agent.

When complexing with cyclodextrins, the molecules of the «guest» substance transform into a nanostructured («encapsulated») state, in which each substrate molecule is placed in the cavity of a native or modified cyclodextrin molecule [6]. This causes significant changes in the physicochemical properties of the molecules of the substance bound by cyclodextrins: the stability of compounds sensitive to oxygen or light increases [6]; the reactivity and activity of the substrate molecules changes; stabilization of easily volatile compounds occurs [9]; the solubility of a number of substances increases [9]; the possibility of converting liquids into powder form is realized [2]; the resistance of the substrate to biodegradation by microorganisms increases [9]; disagreeable odors and taste are masked [10]; the color or color intensity of the compounds changes; the catalytic activity of cyclodextrins, etc., can be observed [9]. Such properties of cyclodextrins and their derivatives makes them suitable for use in analytical chemistry, agriculture, pharmaceuticals, food and cosmetic production [10].

The aim of this work was to obtain inclusion complexes  $N'$ -((5-nitrofuran-2-yl)methylene)isonicotinohydrazide **1** (Fig. 2) with  $\beta$ -cyclodextrin ( $\beta$ -CD) and 2-hydroxypropyl- $\beta$ -cyclodextrin (2-HP- $\beta$ -CD), as well as the establishment of structural features of the obtained supramolecular complexes.

Figure 2.  $N'$ -((5-nitrofuran-2-yl)methylene)isonicotinohydrazide (**1**)

### Experimental

$\beta$ -Cyclodextrin ( $\beta$ -CD) and 2-hydroxypropyl- $\beta$ -cyclodextrin (2-HP- $\beta$ -CD) were used by Fluka, 99 % pure.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Jeol JNM-ECA 400 spectrometer (399.78 and 100.53 MHz

on  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively) in a DMSO- $d_6$  solution at room temperature. Chemical shifts are measured relative to the residual signals of protons or carbon atoms of DMSO- $d_6$ .

To obtain complexes for the inclusion of functionally substituted N'-((5-nitrofuranyl)methylene)isonicotinohydrazide **1** with  $\beta$ -cyclodextrins, the coprecipitation method was chosen, since this method is simple and easy to implement. A concentrated solution of  $\beta$ -cyclodextrin in water was added dropwise to a concentrated solution of N'-((5-nitrofuranyl)methylene)isonicotinohydrazide **1** in DMF in the ratio 1:1. Then they were interfered with a magnetic stirrer at a temperature of 50–60 °C. The identity of the proposed complexes was checked by thin-layer chromatography on Silufol UV-254 plates in the isopropyl alcohol system — 25 % ammonia-water solution 7:2:1. The final product was dried at a temperature of 350 °C in vacuum drying at atmospheric pressure of 0.4 kgf/cm<sup>2</sup>. The inclusion complex of hydrazone **1** with  $\beta$ -cyclodextrin was obtained in powder form. The yield of product **2** was 71.6 %, mp. 300–303 °C. The inclusion complex **3** N'-((5-nitrofuranyl)methylene)isonicotinohydrazide **1** with 2-hydroxypropyl- $\beta$ -cyclodextrin was obtained similarly. The product yield was 70.5 %, mp. 289–292 °C.

### Results and Discussion

In supramolecular chemistry, the size and shape or geometric complementarity of the interacting components play a decisive role; therefore,  $\beta$ -CD and its 2-hydroxy derivative, 2-hydroxypropyl- $\beta$ -CD, were used to obtain inclusion complexes with substrate **1**.

To analyze the physicochemical properties of inclusion complexes of cyclodextrins with substances from various classes of organic and inorganic compounds, as well as aggregates of inclusion complexes, various instrumental methods are used [11]. The choice of specific analysis methods is determined by the physicochemical properties of the complexant substance and the state of aggregation of inclusion complexes [6]. Nanostructures of inclusion complexes formed as a result of substrate-ligand interaction of guest substance molecules with cyclodextrin molecules can be studied and characterized both in dry crystalline form and in the state of solutions [12].

To determine the change in the properties of the ligand substance and the substrate as a result of the formation of nanocomplexes of cyclodextrin cavities obtained in the crystalline state, thermal analysis methods, microscopy methods, spectral, chromatographic methods, etc. can be used [13–15]. To control the physicochemical properties of inclusion complexes it is recommended to use the methods of thermal analysis, scanning electron microscopy, X-ray diffraction analysis, IR spectroscopy, NMR, CD, EPR spectroscopy, microcalorimetry and etc.

For analysis of inclusion complexes, the methods of proton magnetic resonance spectroscopy on  $^1\text{H}$  nuclei and nuclear magnetic resonance spectroscopy on  $^{13}\text{C}$  nuclei are mainly used. The most informative method for confirming the formation of inclusion complexes is  $^1\text{H}$ -NMR spectroscopy [9]. This analysis method allows you to fix the pronounced chemical shift in the vibrational spectra of H-3 and H-5 protons oriented inside the torus cavity, which is due to the placement of the «guest» substance molecule in the hydrophobic cyclodextrin cavity. Moreover, insignificant chemical shifts are observed in the vibrational spectra of H-1, H-2, and H-4 atoms localized on the outer surface of the molecule [16]. The  $^{13}\text{C}$ -NMR spectroscopy method allows one to record chemical shifts in the electronic environment of carbon atoms of the cavity of a cyclodextrin molecule resulting from the van der Waals and electrostatic interaction of the molecules of the «guest» substance with the molecules of the host substance [17–20]. With an increase in the concentration of the «guest» substance in the system, a proportional increase in the chemical shift in the vibrational spectra is observed, due to a shift in the equilibrium state towards the formation of inclusion complexes [21].

The synthesis of the initial N'-((5-nitrofuranyl)methylene)isonicotinohydrazide **1** (substrate) was previously described by us in [11–13]. The substance during screening studies showed pronounced antimicrobial and antifungal activity.

In the  $^1\text{H}$  NMR spectrum of compound **1**, the proton H-4 of the furan fragment appeared as a single-proton doublet at 7.29 ppm. with  $^3J$  4.4 Hz. The remaining furan proton H-3 resonated with the pyridine protons H-15,19 with a three-proton multiplet at 7.76–7.79 ppm. The pyridine protons H-16,18 were manifested by a two-proton doublet at 8.77 ppm. with  $^3J$  5.6 Hz. The proton H-8 at the unsaturated carbon atom and the amide proton H-10 appeared as single-proton singlets at 8.36 and 12.41 ppm. respectively.

In the  $^{13}\text{C}$  NMR spectrum of compound **1**, the signals of the carbon atoms of the furan fragment appeared at 115.08 (C-3), 11.61 (C-4), 151.83 (C-5) and 152.59 (C-2) ppm. The signals of the carbon nuclei of the pyridine ring are observed at 122.07 (C-15,19), 140.35 (C-14) and 150.99 (C-16,18) ppm. The unsaturated carbon atom C-8 resonated at 137.20 ppm. Chemical shift signal at 162.53 ppm corresponds to the carbon atom C-11 of the urea group.

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

In the spectra of the  $^1\text{H}$ - $^1\text{H}$  COSY compound, spin-spin correlations are observed through three bonds of the neighboring methine-methine protons of the  $\text{H}^4$ - $\text{H}^3$  furan ring (cross-peak coordinates, ppm: 7.28, 7.76 and 7.76, 7.28) and aromatic protons  $\text{H}^{15,19}$ - $\text{H}^{16,18}$  (coordinates of cross peaks, ppm: 7.78, 8.76 and 8.7, 7.77) of the pyridine ring. Heteronuclear interactions of protons with carbon atoms through one bond were established using  $^1\text{H}$ - $^{13}\text{C}$ CHMOC spectroscopy (Fig. 3b) for all pairs present in the compound:  $\text{H}^4$ - $\text{C}^4$  (7.27, 116.62),  $\text{H}^3$ - $\text{C}^3$  (7.75, 115.04),  $\text{H}^{15,19}$ - $\text{C}^{15,19}$  (7.76, 122.10),  $\text{H}^8$ - $\text{C}^8$  (8.35, 137.21),  $\text{H}^{16,18}$ - $\text{C}^{16,18}$  (8.77, 150.96).

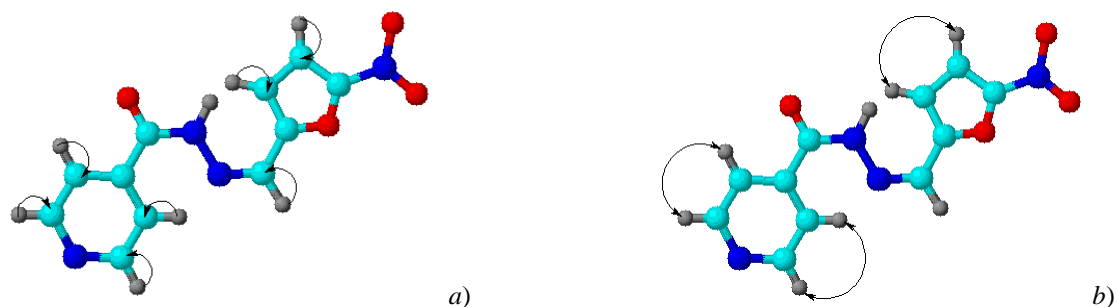


Figure 3. Correlation scheme in the spectra of HMQC (a) and COSY (b) of compound **1**

As a result of the studies, the supramolecular complexes **2** and **3** based on the functionally substituted N'-((5-nitrofur-2-yl)methylene)isonicotinohydrazide with cyclodextrins ( $\beta$ -CD, 2-hydroxypropyl- $\beta$ -CD) were first obtained. The study of supracomplexes with  $\beta$ -CD **2** and 2-HP- $\beta$ -CD **3** showed that in both cases, inclusion complexes of substrate **1** with a cyclodextrin receptor cavity are formed. The greatest change in the chemical shifts of protons in the process of formation of supramolecular complexes occurs with the internal protons H-3 and H-5 of the cyclodextrin cavity. In the formation of the inclusion complex of substrate **1** with  $\beta$ -CD, the greatest change in chemical shifts occurs with protons of the pyridine fragment. In the case of using 2-HP- $\beta$ -CD, a proton of the furan cycle undergoes a greater change in chemical shifts. This indicates the incorporation of the substrate molecule into the cyclodextrin cavity by the pyridine fragment in the case of using  $\beta$ -CD (Fig. 4) and the furanose cycle in the case of 2-HP- $\beta$ -CD (Fig. 5).

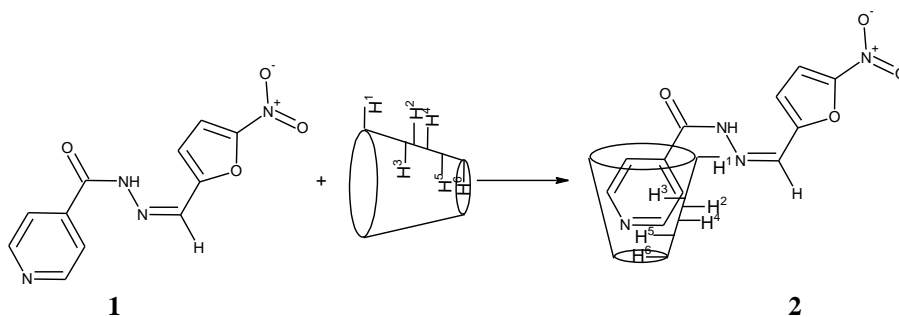


Figure 4. Scheme of the formation of supramolecular complex **2**

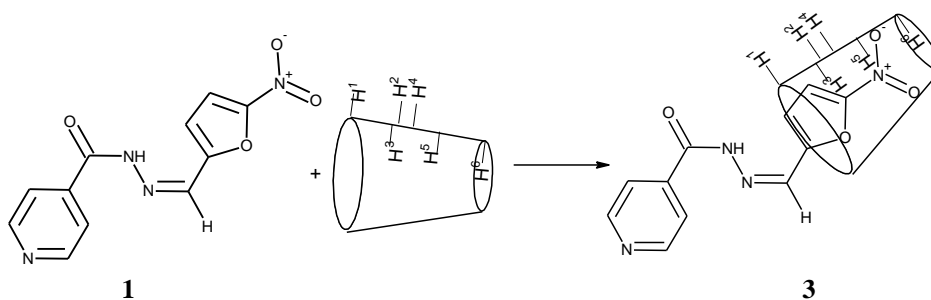


Figure 5. Scheme of the formation of supramolecular complex **3**



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **1** in the free state and in the composition of supramolecular complexes **2** and **3** obtained in DMSO- $d_6$  are presented in Tables 1 and 2.

Table 1

Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei of substrate **1** in the free state ( $\delta_0$ ) and in the composition of complexes **2** ( $\delta_1$ ), **3** ( $\delta_2$ )

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

Table 2

Chemical shifts of  $^1\text{H}$  nuclei of  $\beta$ - and 2-HP- $\beta$ -CD in the free state ( $\delta_0$ ) and in complexes **2** ( $\delta_1$ ) and **3** ( $\delta_2$ ), ppm

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

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

### Conclusions

The supramolecular complexes of  $\text{N}'-((5\text{-nitrofuranyl)methylene})\text{isonicotinohydrazide}$  with  $\beta$ -cyclodextrin ( $\beta$ -CD) and 2-hydroxypropyl- $\beta$ -cyclodextrin (2-HP- $\beta$ -CD) were first obtained and studied in the work. Using the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and two-dimensional NMR COSY ( $^1\text{H}$ - $^1\text{H}$ ) and HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) spectroscopy, the structure of the obtained inclusion complexes was confirmed, and spin-spin interactions of a homo- and heteronuclear nature were established. A comparison of the integral intensities of the  $^1\text{H}$  NMR signals of the initial substrate with  $\beta$ -CD and 2-HP- $\beta$ -CD in supramolecular complexes showed that in both cases complexes are formed with the penetration of the substrate molecule into the internal cavity of the receptor by the pyridine fragment in the case of  $\beta$ -CD and furanose cycle in the case of 2-HP- $\beta$ -CD. It was shown that the obtained supramolecular complexes are able to dissolve in water or form stable aqueous dispersions.

### Acknowledgements

Financial support from the Ministry of Education and Science of the Republic of Kazakhstan (IRN AP05131054-OT-18, 2018–2020) is greatly acknowledged.

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### **N'-((5-нитрофуран-2-ил)метил)изоникотиногидразид негізінде циклодекстриндік нанокешендерді алу және олардың құрылымын физикалық-химиялық әдістермен зерттеу**

Мақалада N'-((5-нитрофуран-2-ил)метил)изоникотиногидразидтің  $\beta$ -циклодекстринмен ( $\beta$ -ЦД) және 2-гидроксипропил- $\beta$ -циклодекстринмен (2-ГП- $\beta$ -ЦД) супрамолекулярлық кешендер алынып, зерттелген. Бір өлшемді  $^1\text{H}$ ,  $^{13}\text{C}$  спектроскопия ЯМР әдістерімен алынған қосу кешендерінің құрылысы расталды. Гомо-және гетероядер табиғатының спин-спинді өзара әрекеттесуін орнатуға мүмкіндік беретін ЯМР COSY ( $^1\text{H}$ - $^1\text{H}$ ) және HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ) екі өлшемді спектроскопия әдістерімен анықталған.

Супрамолекулярлы кешендерде  $^1\text{H}$  ЯМР сигналдарының интегралдық қарқындылығын  $\beta$ - және 2-ГП- $\beta$ -ЦД-мен салыстыру екі жағдайда да рецепторлардың бір молекуласына субстраттың бір молекуласының құрам кешені түзілетіндігін көрсетті.  $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразидтің зерттелетін  $\beta$ -циклодекстриндермен өзара әрекеттесуі кезінде субстрат молекуласының рецептордың қуысына пиридин фрагменімен кіруімен  $\beta$ -ЦД қолданғанда және фураноздық циклмен кіруімен 2-ГП- $\beta$ -ЦД қолданғанда қосу кешендері пайда болатыны байқалды. Алынған супрамолекулярлық кешендер суда еруі немесе тұрақты су дисперсияларын құруы мүмкін.

*Кілт сөздер:* гидразидтер,  $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразид,  $\beta$ -циклодекстрин, 2-гидроксипропил- $\beta$ -циклодекстрин, қосу кешендері, ЯМР спектроскопиясы, супрамолекулярлы кешендер, COSY ( $^1\text{H}$ - $^1\text{H}$ ), HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ).

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## Получение циклодекстриновых нанокмплесов на основе $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразида и исследование их структуры физико-химическими методами

В статье впервые были получены и изучены супрамолекулярные комплексы  $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразида с  $\beta$ -циклодекстрином ( $\beta$ -ЦД) и 2-гидроксипропил- $\beta$ -циклодекстрином (2-ГП- $\beta$ -ЦД). Методами  $^1\text{H}$ ,  $^{13}\text{C}$  ЯМР спектроскопии было подтверждено строение полученных комплексов включения. Строение соединений было изучено также методами двумерной спектроскопии ЯМР COSY ( $^1\text{H}$ - $^1\text{H}$ ) и HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ), позволяющей установить спин-спиновые взаимодействия гомо- и гетероядерной природы. Сопоставление интегральных интенсивностей сигналов  $^1\text{H}$  ЯМР исходного субстрата с  $\beta$ - и 2-ГП- $\beta$ -ЦД-ами в супрамолекулярных комплексах показало, что обоих случаях образуются комплексы состава: одна молекула субстрата на одну молекулу рецептора. Установлено, что при взаимодействии  $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразида с изучаемыми  $\beta$ -циклодекстринами образуются комплексы включения с вхождением молекулы субстрата во внутреннюю полость рецептора пиридиновым фрагментом в случае использования  $\beta$ -ЦД и фуранозным циклом — в случае 2-ГП- $\beta$ -ЦД. Полученные супрамолекулярные комплексы способны растворяться в воде или образовывать устойчивые водные дисперсии.

*Ключевые слова:* гидразиды,  $\text{N}'$ -((5-нитрофуран-2-ил)метилен)изоникотиногидразид,  $\beta$ -циклодекстрин, 2-гидроксипропил- $\beta$ -циклодекстрин, комплексы включения, спектроскопия ЯМР, супрамолекулярные комплексы, COSY ( $^1\text{H}$ - $^1\text{H}$ ), HMQC ( $^1\text{H}$ - $^{13}\text{C}$ ).

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### Features of the extraction of yttrium and lanthanum with an intergel system based on hydrogels of polyacrylic acid and poly-4-vinylpyridine

To predict the sorption activity and selectivity of hydrogels, the effect of mutual activation of polymer networks in the intergel system was studied. The intergel system of the hydrogel of polyacrylic acid ((hPAA)) and the hydrogel of poly-4-vinylpyridine (hP4VP), which was studied at a distance through the volume of the solvent in the absence of direct contact between the polymer networks, were chosen as the object of study. Intergel systems have been investigated using methods for measuring electrical conductivity, pH, and gravimetry. The mutual activation of La<sup>3+</sup> and Y<sup>3+</sup> ions with the intergel system in an aqueous medium was also studied. It has been established that as a result of the remote interaction of the studied hydrogels, their mutual activation occurs, leading to a significant change in their electrochemical and conformational properties. At certain ratios of acidic and basic hydrogels, a significant increase in the sorption of lanthanum and yttrium ions is observed in comparison with the initial hydrogels. These results indicate the appearance of ionized structures with optimal conformation, providing an optimal ligand environment around lanthanum and yttrium ions.

**Keywords:** intergel systems, polyacrylic acid, poly-4-vinylpyridine, hydrogels, remote interaction, La<sup>3+</sup> ions, Y<sup>3+</sup> ions, sorption, desorption.

#### Introduction

It is known that polymer hydrogels having functional groups capable of binding metal ions are classified as highly selective polymer structures. This contributes to the fact that such polymers have a sorption ability with respect to metal ions, including ions of rare earth elements.

According to the phenomenon of the remote interaction of polymer hydrogels in an aqueous medium, nonionic macromolecules that are unable to undergo ionization and subsequent dissociation cannot participate in the process of remote interaction. Therefore, the remote interaction of polymers of various structures leads to their functionalization.

Previous studies showed that the remote interaction of polymer hydrogels leads to a significant change in their electrochemical and conformational properties. As a result of remote interaction, functional groups are formed without counter ions, stabilized by intramolecular interactions; electrochemical and conformational changes in macromolecules lead to a significant increase in the sorption ability of the intergel system, consisting of two hydrogels; the «long-range effect» under certain conditions leads to high selectivity with respect to metal ions [1–4].

In this regard, the aim of this work is to study the sorption ability using an example of an intergel system consisting of hydrogels of polyacrylic acid and poly-4-vinylpyridine with respect to lanthanum and yttrium ions, as well as predicting the possibility of using them to extract rare and rare-earth metals.

### Experimental

To measure the electrical conductivity of the solutions, a MARK-603 conductometer (Russia) was used; the concentration of hydrogen ions was determined using a Metrohm 827 pH-Lab pH meter (Switzerland). The mass was determined on an analytical electronic balance SHIMADZU AY220 (Japan). The concentration of  $\text{La}^{3+}$  and  $\text{Y}^{3+}$  ions was determined on spectrophotometers Perkin Elmer Lambda 35 (USA), Jenway-6305 (Japan).

The studies were carried out in an aqueous medium and in a 0.005 M solution of 6-aqueous lanthanum and yttrium nitrate. Polyacrylic acid hydrogels were synthesized in the presence of a crosslinking agent N,N-methylene-bis-acrylamide and a redox system  $\text{K}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_3$  in an aqueous medium. The synthesized hydrogels were crushed into fine dispersions and washed for a long time with distilled water until a constant value of the electrical conductivity of aqueous solutions was established. A Sigma-Aldrich crosslinked divinylbenzene hydrogel of poly-4-vinylpyridine (hP4VP) was used.

#### Electrochemical studies

Experiments to determine the pH and conductivity were carried out at room temperature. The studies of the intergel system were performed in the following order: each hydrogel in dry form was placed in separate cells from a plastic bag, the pores of which are permeable to low molecular weight ions and molecules, but impermeable to dispersion of hydrogels. Then the cells with dry hydrogels were placed in glasses with aqueous solutions and solutions of lanthanum nitrate. The electrical conductivity and pH of the supra gel were determined in the presence of hydrogels in solution. Adsorption behavior in relation to La (III) in aqueous conditions: studies using periodic and column methods under various conditions: experimental studies of the kinetic and thermodynamic characteristics of the adsorption process, studied in the work, which are indicated in the reference literature and were considered [5–6].

*Method for determination of lanthanum and yttrium ions.* The method for determining lanthanum and yttrium ions in solution is based on the formation of a colored complex compound of the arsenazo III organic analytical reagent with rare-earth metal ions (REM).

The degree of extraction (sorption) was calculated by the formula:

$$\eta = (C_{\text{int}} - C_{\text{res}}) / C_{\text{res}} * 100 \%,$$

where  $C_{\text{int}}$  is the initial concentration of the metal in solution, g/l;  $C_{\text{res}}$  is residual concentration of metal in solution, g/l [7–9].

### Results and Discussion

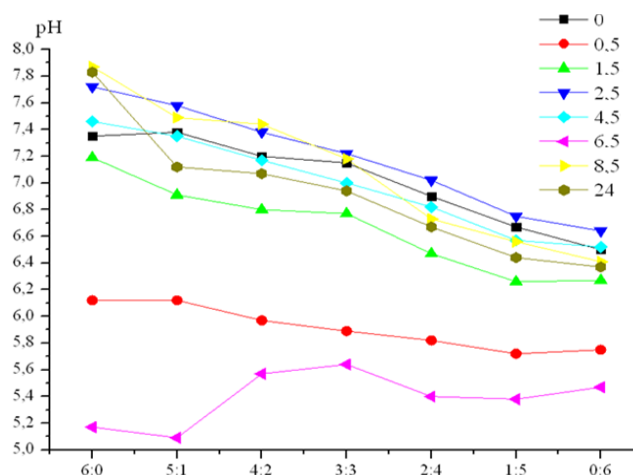
Study of the mutual activation of hPAA:hP4VP hydrogels in the intergel system

The presence of an intergel system in an aqueous solution leads to various processes that affect the electrochemical balance in the solution.

As a result of these interactions, a state arises in which there are no counterions in some of the charged functional groups of hydrogels. The concentration of ionized groups that lack counterions depends on the initial molar ratios of the polymer networks and other factors.

Figure 1 shows the time dependence of the pH of aqueous solutions on the molar ratios of hP4VP. As polyacid predominates, a decrease in the concentration of hydrogen ions with time is observed. Distinct minima are observed in the presence of only polyacids (hPAA:hP4VP = 6:0) after 6.5 hours of interaction. The maximum pH values after 24 hours are observed at a ratio of hPAA:hP4VP = 6:0. As the proportion of polybase increases, the pH of the solution gradually decreases. The lowest pH value is observed in a 5:1 ratio after 6.5 hours of interaction.

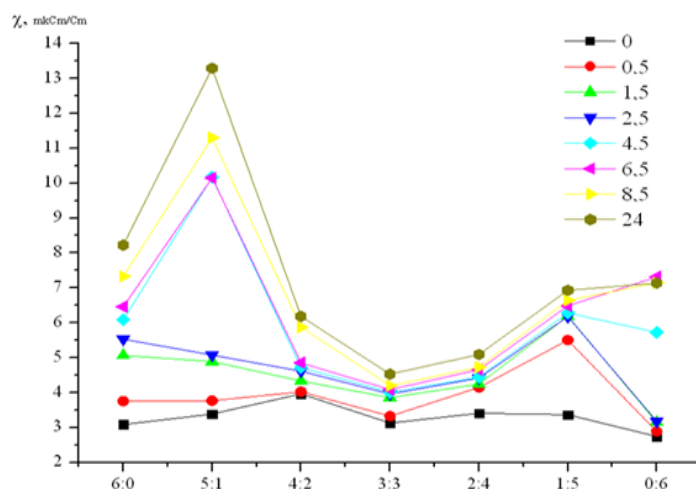
The appearance of an excess of  $\text{H}^+$  ions is due to the high swelling rate and dissociation of COOH groups, as well as the insufficient swelling rate of the main groups and their low concentration. An increase in the content of  $\text{OH}^-$  ions in the aqueous medium is associated with a low swelling rate and a low concentration of COOH groups, as well as a high swelling rate and the interaction of the main functional groups with  $\text{H}^+$  ions. This is possible in the case of a second reaction in which hydroxyl anions are released into the solution. In parallel, the third reaction is taking place, as a result of which the free proton binds to the pyridine ring and the concentration of positively charged ions in the solution decreases sharply.



1 — 0 h; 2 — 0.5 h; 3 — 1.5 h; 4 — 2.5 h; 5 — 4.5 h; 6 — 6.5 h; 7 — 8.5 h; 8 — 24 h

Figure 1. Dependence of the pH of aqueous solutions on the molar ratio of hydrogels hPAA:hP4VP over time

Figure 2 shows the dependence of changes in the electrical conductivity of solutions on the molar ratio of hydrogels over time. During the remote interaction, regions of minimum and maximum electrical conductivity appear, and at the beginning of the interaction, the conductivity of the solutions increases. With a ratio of 5:1, high values of electrical conductivity are observed after 4.5; 6.5; 8.5 and 24 hours. The maximum conductivity values are reached after 24 hours. As can be seen from the figure, the minimum electrical conductivity of aqueous solutions is observed at a ratio of 3:3 for all the time of distance interaction of hydrogels.



1 — 0 h; 2 — 0.5 h; 3 — 1.5 h; 4 — 2.5 h; 5 — 4.5 h; 6 — 6.5 h; 7 — 8.5 h; 8 — 24 h

Figure 2. Dependence of the electrical conductivity of aqueous solutions on the molar ratio of hydrogels hPAA:hP4VP in time

Comparing the values of electrical conductivity and pH, we can conclude that as a result of mutual activation of the hydrogels go into a more highly ionized state. The area of maximum activation of hydrogels is the ratio of hPAA:hP4VP = 5:1. The highest ionization of gP4VP hydrogel occurs at a ratio of 5:1.

The minimum electrical conductivity of the hPAA:hP4VP intergel system is due to the binding of the proton cleaved from the carboxyl group by the vinylpyridine heteroatom. When immersed in an aqueous medium, both hydrogels begin to swell as a result of interaction with water molecules. Carboxyl groups are first ionized, then anions —  $\text{COO}^-$  and hydrogen ions (protons)  $\text{H}^+$  are dissociated into the carboxylate. The ionization of the cationic hydrogel of poly-4-vinylpyridine in an aqueous medium occurs as a result of the addition of hydrogen ions formed during the dissociation of carboxyl groups and water molecules into  $\text{H}^+$ ,  $\text{OH}^-$

ions. The long-range effect of hydrogels leads to the fact that during these interactions the total content of positive charges in the aqueous medium decreases.

High values of electrical conductivity, in turn, indicate that, at certain ratios of two hydrogels, the dissociation of carboxyl groups prevails over the process of proton association by polybasic nitrogen heteroatoms. The reason for this may be a conformational change in the links in the interstitial chains. At certain concentrations, charged  $\text{NH}^+$  groups can form intramolecular cross-links  $\geq \text{N} \dots \text{H}^+ \dots \text{N} \equiv$ , which lead to the folding of macromolecular tangles and a decrease in proton binding.

From the above results, it can be expected that the phenomena of mutual activation of functional hydrogels should be reflected in activation processes with metal ions. To verify this assumption, the mutual activation of the intergel system with respect to lanthanum and yttrium ions was studied.

Figure 3 reflects the change in the concentration of lanthanum ions during its sorption by the hPAA:hP4VP intergel system. First, in all ratios, we observe that the amount of lanthanum ions in the solution is high. As can be seen from the figure, in comparison with the ratios when only polyacid or polybase is present in the solution (ratios 6:0 and 0:6), the ratios at which there are 2 hydrogels in the solution have a much greater sorption ability. A much higher degree of extraction of  $\text{La}^{3+}$  ions at a ratio of 3:3. Moreover, the greatest sorption occurs when the ratio of hPAA:hP4VP = 3:3 after 24 hours of interaction. This is due to the fact that, at this ratio, the hydrogels of polyacrylic acid and poly-4-vinylpyridine are in a highly ionized state due to the mutual activation of hydrogels in intergel systems.

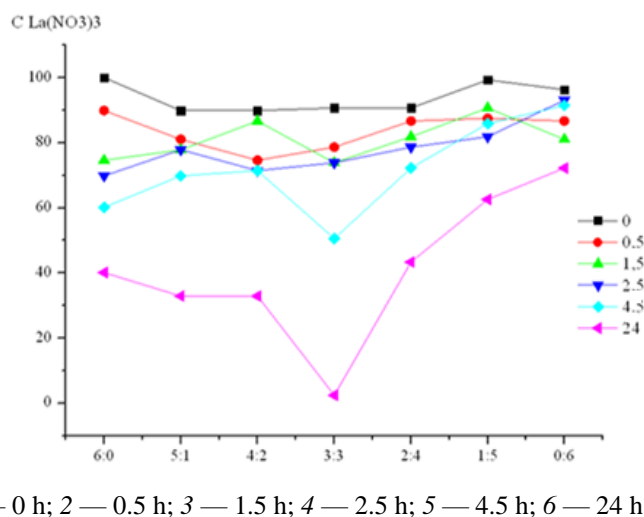


Figure 3. Dependence of the concentration of lanthanum ions on the molar ratio of hydrogels in the hPAA:hP4VP intergel system in the environment of 6-aqueous lanthanum nitrate

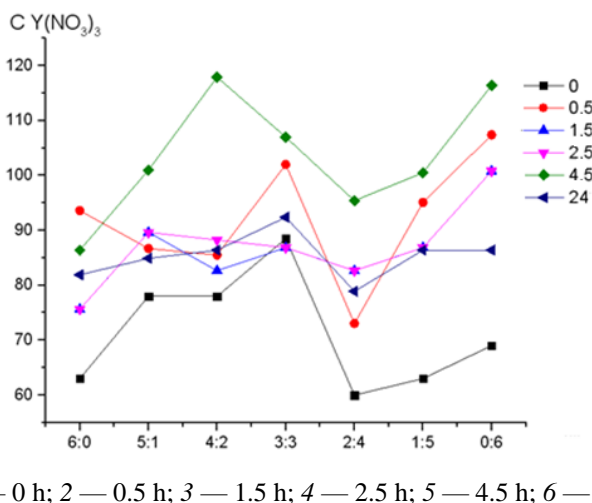


Figure 4. Dependence of the concentration of yttrium ions on the molar ratio of hydrogels in the hPAA:hP4VP intergel system in a medium of 6- yttrium nitrate



The dependence of the concentration of yttrium ions on the molar ratio of hydrogels in time in the hPAA:hP4VP intergel system in a medium of 6- $\gamma$ -yttrium nitrate is shown in Figure 4. The results obtained indicate that mutual activation leads to a significant increase in the sorption properties of polymer hydrogels in the intergel system.

The starting hydrogel of polyacrylic acid has a higher degree of extraction of yttrium ions. As can be seen from Figure 4, the highest activation of yttrium ions occurs at a ratio of 2:4 hPAA:hP4VP. In the figure, one can observe the general regularity of the degree of activation of yttrium ions in the intergel system. The lowest activation point corresponds to a 4:2 ratio after 4.5 hours of interaction. And in a 2:4 ratio of the intergel system, a decrease in the concentration of yttrium ions is observed. The main reason for such a high degree of extraction is the high ionization of polymer structures as a result of their mutual activation. Further, the extraction of yttrium ions by the intergel system decreases and the polybase present in the solution shows the lowest activation with yttrium ions. These results indicate the appearance of ionized structures with optimal conformation, providing an optimal ligand environment around lanthanum and yttrium ions.

Table 1 presents the values of the degree of extraction of lanthanum ions by the hPAA:hP4VP intergel system. It can be seen that in the hPAA:hP4VP intergel pairs, the degree of sorption is much higher compared to individual hydrogels. This is due to the high degree of ionization of the starting polymers in the intergel system during their remote interaction as a result of mutual activation. The highest ionization of hPAA:hP4VP occurs at a ratio of 50 % hPAA – 50 % hP4VP, as a result of which the degree of extraction of lanthanum ions reaches maximum values (97.6 %).

Table 1

**Degree of extraction of lanthanum ions with hydrogels PAA, P4VP**

$\tau$ , h	$\eta(\text{La})$ , %						
	hPAA:hP4VP, %						
	100	83:17	67:33	50:50	33:67	17:83	100
0	0	10.2	10.2	9.4	9.4	0	3.7
0.5	10.2	19	25.4	21.4	13.4	12.6	13.4
1.5	25.4	22.2	13.4	26.2	18.2	9.4	19
2.5	30.2	22.2	28.6	26.2	21.4	18.2	7
4.5	39.9	30.2	28.6	49.5	27.8	14.2	8.6
24	59.8	67.1	67.1	97.6	56.7	37.5	27.8

Table 2 shows the values of the degree of extraction of lanthanum ions by the hPAA: hP4VP intergel system. The highest ionization of hPAA:hP4VP occurs at a ratio of 33 % hPAA – 67 % hP4VP, as a result of which the degree of extraction of yttrium ions reaches maximum values (26.9 %).

Table 2

**Degree of extraction of yttrium ions with hydrogels PAA, P4VP**

$\tau$ , h	$\eta(\text{Y})$ , %						
	hPAA:hP4VP, %						
	100	83:17	67:33	50:50	33:67	17:83	100
0	37	22	10.2	9.4	9.4	0	3.7
0.5	6.4	13.3	14.5	3.2	26.9	4.9	2.6
1.5	24.3	10.3	17.3	13.1	17.3	13.1	9.2
2.5	24.3	10.3	11.7	13.1	17.3	13.1	9.2
4.5	13.6	9.9	2.1	3	4.6	4.5	3.6
24	18.1	15.1	13.6	1.6	21.1	13.6	13.6

### Conclusions

Based on the obtained data on the electrical conductivity, pH, and swelling coefficient, we can conclude that sorption of lanthanum ions by polymer hydrogels occurs. When the molar ratio of hPAA: hP4VP hydrogels is equivalent, the intergel system has the highest sorption ability with respect to lanthanum ions in

comparison with the initial hydrogels. The maximum degree of binding of the polymer chain to yttrium ions is manifested when the ratio of hPAA:hP4VP = 33 %:67 %. The mutual activation of hPAA and hP4VP hydrogels in the intergel system allows one to achieve a significantly higher degree of sorption for the intergel pair than for individual hydrogels. As can be seen from the data obtained, most of the lanthanum is recovered within 24 hours. In this case, the highest sorption occurs at the ratios of 67 % hPAA – 33 % hP4VP and 33 % hPAA – 67 % hP4VP, 67.1 and 56.7 % of lanthanum are recovered, respectively. The largest amount (97.6 %) of lanthanum is recovered at a ratio of 50 % hPAA – 50 % hP4VP at 24 h [10–13].

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## Полиакрил қышқылы мен поли-4-винилпиридин гидрогельдері негізіндегі интергельді жүйеден иттрий мен лантанды алу ерекшеліктері

Гидрогельдердің сорбциялық белсенділігі мен селективтілігін болжау үшін интергельді жүйедегі полимерлік торларды өзара активтендірудің әсері зерттелген. Зерттеу объектісі ретінде полиакрил қышқылының гидрогелі (гПАК) және поли-4-винилпиридиннің (гП4ВП) гидрогелі таңдалды. Интергельді жүйенің рН, электр өткізгіштігі гравиметриялық өлшеу әдістерімен анықталды. Сондай-ақ сулы ортада интергельді жүйемен  $\text{La}^{3+}$  және  $\text{Y}^{3+}$  иондарының өзара активациясы зерттелді. Ең жоғары электр өткізгіштік 24 сағаттан кейін орын алды. Электр өткізгіштігінің ең төменгі мәндері гПАК:гП4ВП = 0:6 интергельді жүйесінде

байқалған. Ол интергельді жүйенің әлсіз диссоциациясымен байланысты. гПАК:гП4ВП интергельді жүйесінде сутегі иондарының концентрациясының ұлғаюы гПАК:гП4ВП = 5:1 арақатынасында көрінген. Зерттелген гидрогельдердің қашықтықтан өзара әрекеттесуі нәтижесінде олардың электрохимиялық және конформациялық қасиеттерінің айтарлықтай өзгеруіне әкеліп соқтыратыны және өзара активтендіру жүргізілгені анықталды. Егер біз осы деректерді электр өткізгіштігі туралы деректер бойынша салыстырсақ, бұл ретте карбоксилді топтардың диссоциациясы процесі протондардың винил пиридинге қосылу процесінен басым болады деген қорытынды жасауға болады. Қышқылдық және негіздік гидрогельдердің белгілі бір арақатынасында бастапқы гидрогельдермен салыстырғанда лантан және иттрий иондарының сорбциясының айтарлықтай өсуі байқалған. Бұл нәтижелер лантан және иттрий иондарының айналасында оңтайлы лигандты ортаны қамтамасыз ететін оңтайлы конформациясы бар иондалған құрылымдардың пайда болуын көрсетеді.

*Кілт сөздер:* интергельді жүйе, полиакрил қышқылы, поли-4-винилпиридин,  $\text{La}^{3+}$  ионы,  $\text{Y}^{3+}$  ионы, сорбция, десорбция.

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## Особенности извлечения иттрия и лантана интергелевой системой на основе гидрогелей полиакриловой кислоты и поли-4-винилпиридина

Для прогнозирования сорбционной активности и селективности гидрогелей было исследовано влияние взаимной активации полимерных сеток в интергелевой системе. В качестве объекта исследования была выбрана интергелевая система «гидрогель полиакриловой кислоты (гПАК) – гидрогель поли-4-винилпиридина (гП4ВП)», которая изучалась на расстоянии через объем растворителя при отсутствии непосредственного контакта между полимерными сетками. Интергелевые системы были изучены методами измерения электропроводности, pH и гравиметрии. Также рассмотрена взаимная активация ионов  $\text{La}^{3+}$  и  $\text{Y}^{3+}$  с интергелевой системой в водной среде. Зависимость удельной электропроводности от молярного соотношения гидрогелей во времени, увеличение электропроводности происходит при соотношении гПАК:гП4ВП = 5:1 на протяжении всего времени удаленного взаимодействия. Максимальная электропроводность была достигнута через 24 ч. Минимальные значения электропроводности отмечены в области интергелевой системой гПАК:гП4ВП = 0:6, что связано с его слабой диссоциацией. Зависимость концентрации ионов водорода гПАК:гП4ВП, увеличение концентрации ионов водорода происходит при соотношении гПАК:гП4ВП = 5:1. Установлено, что в результате дистанционного взаимодействия изучаемых гидрогелей происходит их взаимная активация, приводящая к значительному изменению их электрохимических и конформационных свойств. Эти результаты указывают на возникновение ионизованных структур с оптимальной конформацией, обеспечивающих оптимальное лигандное окружение вокруг ионов лантана и иттрия.

*Ключевые слова:* интергелевая система, полиакриловая кислота, поли-4-винилпиридин, сорбция, десорбция, ионы  $\text{La}^{3+}$ , ионы  $\text{Y}^{3+}$ .

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## **Poly(propylene fumarate phthalate) and acrylic acid radical copolymerization constants and parameters**

Poly(propylene fumarate phthalate) and acrylic acid radical copolymerization in dioxane solution at various molecular ratios of original monomeric mixture was studied in this work for the first time. An unsaturated polyester resin was obtained using the polycondensation reaction. The composition of the obtained poly(propylene fumarate phthalate) was determined according to elemental analysis. The studied copolymers are promising for further study due to their swelling ability, antioxidant activity, and biodegradable ability. Copolymerization reaction kinetics has been studied. The composition of the copolymers was determined using chromatemass spectrometry. Radical copolymerization constants and parameters have been calculated by Mayo-Lewis integral method. Based on the copolymerization constants the Q-e parameters was calculated according to the Alfrey-Price equation. It was proved that non-solvable polymers of a net-shaped structure are formed in the whole range of the researched comonomer ratios during the radical copolymerization of p-PFF with AA. Based on the results presented in the article, we can say that all copolymer compounds based on poly(propylene fumarate phthalate) and acrylic acid demonstrate the ability to control physical and chemical properties. This in turn will allow to create new materials with a pre-defined behavior program. It was found that the unsaturated polyester resin is characterized by a lower reactivity in case of acrylic acid and poly(propylene fumarate phthalate) copolymerization.

**Keywords:** poly(propylene fumarate phthalate), acrylic acid, biodegradable, polycondensation, radical copolymerization, kinetics, copolymerization.

### *Introduction*

Over the past few decades fumaric acid-based polyesters comprising Krebs cycle [1, 2] are of much interest in biomedicine due to great biocompatibility and biodegradability [3, 4]. Moreover, polyester resins are relatively cheap products, which in some cases makes materials based on them competitive comparing to other sorts of plastics [5–8].

Poly(propylene fumarate phthalate) is the most researched material among the. It is a perfect option for cross-linking with various monomers, such as acrylic and methacrylic acid.

Cross-linked poly(propylene fumarate phthalate) can satisfy a number of medical requirements, such as biocompatibility, osteoconductivity, sterilisability and manageability [9–14]. It can be polymerized in situ [15] forming solid composite with mechanical properties identical to those of spongy bone.

In this regard, the poly(propylene fumarate phthalate) (p-PFF) and acrylic acid (AA) copolymerization constants and parameters determination, as well as the development of new methods for vinyl monomers radical polymerization control and polymer characteristics improvement are one of research priorities for high-molecular compounds chemistry development.

External factors sensitive copolymers were previously synthesized by reaction of polyglycolefumarates radical copolymerization with various unsaturated carboxylic acids and dimethylaminoethyl metacrylate [16–21]. Due to this fact, further research in this area appeared to be advantageous.

Reactions of poly(propylene fumarate phthalate)(p-PFF) and acrylic acid (AA) radical copolymerization were studied in this work for the first time.

### *Experimental*

Initial p-PFF was received by fumaric acid, phthalic anhydride and propylene glycol polycondensation at temperatures 423–453 K [22, 23]. The reaction was monitored by determining the acid number and the amount of water emission. The synthesized polyester is a light yellow fusible resinous substance that can dissolve in chloroform and dioxane. Received resin was obtained from original monomers by multiple acetone washing. Received substance content was defined by elemental analysis data.

P-PFP molecular weight was determined by light scattering method at NACH 2100 AN nephelometer and by gel-permeation chromatography, which is 2272 and 2394 atomic mass units.

P-PFP and AA radical copolymerization was performed in solution of dioxane at different original copolymer molecular ratios with benzoyl peroxide (BP) as initiating agent at 333 K. Synthesized polymers were washed by dioxane and dried in vacuum multiple times in order to refine them from remaining unreacted monomers until reaching constant weight.

Contents of received copolymers were defined with potentiometric titration and by a highly efficient chromatograph LC-20 Prominence, Shimadzu (Japan) [24, 25]. In order to find amount of copolymers unreacted double bonds (degree of unsaturation) bromide-bromate method was used [26].

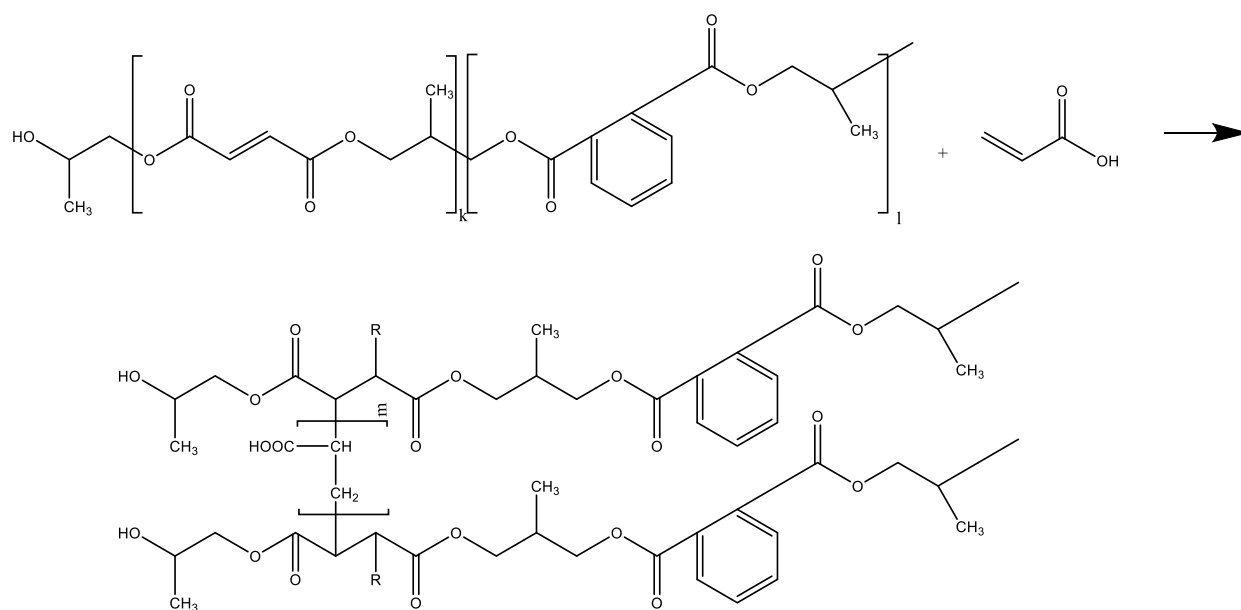
P-PFP and AA radical copolymerization kinetics was investigated by dilatometric method in dioxane. Constants of copolymerization  $r_1$  and  $r_2$  were defined based on contents of copolymers received at deep conversion using Mayo-Lewis integral equation [27].

### Results and Discussion

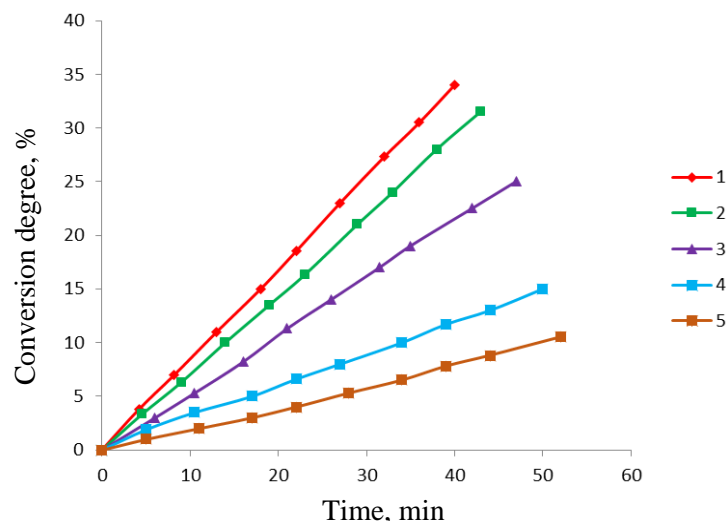
Elaborate development of thorough research in the area of radical copolymerization allows controlling properties of polymers, their structure and molecular mass, and also suggests more methods for producing polymers with the desired properties. As mentioned above, unsaturated polyesters-based products cured with vinyl monomers and having specific physico-chemical and mechanical properties are most desirable. Unsaturated double bonds in p-PFP molecules allow using it as polymeric matrix to receive cross-linked polymers in case of copolymerization with acrylic acid.

P-PFP was received by fumaric acid, phthalic anhydride and propylene glycol polycondensation [22, 23].

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



Copolymerization constant and parameters values are important characteristics when considering monomers relative reaction ability depending on their structure. However, more comprehensive information on monomers relative reaction ability at copolymerization can be obtained from kinetic data (Fig. 1).



1 — 6.77:93.23; 2 — 20.34:79.66; 3 — 44.17:55.17; 4 — 68.42:31.58; 5 — 86.67:13.33 mol.%

Figure 1. p-PFP:AA copolymerization kinetic graph

P-PFP and AA radical copolymerization kinetics at various initial molecular ratios was studied deeply in order to estimate monomers relative activity (Fig. 1). It was found that the reaction rate and copolymer yield increase with increasing AA content in the initial monomer mixture. However, these parameters decrease with increasing p-PFP in the reaction mixture. This seems to be determined by presence of  $-\text{COO}$  carboxyl functional group in acrylic acid chain, which can participate in reactions of polymer transfer followed by molecular mass growth due to branching processes. As can be seen in Figure 1, the radical copolymerization kinetics data indicate a constant process acceleration in the case of AA molecular mass increase in initial monomeric mixture.

As mentioned above, cross-linked insoluble polymers are formed throughout the range of studied copolymer ratios in process of p-PFP and AA radical copolymerization.

Experimental data received after studying radical copolymerization processes in p-PFP – AA systems are shown in Table 1. Copolymer yield ranges from 83 % to 62 %.

Table 1

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

Initial monomer ratio, % by mass		Copolymer content, % by mass		Yield, %
$M_1$	$M_2$	$m_1$	$m_2$	
10.22	89.78	6.77	93.23	83.70
25.00	75.00	20.34	79.66	78.73
50.00	50.00	44.17	55.17	79.33
73.91	26.09	68.42	31.58	71.93
90.00	10.00	86.67	13.33	62.09

As can be seen in Table 1, p-PFP-AA copolymers are enriched with AA components throughout the range of initial mixtures. At that, the proportion of AA components in the copolymer composition increases symbolically with respect to their content in initial monomeric mixture.

Copolymer yield and swelling rating increase as share in original AA mixture rises; this seems to be determined by high degree of branching and cross-linking.

The branching and cross-linking reactions decrease correspondingly with AA molecular concentration reducing since benzene rings cannot participate in homopolymerization reactions. While the copolymer unsaturation degree increases. Besides, the abovementioned reactions are more complicated when p-PFP concentration rises in initial monomeric mixture, which leads to higher viscosity.

Copolymer content dependence on initial mixture composition can be shown more conveniently on content diagram (Fig. 2).

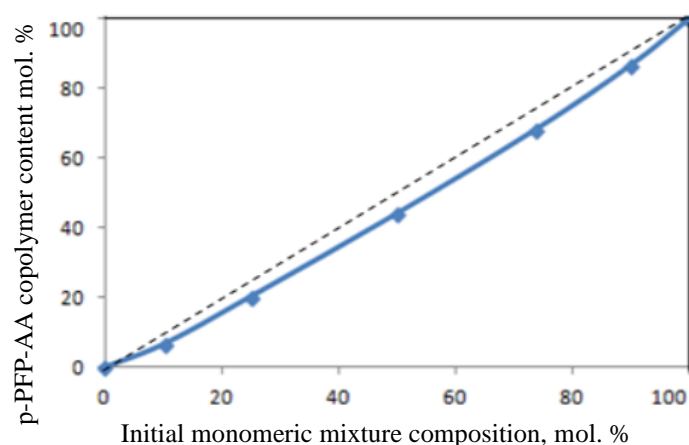


Figure 2. Composition diagram showing p-PFP – AA copolymer content dependence on initial monomeric mixture composition

Copolymer relative activity based on copolymer content and initial monomeric mixture composition has been calculated using Mayo-Lewis integral equation [9], Fineman-Ross and Kelen-Tudos standard methods. Table 2 shows the calculated data that illustrate the higher AA activity in the process of radical copolymerization.

Table 2

**p-PFP – AA binary systems radical copolymerization constants and parameters**

$M_1$	$M_2$	$r_1$	$r_2$	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$	$Q_1$	$e_1$	$Q_2$	$e_2$
p-PFP	AA	0,76	1,21	0,92	1,32	0,83	1,19	1,06	1,15	0,77

As can be seen in Table 2, the relative activity value  $r_1$  in p-PFP-AA system is below one ( $r_1 < 1$ ). This suggests a higher activity of macroradical ending with p-PFP component towards «outer» monomer or radicals, but macroradical ending with AA second co-monomer component tends to react with «inner» monomer. Copolymerization stabilizer derivatives are close to each other, i.e. copolymer macroradicals can be created by static structures.

### Conclusions

Therefore, a brief summary of the studies described in this article shows that new crosslinked polymers can be obtained by poly(propylene fumarate phthalate) and acrylic acid radical copolymerization.

The obtained result demonstrates the ability to control the physicochemical properties of a poly(propylene fumarate phthalate) and acrylic acid based copolymer by changing the content of the polymer composition, which allows you to create new materials with preset properties.

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## **Полипропиленфумаратфталатты акрил қышқылымен радикалды сополимерлеудің константалары мен параметрлері**

Мақалада алғаш рет полипропиленфумаратфталаттың бастапқы мономерлік қоспаның түрлі мольдық қатынасында диоксан ортасында акрил қышқылымен бинарлы радикалды сополимерленуі зерттелген. Поликонденсация реакциясымен қанықпаған полиэфирлі шайыр алынды. Сополимерлену үрдісінің кинетикасы зерттелді. Хромато-масс спектроскопия әдісін қолдану арқылы синтезделген сополимерлердің құрамы нақтыланған. Майо-Льюистің интегралдық әдісімен радикалды сополимерлену константалары мен параметрлері анықталған. Алфрей-Прайс теңдеуі бойынша сополимерлену константасының негізінде Q-е параметрлері есептелген. п-ПФФ пен АҚ радикалды сополимерлеу кезінде сомономерлердің зерттелген ара қатынасының барлық интервалында торлы құрылымның ерімейтін полимерлері

түзілетіндігі дәлелденді. Мақалада келтірілген нәтижелер бойынша полипропиленфумарат пен акрил қышқылы негізіндегі сополимерлердің барлық қосылыстары физика-химиялық қасиеттерді басқару мүмкіндігін көрсетеді деп айтуға болады. Бұл өз кезегінде алдын ала берілген бағдарлама тәртібі бойынша жаңа материалдарды жасауға мүмкіндік береді. Акрил қышқылын полипропиленфумаратфталатпен сополимерлеу кезінде қанықпаған полиэфир шайыры аз реакциялық қабілеттілікпен сипатталған.

*Кілт сөздер:* полипропиленфумаратфталат, акрил қышқылы, биоыдырағыштық, поликонденсация, радикалды сополимерлену, кинетика, сополимерлену.

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### Константы и параметры радикальной сополимеризации полипропиленфумаратфталата с акриловой кислотой

В статье впервые исследована бинарная радикальная сополимеризация полипропиленфумаратфталата с акриловой кислотой в растворе диоксана при различных мольных соотношениях исходной мономерной смеси. Реакцией поликонденсации получена ненасыщенная полиэфирная смола. Состав полученного полипропиленфумаратфталата устанавливали по данным элементного анализа. Исследованные сополимеры перспективны для дальнейшего изучения их набухающей способности, антиоксидантной активности, биodeградируемой способности. Исследована кинетика реакции сополимеризации. Состав сополимеров определен с помощью хромато-масс-спектропии. Параметры радикальной сополимеризации и константы рассчитаны интегральным методом Майо-Льюиса. Параметры Q-е рассчитаны на основании констант сополимеризации по уравнению Алфрей-Прайса. Было доказано, что нерастворимые полимеры сетчатой структуры во всем интервале исследованных соотношений сомономеров образуются при радикальной сополимеризации п-ПФФ с АК. По приведенным в статье результатам можно заключить, что все соединения сополимеров на основе полипропиленфумаратфталата и акриловой кислоты демонстрируют возможности управления физико-химическими свойствами. Это, в свою очередь, позволит создать новые материалы с заранее заданной программой поведения. Установлено, что при сополимеризации полипропиленфумаратфталата с акриловой кислотой ненасыщенная полиэфирная смола характеризуется меньшей реакционной способностью.

*Ключевые слова:* полипропиленфумаратфталат, биodeградируемость, акриловая кислота, поликонденсация, радикальная сополимеризация, кинетика, сополимеризация.

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## Study of acid properties of new polymeric complexes of maleic acid polymethylvinyl ether cross-linked by polypropylene glycol

Dissociation course of polymethylvinyl ether of maleic acid cross-linked by polypropylene glycol (PMVE-MA with PPG) was investigated using classical potentiometric titration and colloid titration. It is assumed, that in the course of colloid titration monovalent counter-ions are replaced by the oppositely charged polycation, therefore it was determined the general concentration of anionic groups of hydrogel of polymethylvinyl ether of maleic acid cross-linked by polypropylene glycol. The apparent constant of dissociation (pseudo constant of dissociation) depends on the forming of the polyelectric complex but does not depend on the degree of dissociation. While it is known that potentiometric titration are determined by the apparent constant of dissociation that decreased simultaneously with the increase of the dissociation degree. Protons releasing from acid groups of hydrogel of polymethylvinyl ether of maleic acid cross-linked by polypropylene glycol leads to the formation of the complex with stronger cationic polyelectrolyte. Therefore, comparison of the results of potentiometric and colloid titration makes it possible to take in the information about the interrelation of acid characteristics of the surface of PMVE-MA with PPG and its functional properties. As a result we can define its application area for creation of new high-efficient composite material.

**Keywords:** polyelectrolyte, colloid titration, potentiometric titration, dissociation, hydrogel.

### Introduction

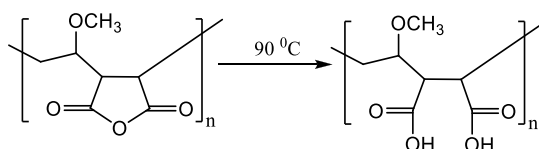
In recent decades hydrogels are widely used for producing the composite materials, filtering elements for liquid and gaseous mediums, adsorbents used for cleaning the water from heavy and toxic metals and gathering the oil and oil-product, carriers of nanoparticles of different nature [1]. Their application area depends on physical and chemical compositions of polymers, and structural and acid-base surface characteristics of polymers [2]. It is necessary know the protolytic properties of polymer surfaces, the origin and the number of active sites for the determination the degree of adsorption activity and selectiveness of polymer materials. Inhomogeneity and high degree of dispersion of these materials make it more difficult to control the surface adsorptive and acid-base properties of polymer with the use of the method of surface analysis (the study of moistening (wetting) phenomenon by the use of test liquids).

At the present day adsorptive-chemical method mainly used for the defining surface acidity of finely dispersed materials [3]. This method is practically not used for the study of polymer materials surface. Considering that active sites of hydrogel surfaces are characterized with weak protolytic properties, it will be reasonable to use methods of potentiometric and colloid titration in non-aqueous or mixed solvents in order to estimate their quantity and values of pK (these methods are capable to strengthen donor-acceptor properties).

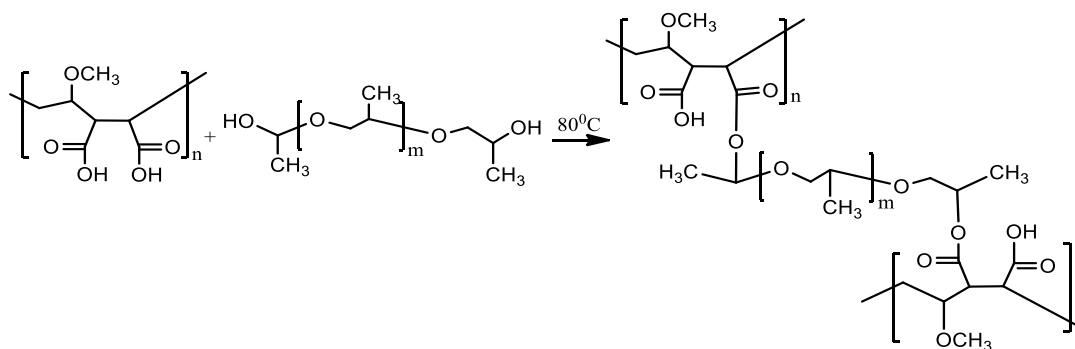
The article is devoted to the experimental evaluation of apparent constant of dissociation (pseudo constant of dissociation) (pK) of hydrogel of PMVE-MA with PPG in water and aqueous organic media by the use of potentiometric and colloid titration.

### Experimental

Hydrogel of polymethylvinyl ether of maleic acid, cross-linked by polypropylene glycol (PMVE-MA with PPG) was used as the object of the research:



Poly(methyl-vinyl-co-maleic acid) or polymethylvinyl ether of maleic acid (PMVE-MA) were obtained by the hydrolysis of polymethylvinyl ether of maleic anhydride (PMVE-MAH). Process was performed on the unit composed of round-bottomed flask (volume 100 ml) and backflow condenser. Initial mixture was prepared from 0.65 g PMVE-MAH and 20 ml distilled water. Hydrolysis was carried out during 2 hours at 90 °C. Aqueous solution of polypropylene glycol (PPG) was gradually added into obtained solution of polymethylvinyl ether of maleic acid (PMVE-MA) up to obtaining the homogeneous mixture. Excess water was removed by the use of rotary evaporator. Reaction mixture was solidified 24 hours at 80 °C. The gel of PMVE-MA with PPG [4] was obtained as a result of the esterification reaction among polymethylvinyl ether of maleic acid and polypropylene glycol:



Potentiometric titration of hydrogel of PMVE-MA with PPG was performed in water and aqueous organic media 0.05 M using the NaOH solution in the presence of 0.1 M NaCl accurate within 0.001 units of pH. The titration was carried out using «I-160MI» ionomer with the function of push-button controlled mixing. The temperature was kept constant at 22 °C. Ethyl alcohol and acetone were chosen as organic solvents for the purpose of intensification of acidic sites. These solvents are characterized by the more distinctive basic properties than water and their acidity scale span is longer (ethanol 19.5; acetone 32.5) and consequently the discriminating fineness (differentiating ability) is greater. Mixed solvent «water – ethyl alcohol» (70 % by ethanol weight), «water – acetone» (70 % by acetone weight) is the most perspective solvent for the study the slightly acidic properties of carbonaceous resin (carboxylic cation exchange resin).

Colloid titration of hydrogel of PMVE-MA with PPG 0.05 M was performed by the use of NaOH solution in the 0.1 M NaCl presence.

The curves of potentiometric and colloid titration and the dependency of  $pK_a$  on the degree of dissociation  $\alpha_D$  for hydrogel of PMVE-MA with PPG were obtained.

### Results and Discussion

With the aim to study the process of dissociation of polymethylvinyl ester of maleic acid, linked with polypropyleneglycole, we obtained the curves of potentiometric and colloid titration and dependence of  $pK_a$  on the degree of dissociation  $\alpha_D$  for hydrogel.

The dependency of the dissociation degree  $\alpha_D$  of hydrogel of PMVE-MA with PPG in neutral medium ( $\alpha_N = 0.96$ ) on the polymer concentration  $c_p$  are presented in Figure 1. The degree of weak acid dissociation  $\alpha_D$  was defined according to the equation 1:

$$\alpha_D = \frac{c_{A^-}}{c_{A^-} + c_{HA}} \quad (1)$$

As can be seen in Figure 1, the dissociation level of the acid is decreased in presence of organic solvents, which is confirmed with constant values of autoprotolysis of these solvents (ethanol, acetone), as well as with values of dipole moment and dielectric capacity.

Dissociation of hydrogel of polymethylvinyl ester of maleic acid, linked with polypropyleneglycole, was studied by method of potentiometric titration as well (Fig. 2, a, b and c).

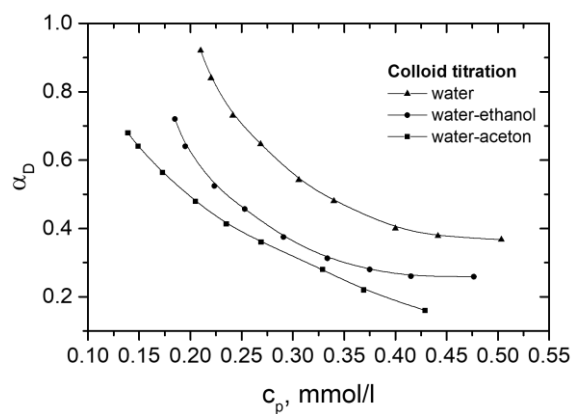
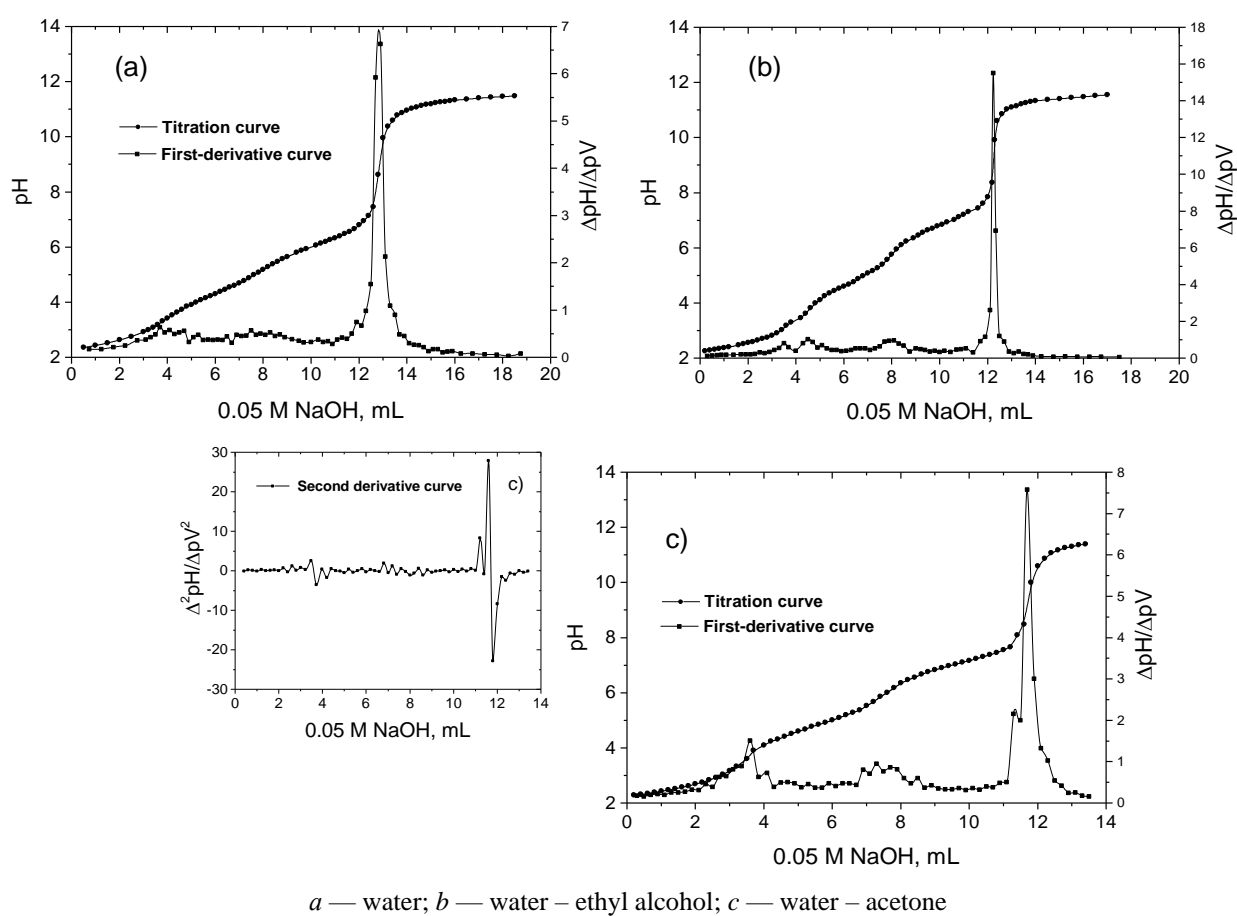
Figure 1. Dependence of dissociation level  $\alpha_D$  on polymer concentration  $c_p$ 

Figure 2. Integral and differential curves of titration of hydrogel of PMVE-MA with PPG in the presence of NaCl electrolyte, across different environments

According to the literature data water, acetone and ethanol have the following values of dipole moment ( $\mu$ , D) and dielectric permeability ( $\epsilon$ ) [5] (at 20 °C) (Table 1):

Table 1

## Dipole moment and dielectric permeability

Solvent	$\mu$ , D	$\epsilon$
Water	1.8	78.5
Ethanol	1.7	24.3
Acetone	2.7	20.7

Figure 2a presents the titration curve of hydrogel of PMVE-MA with PPG, which functional groups are entirely protonated by the solvent of sodium hydroxide in aqueous media. As can be seen in Figure 2a, the differential curve has poorly resolved jumps of titration. The same dependency was obtained for the titration curves of hydrogel in water-ethanol mixtures (Fig. 2b). Replacing ethanol in the water-organic mixture to acetone being the less polar solvent we obtain the titration curves (Fig. 2c) that significantly differ, in the case of using the most polar solvent jump of titration will be sharper.

Addition of organic solvents decreases the level of dissociation, and thus charge quantity of macromolecule is decreased as well, and its shape is changed to nodular one. Here is cumulative effect in increase of availability of ionogenic groups and decrease of steric factor.

Observed indexes pH are graphically determined depending on neutralization degree  $\alpha_N$ , which has been calculated according to the equation 2:

$$\alpha_N = \frac{c_{NaOH}}{c_p}, \quad (2)$$

where  $c_{NaOH}$  is the concentration of added titrating solution, and  $c_p$  is the concentration of polymer in functional groups equivalent.

Both types of concentration are adjusted taking into dilution procedure. Taking into the consideration the simultaneous change of the titration curves and the decrease of ionic strength, it was assumed that there is the influence of electrostatic interaction (Coulomb interaction) as it was noted by authors of the work [6].

The degree of dissociation  $\alpha_D$  was estimated according to the equation 3:

$$\alpha_D = \alpha_N + \frac{c_{H_3O^+} - c_{OH^-}}{c_p}, \quad (3)$$

where  $\alpha_N$  is the neutralization degree and  $c_p$  is the total concentration of hydrogel of PMVE-MA with PPG in functional groups equivalent.

Concentration of hydroxonium  $c_{H_3O^+}$  was obtained from measured pH. Concentration of hydroxide  $c_{OH^-}$  was estimated using this value from ionic product of water  $K_w$  ( $K_w = 1.01 \times 10^{-14} \text{ mol}^2/\text{L}^2$  at 22 °C).

On the titration curves (Fig. 3) we can see the jumps corresponding to double-stage dissociation of hydrogel of PMVE-MA with PPG. The degree of dissociation  $\alpha_D$  increases along with growth of pH.

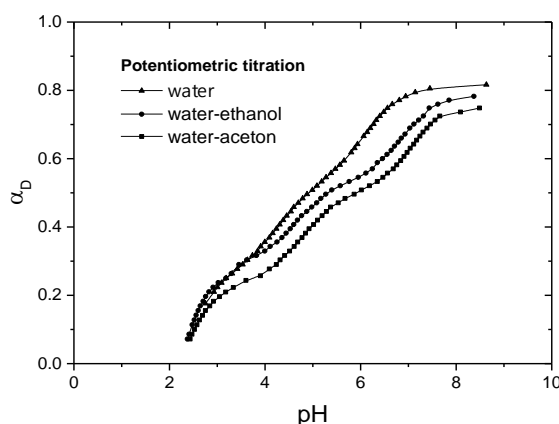


Figure 3. Dependence pH on the neutralization degree  $\alpha_N$  of hydrogel of PMVE-MA with PPG in the presence of 0.1 M NaCl determined by the potentiometric titration

In Figures 4 and 5 experimental data of potentiometric titration of hydrogel of PMVE-MA with PPG were presented as the functions of apparent constant of dissociation (pseudo constant of dissociation) pK on the degree of dissociation  $\alpha_D$ . They were calculated according to Henderson-Hasselbach equation (equation 4) at the values of dissociation degree  $\alpha_D$  ( $0 \leq \alpha_D \leq 1$ ) and according to Lifson-Katchalsky theory (equation 5).

$$pK = pH - \log \frac{\alpha_D}{1 - \alpha_D}; \quad (4)$$

$$pK = pK_0 + \Delta pK(\alpha_D), \quad (5)$$

where  $K_0$  — ionization constant of functional groups of the polymer, and  $\Delta pK(\alpha_D)$  represents the contribution of electrostatic interaction (Coulomb interaction) of functional groups. It can be determined using the integration of the area under the curve  $pK - f(\alpha)$ .

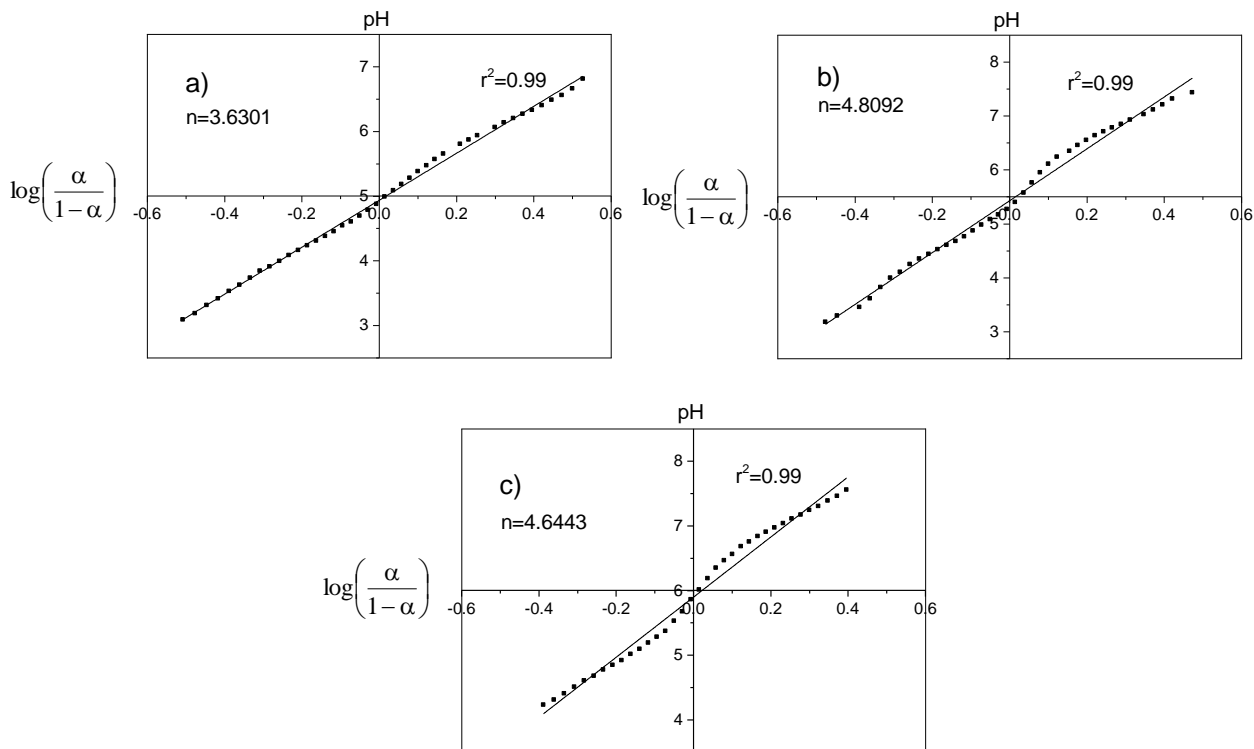


Figure 4. Curves of Henderson-Hasselbalch for potentiometric titration of hydrogel PMVE-MA with PPG in presence of electrolyte NaCl, in different media: a) water; b) water-ethyl alcohol; c) water-acetone

The apparent constant of dissociation (pseudo constant of dissociation)  $pK$  for hydrogel of PMVE-MA with PPG depends on the degree of dissociation  $\alpha_D$  evaluated according to the data of potentiometric and colloid titration (Fig. 5).

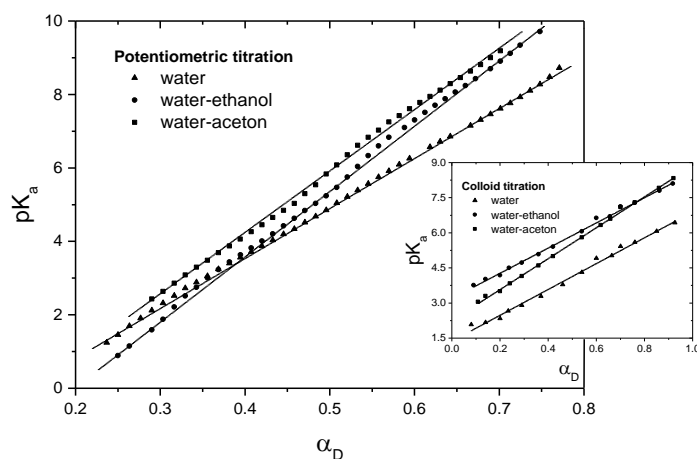


Figure 5. Dependency  $pK$  on the degree of dissociation  $\alpha_D$  for hydrogel of PMVE-MA with PPG in the presence of NaCl obtained by the potentiometric and colloid titration

Consequently, surface acid sites of hydrogel of PMVE-MA with PPG can be identified as carboxylic groups. This is confirmed by the results of IR-spectroscopy of hydrogel of PMVE-MA with PPG. In infra-red spectrum



absorption bands have been found in the areas of  $1712\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$ . They are corresponding to valent asymmetrical and symmetrical oscillations (vibrations) of carboxylic group  $\text{C}=\text{O}$  [7].

The aim of the research was the definition of apparent constant of dissociation (pseudo constant of dissociation)  $K^{\#}$  of hydrogel of PMVE-MA with PPG according to the experimental data of colloid titration. For this purpose it was performed the computation according to equation system used for mathematical processing of the titration curves of the monobasic weak acid (HA) by (NaOH) strong base. Using these equations we determined the dissociation constant of weak acid according to mass action law (Guldberg and Waage's Law of Mass Action) (equation 6), ionic product of water (equation 7), condition of electrical neutrality (equation 8) and the expression for the mass balance (equation 9) [8, 9].

$$K_a = \frac{c_{H_3O^+} \cdot c_{A^-}}{c_{HA}}; \quad (6)$$

$$K_w = c_{H_3O^+} \cdot c_{OH^-}; \quad (7)$$

$$c_{H_3O^+} + c_{Na^+} = c_{OH^-} + c_{A^-}; \quad (8)$$

$$c_{A^-} + c_{HA} = c_p. \quad (9)$$

After the transformation we obtain the cubic equation:

$$c_{H_3O^+}^3 + c_{H_3O^+}^2(c_{Na^+} + K_a) + c_{H_3O^+}(c_{Na^+}K_a - c_pK_a - K_w) - K_aK_w = 0. \quad (10)$$

As  $c_{H_3O^+}^3 \gg K_aK_w$  then the equation takes the following form:

$$c_{H_3O^+} = -\frac{c_{Na^+} + K_a}{2} + \sqrt{\left(\frac{c_{Na^+} + K_a}{2}\right)^2 - K_a(c_{Na^+} + c_p) + K_w}. \quad (11)$$

Replacing  $c_{Na^+} = \alpha_N \cdot c_p$  we obtain the dependence:

$$c_{H_3O^+} = -\frac{\alpha_N c_p + K_a}{2} + \sqrt{\left(\frac{\alpha_N c_p + K_a}{2}\right)^2 - K_a c_p (1 - \alpha_N) + K_w}. \quad (12)$$

The degree of dissociation  $\alpha_D$  for hydrogel of PMVE-MA with PPG and the apparent constant of dissociation (pseudo constant of dissociation)  $K_a$  depending on  $c_p$  and  $\alpha_N$  were estimated according to the equations 12 and 3 (Table 2).

Table 2

Value of  $pK_a$  and  $n$  for hydrogel PMVE-MA with PPG at  $t = 25\text{ }^\circ\text{C}$  in different media

Solvent	$pK_a^{\#}$	$n$ (equat. 4)	$pK_a$
Water	$1.4 \pm 0.1$	3.6301	$1.8 \pm 0.1$
Water – Ethyl alcohol	$3.2 \pm 0.2$	4.8092	$3.4 \pm 0.1$
Water – Acetone	$2.3 \pm 0.1$	4.6443	$2.5 \pm 0.2$

Calculated values  $pK_a^{\#}$ ,  $pK_a$  and  $n$  are represented in the Table 2. As can be seen, obtained results comply with each other well.

### Conclusions

Dissociation indexes of the hydrogel of PMVE-MA with PPG were determined by the potentiometric titration in water and water-organic medium. Index of apparent constant of dissociation (pseudo constant of dissociation)  $pK$  depends on the change of dissociation degree  $\alpha_D$  for the studied polymer. It was necessary to extrapolate  $pK$  and  $\alpha_D = 0$  for the purpose of determination of  $pK_0$ .

Contrary to data of potentiometric titration, the apparent constant of dissociation (pseudo constant of dissociation)  $pK^{\#}$  was determined by the use of colloid titration with the oppositely charged polycation is essentially independent of the degree of dissociation  $\alpha_D$ . In the case of the hydrogel of PMVE-MA with PPG

the results of colloid titration do not point on the presence of two different ionized groups. This is explained by the fact that in the process of titration the monovalent counter-ion entirely replaced into polycation. Therefore we can measure the general concentration of polyacids anionic groups in hydrogel. Using the dissociation constants determined by the colloid titration, it becomes possible to determine the degree of dissociation and properly the charge of hydrogel of PMVE-MA with PPG for the wide spectrum of concentrations and neutralization degree in the case if there will be the oppositely charged macromolecules or surfaces in them. This has importance for the practical use of hydrogels if there is the replacement of counter-ions (for example, in adsorption process).

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## Полипропиленгликольмен тігілген, малеин қышқылының полиметилвинилді эфирінің жаңа полимерлік кешендерінің қышқылдық қасиеттерін зерттеу

Полипропиленгликольмен тігілген, малеин қышқылының полиметилвинил эфирінің (ППГ-мен ПМВЭ-МҚ) диссоциациясының барысы мынадай әдістермен зерттелді: классикалық потенциометриялық титрлеу және коллоидтық титрлеу. Коллоидты титрлеу барысында бірвалентті кері иондар қарсы зарядталған поликатионмен ауыстырылды, осылайша полипропиленгликольмен тігілген малеин қышқылының полиметилвинил эфирінің негізіндегі гидрогелінің аниондық топтарының жалпы концентрациясы анықталды. Диссоциацияның көрінетін константасы бұл ретте полиэлектрлік кешеннің қалыптасуына байланысты болады, алайда диссоциация дәрежесіне байланысты емес. Бұл орайда потенциометриялық титрлеу диссоциация деңгейінің өсуімен бір мезгілде азайтылатын диссоциацияның көрінетін константасын анықтауға болатыны белгілі. Полипропиленгликольмен тігілген, малеин қышқылының полиметилвинил эфирінің қышқылы негізіндегі гидрогельдің қышқылдық топтарынан протондарды босату қатты катионды полиэлектролиті бар кешенді қалыптастыруға алып келді. Осылайша, потенциометриялық және коллоидтық титрлеу нәтижелерін салыстыру ППГ-мен тігілген ПМВЭ-МҚ беттерінің қышқылдық сипаттамаларының және оның функционалдық қасиеттерімен өзара байланысы туралы ақпарат алуға мүмкіндік береді. Осының арқасында жаңа, тиімділігі жоғары композициялық материалдарды жасау мақсатында оны қолдану аймағын анықтау мүмкіндігі ашылды.

*Кілт сөздер:* полиэлектролит, коллоидті титрлеу, потенциометриялық титрлеу, диссоциация, гидрогель.

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**Исследование кислотных свойств новых полимерных  
комплексов полиметилвинилового эфира малеиновой кислоты,  
сшитого полипропиленгликолем**

Ход диссоциации полиметилвинилового эфира малеиновой кислоты, сшитого полипропиленгликолем (ПМВЭ-МК с ППГ), был исследован методами классического потенциометрического титрования и коллоидного титрования. Предположено, что в ходе коллоидного титрования одновалентные противоионы заменяются противополюсно заряженным поликатионом, таким образом, определяется общая концентрация анионных групп гидрогеля полиметилвинилового эфира малеиновой кислоты, сшитого полипропиленгликолем. Кажущаяся константа диссоциации при этом зависит от формирования полиэлектрического комплекса, но не связана со степенью диссоциации. Как известно, потенциометрическим титрованием определяют кажущуюся константу диссоциации, которая уменьшается одновременно с ростом степени диссоциации. Высвобождение протонов из кислотных групп гидрогеля полиметилвинилового эфира малеиновой кислоты, сшитого полипропиленгликолем, приводит к формированию комплекса с более сильным катионным полиэлектролитом. Следовательно, сравнение результатов потенциометрического и коллоидного титрования позволяет получать информацию о взаимосвязи кислотных характеристик поверхности ПМВЭ-МК с ППГ и его функциональными свойствами. Благодаря этому открывается возможность определения области его применения для создания новых высокоэффективных композиционных материалов.

*Ключевые слова:* полиэлектролит, коллоидное титрование, потенциометрическое титрование, диссоциация, гидрогель.

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## **Change in the heat of D-glucose dissolution in water exposed to electromagnetic field**

The article is devoted to the study of the influence of weak electromagnetic fields of 90, 110 and 170 MHz frequency on water properties. The calorimetric measurement of the integral heat of dissolution of non-electrolyte ( $\alpha$ -D-glucose) was chosen as an indirect method to study the change in water properties. The heat of  $\alpha$ -D-glucose dissolution was measured in relation to field frequency for the first time. The results of calorimetric measurements of the thermal effects of the carbohydrate dissolution in field-exposed water compared with unirradiated are presented. The measurements were carried out with a Beckman thermometer. The dependence of the relative heat of  $\alpha$ -D-glucose dissolution on time after field exposure was established. A cumulative character takes place for the 90 MHz and 110 MHz frequencies. That is reflected in the gradual increase of endoeffect. The dependence has a maximum on the third day in the case of 170 MHz. A sharp change in the heat of dissolution was observed within three days for the 90 MHz and 110 MHz frequencies. Further a weak time dependence is registered after twenty days. In general, there is an increase in the endothermicity of the  $\alpha$ -D-glucose dissolution process. The assumption has been made that the hydration heat of a carbohydrate molecule in field-exposed water reduces due to the increased intermolecular interactions between water particles and weakened interactions between water particles and carbohydrate molecules.

*Keywords:* electromagnetic field, glucose, heat of dissolution, calorimetry, hydration, thermodynamics, carbohydrate solutions, frequency.

### *Introduction*

Interest in the impact of weak physical fields on different objects is increasing every year. This is primarily due to the fact that the density of such fields of artificial origin grows, covering the region of ever higher frequencies for communication and navigation and increasing the density of broadcasting on the previously used ranges. In this regard, it is interesting to study the problems of efficiency and effectiveness of field impact in various processes. Water and aqueous solutions is one of the common objects of influence. It is known that fields influence the properties of water and aqueous solutions. These effects are explained by a change in the energy of water molecules interaction in a liquid state, i.e. the change in the hydrogen bond energy. Earlier a method to quantify the change in the energy of hydrogen bonds due to the influence of a magnetic field by calorimetric estimation of the heat of solids dissolution was proposed [1].

Internal energy  $dU$  and enthalpy  $dH$  are the thermodynamic functions that describe intermolecular interactions. They are related by the equation  $dH = dU + pdV$ . The volume change is minimal within solution formation process, therefore the equality of internal energy and enthalpy can be assumed. The enthalpy of dissolution (or the thermal effect of dissolution at constant pressure) can be determined experimentally by the calorimetric method.

Previously, experiments have been conducted to measure the thermal effects of salt dissolution. Starting from the fundamental works of Klassen [2] it was shown that the heat of salts dissolution in magnetized and normal water is noticeably different. In an article [3], it was found that the thermal effect of dissolution for potassium chloride during water magnetization within eight hours changes by 25 %. The results on the change in the thermodynamic properties of crystalline hydrates grown from solutions exposed to low-power high-frequency (HF) electromagnetic fields in the range of 30–200 MHz are no less interesting [4]. The presented data shows a multidirectional effect depending on the field frequency. The explanation is based on the assumption of structural reorganization of water and water clusters and changes in the degree of ion hydration, which is also confirmed by experimental data on the measurement of the electrical conductivity of salt solutions in field-affected water [5].

However, a small number of experiments with the dissolution of non-electrolytes in field-exposed water are known to date. Thermal effects of propanol-1 — water mixing are presented in [6]. When using water exposed to a high-frequency electromagnetic field, the heats of mixing noticeably change both towards the

increase of thermal effect and towards its decrease depending on the field frequency. The changes in the heat of mixing are also dependent on the exposure time and the initial temperature. The authors assume that the observed phenomena occur due to the changes in the energy of interaction of propanol molecules with a structurally reorganized solvent.

In the above studies, we measured either the heat of mixing of two liquids or the heat of dissolution (dehydration) of inorganic salts. To supplement the experimental data, it is of interest to study the dependence of the dissolution enthalpy of a non-electrolyte solid in treated water on the frequency of high-frequency (HF) field.

Natural monosaccharides such as glucose are unique on their properties. Having a chiral atom in its structure and exhibiting optical activity, these molecules are characterized by high hydration capacity due to the presence of a large number of hydroxyl groups. There are other unique properties that ensure the cycle opening in aqueous solution and the conformational transformation of molecules of these carbohydrates [7]. The interest in the thermodynamics of carbohydrates aqueous solutions has not only exhausted, but has increased even more. One of the reasons is the fact that carbohydrate aqueous solutions serve as a good model of solvation interactions [8].

Carbohydrate molecules are bifunctional in relation to their hydration capacity. Hydration includes a specific hydrophilic hydration through the formation of hydrogen bonds between hydroxyl carbohydrate groups and water particles, as well as a specific hydrophobic hydration through intermolecular interactions between CH– and CH<sub>2</sub>– carbohydrate groups and water particles [8].

Application of molecular dynamics methods to aqueous solutions of  $\beta$ -D-glucose made it possible to model the structure of hydrogen bonds. Calculations showed that the hydrogen-bond network differs little from the network in the crystal structure [9]. It is assumed that when considering the interaction of water with carbohydrate molecules, it is necessary to take into account the complementarity of the geometry of the location of hydroxyl groups and the structural matrix of the solvent [8]. Franks [10, 11] first studied the problem of stereospecific hydration of carbohydrates. The specificity of hydration is determined by the ratio of the number of axial and equatorial hydroxyl groups with a preferred hydration of the latter [12]. According to Franks, hydration is ensured by a good agreement between the geometry of the equatorial OH-groups and the water matrix. The distance between the oxygen atoms in equatorial hydroxyls is 0.485 nm, which lies in the region of the second maximum of the radial function of water distribution (0.49 nm). This fact suggests that the carbohydrate molecule is embedded in the structure of the hydrogen bonds of the solvent [8]. It follows that when glucose dissolves, the dynamic structure of hydrogen bonds is perturbed and recovered, with some water particles being replaced by glucose molecules. In [13] it was assumed that after the dissolution of the carbohydrate the hydrogen-bond network is structured.

Given the above, the research was aimed at the study of changes in the heat of glucose dissolution in water exposed to high-frequency electromagnetic field of certain frequencies.

### *Experimental*

To estimate the changes in the intermolecular interactions of glucose and field-exposed water, we used the literature data on the integral heats of dissolution. According to these data, the thermodynamic characteristics of  $\alpha$ -D-glucose dissolution in water at 298.15 K are as follows:

$\Delta H^\circ = 11.028 \pm 0.017$  kJ/mol — integral heat of dissolution at infinite dilution;

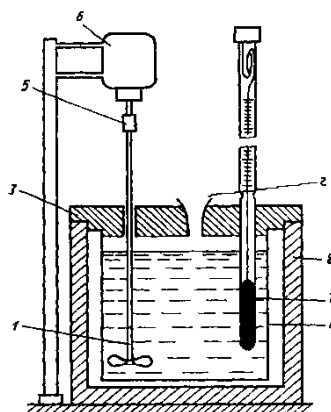
$T\Delta S^\circ = 18.1$  kJ/mol — entropy factor;

$\Delta G^\circ = 7.1 \pm 0.5$  kJ/mol — change in Gibbs dissolution energy.

The integral heat of  $\alpha$ -D-glucose monohydrate dissolution at infinite dilution is 19 kJ/mol [8].

The frequencies of the electromagnetic field of 90, 110 and 170 MHz were chosen as the most effective, based on previous studies in the field of water systems [15].

The G4-119A high-frequency generator was used to exert a field effect on water. A sample of deionized water was placed in an axial-type cell, the design of which is described in [15]. The cell was connected to a generator, which was used to set a certain frequency of HF field. The field exposure with a certain frequency lasted continuously for two hours. At the end of the field exposure, the water sample was either used immediately or placed in an airtight container and used at different time intervals after the field action. The measurements were carried out on a calorimetric setup, the scheme of which is shown in Figure 1.



1 — stirrer; 2 — hole for introducing a soluble substance; 3 — lid; 4 — inner coating;  
5 — stirrer fixing; 6 — motor; 7 — Beckman thermometer; 8 — outer coating

Figure 1. Scheme of calorimetric setup

For calorimetric measurements, we weighed 2.000 g of  $\alpha$ -D-glucose monohydrate accurate to 0.001 g and placed the sample in a control tube, afterwards the tube was weighed. A pipette was used to measure 100 ml of water, which was poured into a 400 ml porcelain beaker, which was then put into a calorimeter. Thereupon, we placed a tube with glucose and a Beckman metastatic thermometer through a hole 2. The control tube was kept in a calorimeter until a uniform variation of temperature over time was established. When the range of readings became uniform, we quickly emptied glucose out of the control tube through hole 2. After the start of the main period, the thermometer readings were recorded every 30 seconds. We completed the measurement when a uniform variation of temperature was established. The control tube was weighed, and the specified mass of dissolved glucose was calculated. The temperature drop corrected for heat exchange was found using the graphical method. A similar experiment was carried out with field-exposed water. Each experiment was repeated twice. The relative change in the dissolution enthalpy was calculated by the formula:

$$\Delta H_r = \frac{\Delta H_{ex} - \Delta H_c}{\Delta H_c} \cdot 100\%, \quad (1)$$

$\Delta H_r = \frac{\Delta H_{ex} - \Delta H_c}{\Delta H_c} \cdot 100\%$ , where  $\Delta H_r$  is the relative change in the heat of dissolution, %;  $\Delta H_{ex}$  is the heat of dissolution in field-exposed water, kJ/mol;  $\Delta H_c$  is the heat of dissolution in the control experiment (without field exposure), kJ/mol.

According to formulas 1–3, the data were reduced to the same mass of glucose sample:

$$\frac{\Delta H_{ex} \cdot m_{ex}}{M_g} = C \cdot \Delta T_{ex} \quad (2)$$

By subtracting (1) from (2), dividing the difference by (1) and performing the simplest transformations, we obtained:

$$\frac{\Delta H_{ex} - \Delta H_c}{\Delta H_c} = \frac{m_c \cdot \Delta T_{ex} - m_{ex} \cdot \Delta T_c}{m_{ex} \cdot \Delta T_c}, \quad (3)$$

where  $m_c$  is the mass of glucose in the control experiment;  $m_{ex}$  is the mass of glucose in the experiment with field exposure;  $C$  is the calorimeter constant, J/K;  $\Delta T_c$  — temperature change during dissolution in the control experiment K;  $\Delta T_{ex}$  — temperature change during dissolution in the experiment with field exposure;  $M_g$  is the molar mass of glucose monohydrate, g/mol.

Thus, there is no need to determine the calorimeter constant for each experiment, if we compare the heats of dissolution under control.

The heat of glucose dissolution was measured immediately after field action (0 days), on days 3, 11, and 21. We also used two water samples subjected to field effect 60 days ago (110 and 170 MHz) and 133 days ago (90 MHz).

### Results and Discussion

Obtained dependences of heat of glucose dissolution on time of water exposure (90, 110 and 170 MHz) are presented in Figures 2–4.

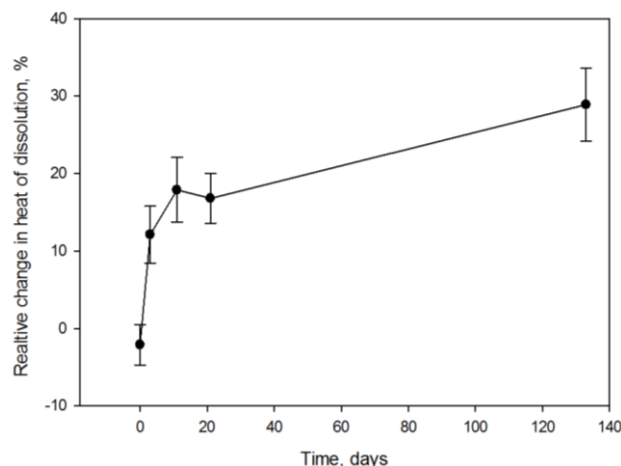


Figure 2. Dependence of heat of glucose dissolution on time of water exposure. Frequency of field exposure — 90 MHz

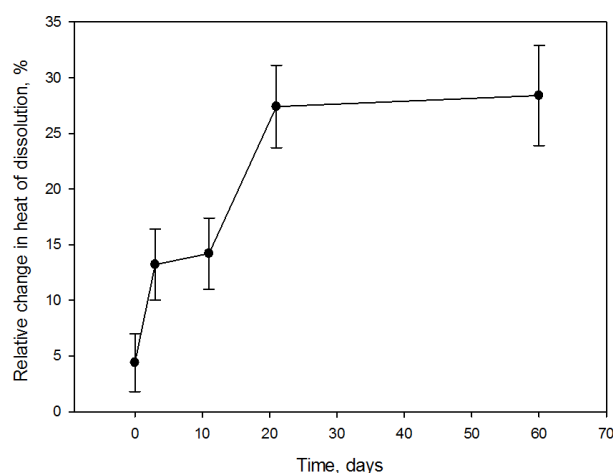


Figure 3. Dependence of heat of glucose dissolution on time of water exposure. Frequency of field exposure — 110 MHz

In all cases the dependence of the field effect on the time of water exposure is clearly observed. The heat of dissolution measured immediately after the field effect does not differ from the control one. For each of the frequencies, a sudden change in the heat of dissolution takes place on the third day after the exposure. The time dependence of the effect for the frequencies of 90 MHz and 110 MHz is similar: after the third week a «saturation» of the effect is observed, i.e. it becomes time-independent. For the 170 MHz frequency, there is an extreme dependence; the maximum is reached on the third day. Experimental data correlate with other data given in [14], which reports an increase in field effect during the week.

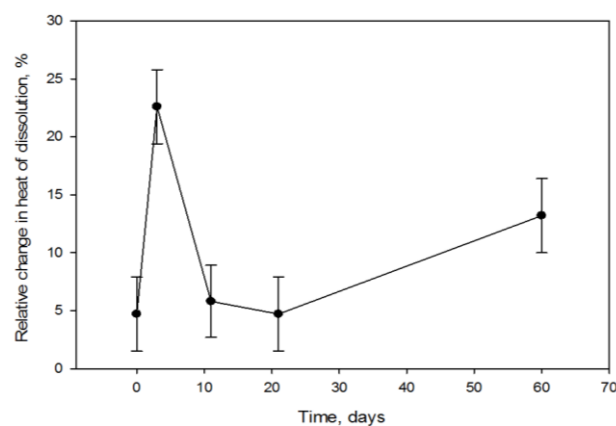


Figure 4 Dependence of heat of glucose dissolution on time of water exposure. Frequency of field exposure — 170 MHz

The solubility enthalpy can be represented as the sum of two opposite in sign components:

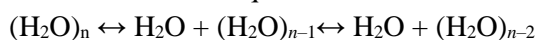
$$\Delta H_{\text{dissol}}^0 = \Delta H_{\text{cell}}^0 + \Delta H_{\text{hydrat}}^0, \quad (4)$$

where  $\Delta H_{\text{dissol}}^0$  is the dissolution enthalpy;  $\Delta H_{\text{cell}}^0$  is the enthalpy of the crystal lattice of glucose ( $> 0$ );  $\Delta H_{\text{hydrat}}^0$  is the hydration enthalpy ( $< 0$ ).

As can be seen from the literature data [8], the heat of  $\alpha$ -D-glucose dissolution is positive. It means that the energy of the crystal lattice prevails over the energy of hydration. The enthalpy of the crystal lattice can be considered constant in all calorimetric experiments, since only water was exposed to the field. Although we used the monohydrate, the heat of hydration cannot be considered equal to zero. An additional intermolecular interaction between water and glucose may occur.

In all cases (except for the first point in Figure 2), a change in the thermal effect towards endothermic values is observed. Based on Franks' assumption that a carbohydrate molecule is embedded in the solvent hydrogen bond network, we can assume an increase in the interactions of homogeneous particles: water — water and carbohydrate — carbohydrate. Additional hydration of the monohydrate occurs either to a lesser extent in the field-exposed water, or does not occur at all, or dehydration occurs. This correlates with a change in the heat value in a positive direction, i.e. the predominance of the energy of the crystal lattice over the energy of hydration.

Taking into account the existence of short-lived water molecules associates (clusters), formed by hydrogen bonds, we can assume that the HF field shifts the equilibrium:



which is characterized by the equilibrium constants  $K_1$  and  $K_2$ .

The values of the constants depend on the strength of interaction of the water molecule with the collective aggregate, which, in turn, essentially depends on the number of particles in the aggregate and the perfection of its structure. If, based on the data of some researchers [16, 17], we consider the energy of separation of water molecule from the  $n > 10$  aggregate, about 30 kJ/mol and take the size of an aggregate of hundreds or thousands of water molecules, then the values of  $K_1$  and  $K_2$  will differ slightly. Despite the fact that clusters exist for a very short time (a few picoseconds) due to heat motion, they may be formed again. Under this assumption, the time dependence can be explained by the time it takes to reach a new equilibrium between different particles in water. Based on the Figures 2–4, it is possible to conclude that the time to reach equilibrium in the case of frequencies of 90 MHz and 110 MHz is approximately three weeks. At 170 MHz frequency, an unstable equilibrium occurs on the third day, which, for reasons unknown so far, relaxes to the original.

### Conclusion

Summarizing all the above mentioned it is possible to come to the following conclusion:

1. Preliminary field effect on water with frequencies of 90, 110 and 170 MHz increases the endothermicity of  $\alpha$ -D-glucose dissolution;
2. For 90 and 110 MHz frequencies a cumulative time effect is observed, with «saturation» after 21 days. For 170 MHz frequency the maximum effect occurs on the third day;
3. It has been suggested that the interaction of water-water particles increases as a result of the field effect on the solvent that explains the decrease in the enthalpy of carbohydrate hydration;
4. For the first time, it was found that the field effect depends on water exposure time after the field action. The maximum effect for different frequencies is observed under different exposure time.

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### **Электромагниттік өріс нәтижесінде суда D-глюкозаның еріген жылу әсерінің өзгеруі**

Мақала судың қасиеттеріне арналған (90, 110 және 170 МГц) мегартерлердің әлсіз электромагниттік өрістерінің әсерін зерттеуге арналған. Электролит емес,  $\alpha$ -D-глюкозаны ерітудің интегралдық жылуының калориметриялық өлшемі судың қасиеттерін өзгертудің жанама әдісі ретінде таңдалған. A-D-глюкозаның ерітіндісінің жылуын өлшеу бірінші рет өріс жиілігінің функциясы ретінде өлшенді. Бекманның термометрімен салыстыруға келмеген, өрістегі суда көмірсулардың ерітіндісінің жылу әсерлерін калориметрикалық өлшеу нәтижелері келтірілген. Дала әсерінен кейінгі уақытқа  $\alpha$ -D-глюкозаны ерітудің салыстырмалы жылу тәуелділігі анықталды. 90 МГц және 110 МГц жиіліктер үшін кумулятивтік сипат бар, ал 170 МГц болған жағдайда тәуелділіктің үшінші күні ең жоғары мәнге ие. 90 МГц және 110 МГц жиіліктер үшін үш күн ішінде еріген жылудың күрт өзгеруі байқалды, содан кейін жиырмасыншы күннен кейін уақытқа тәуелділік аз болады. Жалпы,  $\alpha$ -D-глюкозаны еріту процесінің эндотермиялықтығы анықталды. Суға әсер ететін судағы көмірсулар молекуласының гидратталуының жылу су бөлшектерінің аралық молекулалық өзара әрекеттесуі және су бөлшектерімен көмірсулар молекулалары арасындағы өзара әрекеттердің әлсіреуі салдарынан азаяды деп болжануда.

*Кілт сөздер:* электромагниттік өріс, глюкоза, еріген жылу, калориметрия, ылғалдау, термодинамика, көмірсулардың ерітінділері, жиілігі.

Б.П. Шипунов, А.В. Рябых

### **Изменение теплового эффекта растворения D-глюкозы в воде в результате действия электромагнитного поля**

Статья посвящена исследованию влияния слабых электромагнитных полей мегагерцового диапазона (90, 110 и 170 МГц) на свойства воды. В качестве косвенного метода изучения изменения свойств воды было выбрано калориметрическое измерение интегральной теплоты растворения неэлектролита —  $\alpha$ -D-глюкозы. Впервые произведено измерение теплоты растворения  $\alpha$ -D-глюкозы в зависимости от частоты электромагнитного поля, которое воздействовало на воду. Приведены результаты калориметрических измерений тепловых эффектов растворения углевода в воде, подвергшейся полемому воздействию, по сравнению с необлученной. Измерения проводились с помощью термометра Бекмана. Установлена зависимость относительной теплоты растворения  $\alpha$ -D-глюкозы от времени после полевого воздействия. Для частот 90 и 110 МГц имеет место накопительный характер, что выражается в постепенном увеличении эндозффекта, а в случае 170 МГц зависимость возникает максимум на третьи сутки. Для частот 90 и 110 МГц наблюдается резкое изменение теплоты растворения в течение первых трех суток, затем, после двадцатых суток, прослеживается слабая зависимость от времени. В целом, наблюдается увеличение эндотермичности процесса растворения  $\alpha$ -D-глюкозы в результате полевого

воздействия на воду. Наблюдаемые эффекты объясняются на основе предположения об уменьшении теплоты гидратации молекулы углевода в воде, подвергшейся полювому воздействию, вследствие усиления межмолекулярных взаимодействий между частицами воды и ослабления взаимодействий между частицами воды и молекулами углевода.

**Ключевые слова:** электромагнитное поле, глюкоза, теплота растворения, калориметрия, гидратация, термодинамика, растворы углеводов, частота.

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### Relationship of associated clusters degree with metal ionization according to the cluster-associate model

This article deals with a cluster-associate model of kinematic viscosity of liquid metals. This model was derived from the concept of chaotized particles. According to the proposed model, the authors calculated average values clusters association degree contained in liquid metal. 28 metals of the second — sixth periods of D.I. Mendeleev element table were studied for calculation. The authors compare the first potential of metal ionization with the obtained values of clusters association degree. This comparison showed a regular change in clusters association degree closely connected with the change in the first ionization potential. In combination with the Fraenkel equation, an approximate equation was obtained to calculate activation energy. The obtained equation for the cluster-associate pattern of viscosity temperature dependence is used in calculating the activation energy of viscous melt flow for twenty-eight metals. The obtained results on activation energy were compared to experimental data. This comparison showed that the activation energy data obtained from the proposed model is described better by the approximating dependence. Tables and figures are given in the work for visual confirmation of the obtained results. Thus, in the process of comparing the first potential of metal ionization for all periods of D.I. Mendeleev element system with clusters association degree, their regular connection was revealed. This connection makes it possible to assert the functional aspect of the cluster-associate pattern.

**Keywords:** viscosity, chaotized particles, degree of cluster association, cluster-associate pattern, liquid metals, activation energy, crystal mobile particles, ionization potential, modified Fraenkel equation.

#### Introduction

In 2008 in the Chemical and Metallurgical Institute named after Zh. Abishev doctors of technical sciences V.P. Malyshev and A.M. Turdukozhayeva developed a concept of chaotized particles based on Boltzmann distribution. According to the concept, three aggregate states of the substance are considered from a single point of view by its structure less component. In all cases, particles which differ only in the energy magnitude of chaotic motion are considered. According to the concept of chaotized particles in each of the three aggregate states there are *crystal mobile*, *liquid mobile* and *vapor mobile* particles. However with the temperature rise and overcoming of various chaotization energy barriers, the proportion of these particles changes.

The proportion of these particles is calculated according to the equations

$$P_{crm} = 1 - \exp(-T_m / T)$$

$$P_{vm} = \exp(-T_b / T)$$

$$P_{lqm} = 1 - P_{crm} - P_{vm} - \exp(-T_m / T) - \exp(-T_b / T).$$

Here  $P_{cm}$  is the proportion of crystal mobile particles;  $P_{vm}$  is the proportion of vapor mobile particles;  $P_{lqm}$  is the proportion of liquid mobile particles;  $T$  — temperature;  $T_m$  — melting temperature,  $T_b$  — boiling temperature.

Earlier in the work [1] three models were proposed with the consideration of different content of crystal mobile, liquid mobile and vapor mobile particles. But the need to test each of the three viscosity models and to choose the most adequate brings some elements of uncertainty in the design method of such a dependence, in addition complicating the data processing procedure. This led us to develop a single cluster-associate model

$$\nu = \nu_r (T_r / T)^a. \quad (1)$$

According to the concept of chaotized particles, a cluster is a probabilistic form of the existence of various low-energy complexes from crystal mobile particles. Calculations of clusters proportion and quantity for a mole of substance at the melting and boiling point have shown that the concept of chaotized particles allows to quantify the formation of clusters with their distribution by the number of particles in the liquid at any temperature.

In the same work [1], the model validity (1) to the calculation of liquid metals viscosity was shown. It has been shown that the model (1) for many metals most adequately describes the temperature dependence of viscosity and can be used to calculate the viscosity at high temperatures without the performance of experiment. For many metals equations for viscosity were derived.

### Experimental

In the work [2] three models (taking into account crystal mobile, liquid mobile and vapor mobile particles) of kinematic viscosity of metals were compared with their ionization potentials for all periods of D.I. Mendeleyev element system, analysis of which revealed regular connection of values of this potential with model numbers ranked by increase of temperature influence on viscosity. In this work we will compare cluster-associate pattern (1) by the degree of clusters association with the first ionization potential of the considered metals for all periods of D.I. Mendeleyev element system.

This comparison is shown in Table 1 and Figure 1.

Table 1

Comparison of the first ionization potentials of the metal with the degree of cluster association

Period	Me	Valence shell	$I_1$ , eV	$\bar{a}$	Period	Me	Valence shell	$I_1$ , eV	$\bar{a}$
2	Li	$2s^1$	5.390	1.01	5	Rb	$5s^1$	4.176	1.22
	Be	$2s^2$	9.320	9.51		Sr	$5s^2$	5.692	2.01
3	Na	$3s^1$	5.138	1.35		Ag	$4d^{10}5s^1$	7.574	1.82
	Mg	$3s^2$	7.644	2.57		Cd	$4d^{10}5s^2$	8.991	1.80
	Al	$3s^2p^1$	5.984	1.03		In	$4d^{10}5s^25p^1$	5.785	0.96
4	K	$4s^1$	4.339	1.22		Sn	$4d^{10}5s^25p^2$	7.342	0.97
	Ca	$4s^2$	6.111	1.68		Te	$4d^{10}5s^25p^4$	9.01	2.77
	Fe	$3d^64s^2$	7.87	3.54	6	Cs	$6s^1$	3.894	1.19
	Co	$3d^74s^2$	7.86	3.05		Ba	$6s^2$	5.211	1.56
	Ni	$3d^84s^2$	7.63	1.92		Au	$4f^{14}5d^{10}6s^1$	9.22	1.44
	Cu	$3d^{10}4s^1$	7.724	1.65		Hg	$4f^{14}5d^{10}6s^2$	10.43	0.90
	Zn	$3d^{10}4s^2$	9.391	1.90		Tl	$4f^{14}5d^{10}6s^26p^1$	6.106	1.32
	Ga	$3d^{10}4s^24p^1$	6.00	0.91		Pb	$4f^{14}5d^{10}6s^26p^2$	7.145	0.79
	Ge	$3d^{10}4s^24p^2$	7.88	2.81		Bi	$4f^{14}5d^{10}6s^26p^3$	7.287	1.36

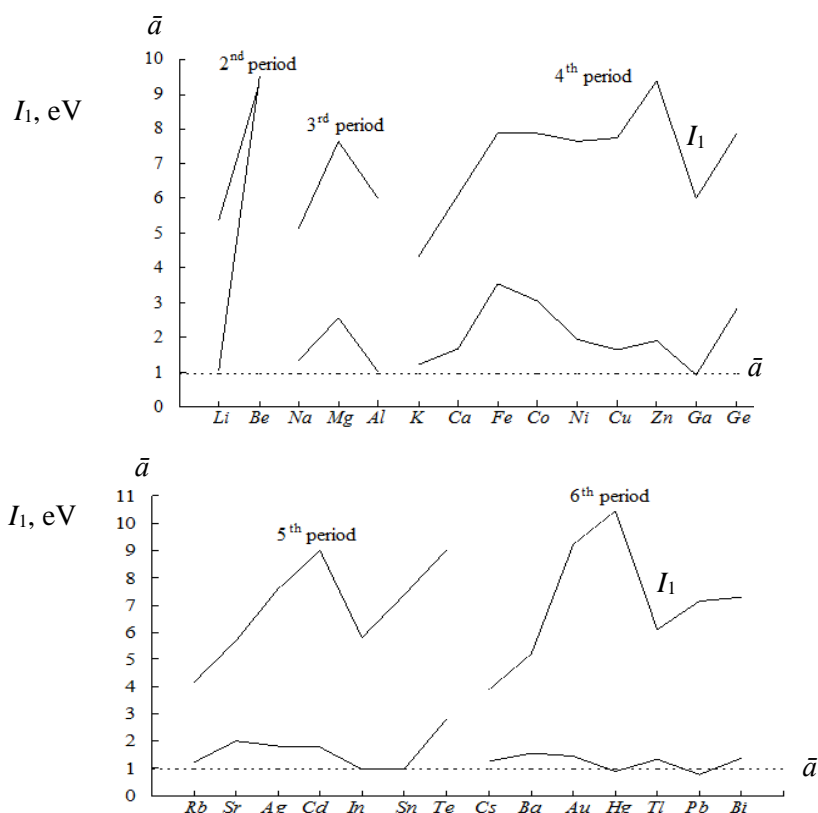
As can be seen from the table and the figure, in general there is a symbate (consistent) change in the degree of clusters association with the increase or decrease of the first potential value of metal ionization for all periods of Mendeleyev element system. Some departure of this model becomes apparent for silver in the fifth period and for gold, mercury, thallium and lead in the sixth period, that is connected with big tendency to clusters association from metal atoms for beryllium, with influence of  $4d$ -subshell for silver, with completion

of 4*f*- and 5*d*-subshells development for metals of the sixth period, and mercury and lead also have 6*s*-subshell accompanied by lanthanide contraction and sharp increase in ionization potential.

The average value of cluster association for 28 metals is  $\bar{a} = 1.94$ . The obtained values of clusters association degree of the tested metals were checked for range uniformity according to equations [3]:

$$r_{\min}^{\max} = \frac{|\bar{x} - x_{\min}^{\max}|}{S(x)\sqrt{\frac{n-1}{n}}} \leq r_{cr}, \quad S(x) = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}},$$

where  $x_{\min}^{\max}$  is the minimax value of the range;  $\bar{x}$  is the average value;  $S(x)$  is the mean-root-square error and  $n$  is the volume of the range,  $r_{cr} = 1.483f^{0.187}$  [3; 15] where  $f = n - 2$ .



$I_1$  is the first ionization potential;  $\bar{a}$  — average degree of cluster association

Figure 1. Dependence of ionization potential and average value of clusters association degree for 28 metals in order of increasing of their atomic number

This test showed that for 28 metals, the range is not uniform: mean-root-square error  $S(x) = 1.645$ ; in equation  $r_{\min}^{\max} \leq r_{cr}$  is not observed  $r_{\min}^{\max} = 4.68 > r_{cr} = 2.73$ ;  $x_{\min}^{\max} = 9.51$  (for Be).

Therefore, it is necessary to eliminate the «jumping out» value, i.e. the beryllium data. The high value of association degree of beryllium clusters is connected with its high position in the periodic table, partial possession of covalent links, high tendency to associate clusters of metal atoms, and high ionization potential. Beryllium generally refers to semi-metals, which causes its exclusion from a variety of metals.

The elimination of beryllium and reduction of range up to 27 metals leads to validity of range uniformity:  $S(x) = 0.780$ ;  $r_{\min}^{\max} = 2.46 < r_{cr} = 2.71$ ;  $x_{\min}^{\max} = 3.54$  (for Fe).

In this case for 27 metals  $\bar{a} = 1.66 \pm 0.32$ .

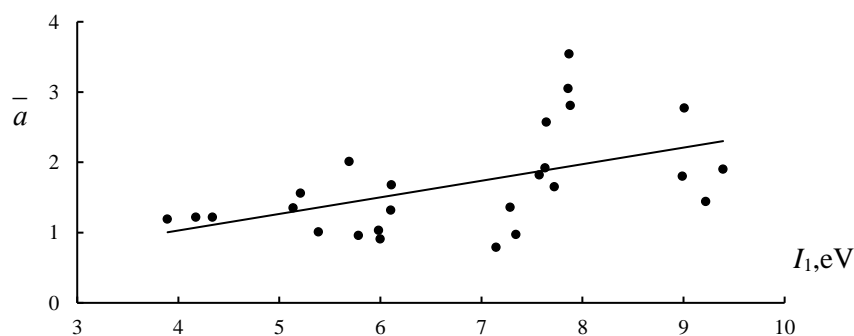
### Results and Discussion

Research for calculation of clusters association degree are conducted on the most uniform simple substances — metals, therefore this indicator has low values and changes within ~1–4 (excepting beryllium) (Table 1). Without this semimetal, and in addition lower than normal associated mercury ( $\bar{a} = 0.9$ ) at its anomalously high ionization potential (10.43 eV), generally regular and probably significant, although weakly expressed as cendant dependence of cluster association with metal ionization potentials is observed

$$\bar{a} = 0.09 + 0.24I_1, R = 0.70, t_R = 6.7 > 2. \quad (2)$$

The weakness of this connection is explained by the secondary nature of associates formation in comparison with the primary processes of elementary  $n$ -particle clusters formation from crystal mobile particles, as it was demonstrated earlier on the example of more evident interconnection of the standard three models with metal ionization potentials. The conformity consists in a great tendency to association of ionic complexes — clusters, which have stronger attraction of universal mobile electrons.

The relationship between cluster association and ionization potential for 26 metals, without mercury and beryllium, is shown in Figure 2.



$I_1$  is the first ionization potential;  $\bar{a}$  — average degree of cluster association.  
Points are data from Table 1, line — according to the equation (2) without data on Be and Hg

Figure 2. Relationship between cluster association and metal ionization potential

Ya.I. Fraenkel, on the basis of activation motion mechanism, obtained in 1927 the equation of dependence of dynamic viscosity on temperature

$$\eta = A \exp\left(\frac{E_a}{RT}\right), \quad (3)$$

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

As the kinematic viscosity is connected with dynamic viscosity on a formula  $\nu = \eta/\rho$  ( $\rho$  — melt density), because of very weak dependence of density on temperature (several percent in all range of liquid state) in comparison with 3–4 multiple change of viscosity in the same range [4], it is possible to change directly in the equation (3) apparent viscosity  $\eta$  to kinematic viscosity  $\nu$ , having respectively corrected parameters  $A$  to  $A'$  and activation energy  $E_a$  to estimated value  $E'_a$

$$\nu = A' \exp\left(\frac{E'_a}{RT}\right). \quad (4)$$

Table 2 shows the activation energy values obtained from the modified Fraenkel equation (4) based on experimental (information) and calculated on cluster-associate model (1) data for 28 metals of D.I. Mendeleev periodic system.

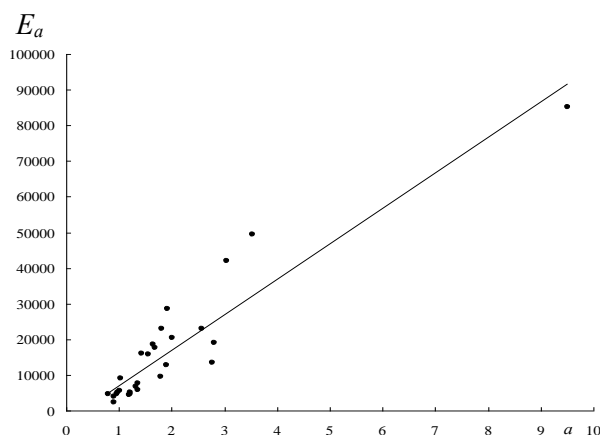
The activation energy values for the calculated data range from 2868 J/mole (mercury) to 128017 J/mole (beryllium). The correlation coefficient for the calculated activation energy values  $E'_a$  (calc) in comparison with experimental  $E_a$  (inf) comprised 0.8580 with its signification  $t_R = 16.6 > 2$  including beryllium. At its exception the correlation coefficient is much higher than  $-R = 0.9552$  with its signification  $t_R = 55.6 > 2$ .

Table 2

Activation energy values for experimental ( $E_a(\text{inf})$ ) and calculated on cluster-associate model (1) ( $E_a'(\text{calc})$ ) data for 28 metals

Element	$E_a(\text{inf})$ , J/mole	$E_a'(\text{calc})$ , J/mole	Element	$E_a(\text{inf})$ , J/mole	$E_a'(\text{calc})$ , J/mole
Li	5463	5920	Rb	4548	5055
Be	85231	128017	Sr	20453	22723
Na	5803	6485	Ag	22981	21684
Mg	22915	22150	Cd	9487	10867
Al	9029	8871	In	4681	5629
K	5138	5812	Sn	5155	5496
Ca	17635	20171	Te	13478	21476
Fe	49404	55540	Cs	4498	5072
Co	41971	46835	Ba	15889	17543
Ni	28610	29757	Au	16038	17294
Cu	18450	22133	Hg	2262	2868
Zn	12713	14134	Tl	6652	9154
Ga	3850	4074	Pb	4714	4448
Ge	19098	31004	Bi	7649	8447

Figures 3 and 4 show the comparison of the obtained range of activation energy data for experimental and calculated on cluster-associate pattern viscosity with the degree of cluster association for the metals under investigation,  $E_a = f(\bar{a})$ .



$E_a$  is the activation energy, J/mole;  $\bar{a}$  is the average degree of cluster association.

Points are experimental data, line is approximation of experimental data by equation  $E_a = A + B\bar{a}$

Figure 3. Dependence of activation energy for experimental data on the degree of clusters association for 28 metals

As can be seen from the figures, the activation energy data obtained by processing the calculated values from the generalized pattern are described better by the approximate dependence.

The approximate equation for experimental data on viscous flow activation energy is expressed as:

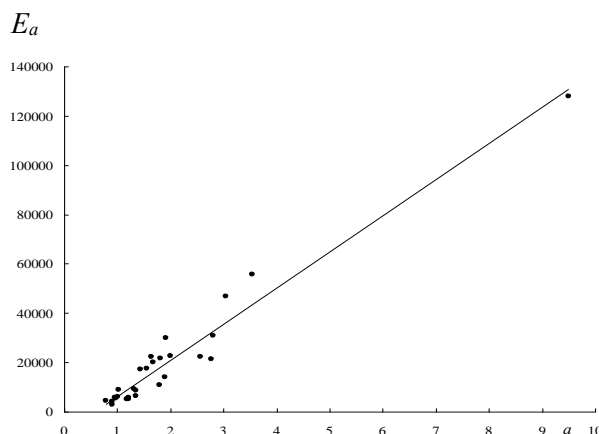
$$E_a(\text{inf}) = B\bar{a} + A = 9957 \bar{a} - 2731. \quad (5)$$

For calculated on cluster-associate model (1):

$$E_a'(\text{calc}) = B'\bar{a} + A' = 14695 \bar{a} - 8525. \quad (6)$$

The approximation dependability value for the information data on viscous flow activation energy depending on the degree of cluster association gives 0.9277, for the calculated from the model (1) — 0.9754.

Virtually, the coefficient  $B$  in equation (5) and  $B'$  in equation (6) make up the value of the activation energy corresponding to one cluster and are expressed as J/(mole·cluster). For experimental data, this coefficient is equal on average to ~10 kJ/(mole·cluster), and for calculated values is equal to ~15 kJ/(mole·cluster).



$E_a$  is the activation energy, J/mole;  $\bar{a}$  is the average degree of cluster association. Points are experimental data, line is approximation of data calculated according to the model (1) by equation  $E_a' = B' \bar{a} + A'$

Figure 4. Dependence of activation energy calculated on model (1) on the degree of clusters association for 28 metals

Shown above calculations confirm the functional nature of the cluster-associate pattern, taking into account the degree of clusters association from crystal mobile particles, which are the basis of a single model, and allow to consider the obtained approval as another proof of objectivity of chaotized particles concept.

### Conclusions

1. The interconnection of clusters association degree in cluster-associate pattern of metals viscosity with their ionization potentials for all periods of D.I. Mendeleyev element system reveals their regular relation similar to the previously proposed [2] three separated patterns. This confirms the functional nature of the new pattern, which retains clusters from crystal mobile particles as a physical basis, with additional consideration of their association.

2. Analysis of activation energy values obtained from the modified Fraenkel equation on the basis of experimental (information) and calculated on cluster-associate pattern data for 28 metals showed their adequate straight-line dependence, moreover the description of their interconnection with the degree of clusters association on the basis of the calculated from the proposed pattern activation energy values is more accurate.

3. The obtained data based on the new cluster-associate pattern can be considered as another confirmation of the concept fruitfulness of chaotized particles.

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### Кластерлік-ассоциативті модель бойынша металдардың иондың потенциалының ассоцирленген кластерінің дәрежесінің өзара байланысы

Мақалада сұйық металдардың кинематикалық тұтқырлығының кластерлік-ассоциаттық моделі қарастырылған. Бұл модель хаотизирленген бөлшектер тұжырымдамасының негізінде алынды. Ұсынылған үлгіге сәйкес авторлар сұйық металдағы кластерлердің ассоциациялану дәрежесінің орташа мәндерін есептеді. Есептеу үшін Д.И. Менделеевтің элементтері кестесінің екінші — алтыншы кезеңдерінің 28



металдары зерттелген. Авторлардың жұмысында металдарды иондаудың бірінші әлеуетін кластерлердің ассоциациялану дәрежесінің алынған мәндерімен салыстыру келтірілген. Бұл салыстыру бірінші иондау әлеуетінің өзгеруімен тығыз байланыста кластерлер қауымдастығы дәрежесінің заңды өзгеруін көрсетті. Френкель теңдеуімен біріктірілгенде активтендіру энергиясын есептеу үшін аппроксимирлеуші теңдеуі алынды. Тұтқырлықтың температуралық тәуелділігінің кластерлік-ассоциаттық моделі үшін алынған теңдеу жиырма сегіз металл үшін балқыманың тұтқыр ағысын активтендіру энергиясын есептеу кезінде пайдаланылған. Активтендіру энергиясы бойынша алынған нәтижелерді авторлар эксперименталды мәліметтермен салыстырды. Бұл салыстыру ұсынылған модель бойынша алынған белсендіру энергиясы бойынша деректер аппроксимациялық тәуелділіктен жақсы сипатталатынын көрсетті. Алынған нәтижелерді көрнекі растау үшін жұмыста кестелер мен суреттер келтірілген. Осылайша, Д.И. Менделеев элементтері жүйесінің барлық кезеңдері бойынша металдарды иондаудың бірінші әлеуетін кластерлер ассоциациясының дәрежесімен салыстыру кезінде олардың заңды байланысы анықталды. Бұл байланыс кластерлік-қауымдасқан модельдің функционалдық сипаты туралы бекітуге мүмкіндік береді.

*Кілт сөздер:* тұтқырлық, ретсізделген бөлшектер, ассоциирленген кластердің дәрежесі, кластерлі-ассоциативті модел, сұйық металдар, активтендіру энергиясы, кристалл қозғалысты бөлшектер, иондау әлеуеті, Френкельдің модификацияланған теңдеуі.

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### **Взаимосвязь степени ассоциированности кластеров с потенциалами ионизации металлов по кластерно-ассоциатной модели**

В статье рассмотрена кластерно-ассоциатная модель кинематической вязкости жидких металлов. Модель была получена на основе концепции хаотизированных частиц. Авторами, согласно предложенной модели, были рассчитаны средние значения степени ассоциированности кластеров, содержащихся в жидком металле. Для расчета были исследованы 28 металлов второго – шестого периодов таблицы элементов Д.И. Менделеева. Кроме того, приведено сопоставление первого потенциала ионизации металлов с полученными значениями степени ассоциированности кластеров. Данное сопоставление показало закономерное изменение степени ассоциации кластеров в тесной связи с изменением первого потенциала ионизации. В комбинации с уравнением Френкеля получено аппроксимирующее уравнение для расчета энергии активации. Уравнение для кластерно-ассоциатной модели температурной зависимости вязкости использовано при расчете энергии активации вязкого течения расплава для двадцати восьми металлов. Полученные результаты по энергии активации авторы сравнили с экспериментальными данными. Результаты сопоставления показали, что данные по энергии активации, полученные по предлагаемой модели, описываются лучше аппроксимирующей зависимостью. В работе для большей наглядности полученных результатов приведены таблицы и рисунки. Таким образом, при сопоставлении первого потенциала ионизации металлов по всем периодам системы элементов Д.И. Менделеева со степенью ассоциации кластеров выявлена их закономерная связь, которая позволяет утверждать о функциональном характере кластерно-ассоциатной модели.

*Ключевые слова:* вязкость, хаотизированные частицы, степень ассоциированности кластеров, кластерно-ассоциатная модель, жидкие металлы, энергия активации, кристаллоподвижные частицы, потенциал ионизации, модифицированное уравнение Френкеля.

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## **Hydrothermal grown iron oxide films on the surface of titanium and conductive glasses and their current characteristics in water photolysis**

The relevance of photolysis on semiconductor electrodes since the pioneer work of Fujishima and Honda on metallic titanium does not lose sharpness due to new possibilities for developing new materials, such as conductive glasses, for which photolysis cells with semi-transparent semiconductor layer can be created. We have compared properties of such glasses with a metal for hydrothermal conditions of iron oxide synthesis. Iron oxide films have also been obtained by introducing a number of cations to modify semiconductor systems ( $\text{Fe}_2\text{O}_3$ ). It turned out that the nature of the substrate significantly affects the properties of the formed conductive film, which ultimately forms the level of anodic photocurrents in the layer of iron oxide semiconductor. We have investigated current characteristics of such films; it was shown that charging processes occur better on metallic titanium than on conductive glasses. We consider that the metal substrate significantly reduces regeneration processes both in the semiconductor layer and at the interface. Thus, formed  $\text{Ti}/\text{Fe}_2\text{O}_3$  electrolyte heterojunction is more efficient than the conducting glass/ $\text{Fe}_2\text{O}_3$  electrolyte system. However, this does not mean that glass is less promising for photolysis systems. It is necessary to achieve more acceptable conditions for the synthesis of semiconductor material.

**Keywords:** iron oxide, conductivity, spectrum, current-voltage characteristic, anode photocurrent, band gap, semiconductor, doping.

### *Introduction*

Semiconductor transition metal oxides are known for their properties as anode materials for the model processes of water photoelectrolysis [1]. Among this variety of anode materials ( $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ , etc.), iron oxide has always attracted itself as an optimal material from point of view of its optical characteristics — the band gap width equals 2.1 eV, herewith the photo corrosion for this material is minimal. On the other hand, this material has intrinsic essential disadvantages, namely increased recombination [2, 3] and it's very limited thickness of an active layer, just a few nanometers [4]. From this point of view, the production of  $\text{Fe}_2\text{O}_3$  films in hydrothermal conditions is always attractive, because this method is an universal one and it allows to vary the properties of films in very wide range, both in thickness and in composition.

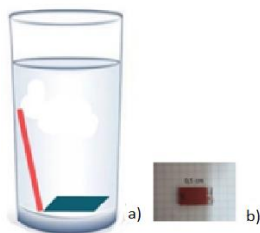
It was shown earlier that under the studied conditions of hydrothermal synthesis [5] at certain concentration ranges of iron chloride (III) it is possible to dope titanium dioxide films with iron ions. It gives a significant improvement of current characteristics of photoelectrodes. It was of interest to study the formation of iron oxide films under the same conditions on pure films of metallic titanium and on a conducting glass. For that we raised concentration of the electrolyte  $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$  solution, which allowed to grow films of pure iron oxide on the surface of titanium and conductive glass in hydrothermal conditions.

### *Experimental*

The investigations were conducted on metallic titanium plates of size  $1.5 \times 1.5$  cm (VT6 titanium grade) of composition Ti-6.25 Al-4.1 with small admixture of aluminum and vanadium (Government Standard 19807–91) with a current collector of the same titanium, as well as on conductive glass Fluorine Tin Oxide (FTO) with conductivity less than  $15 \text{ ohms/cm}^2$  of firm «LATECH».

Previously we applied 2.0–2.5 g/l  $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$  solution for modification of titanium dioxide films on the metallic titanium with hydrochloric acid solution acidifying. We raised the concentration of iron chloride to 5–10 g/l, which allowed us to form under the same conditions (190 °C, 5 hours) iron oxide films in an autoclave.

Hydrothermal synthesis of films was carried out in a laboratory autoclave under pressure of 0.5 MPa with plates position shown in Figure 1. After the hydrothermal synthesis, the films were washed with distilled water, dried and then annealed in air at 500 °C for 1 hour. In parallel, plates of conductive glasses were processed in the same fluoroplastic glass. Then the plates after washing with water were also annealed at 500 °C for an hour.



*a* — titanium plate (vertical position) and glass plate (horizontal position);  
*b* — the size of the glass electrode with iron oxide layer

Figure 1. Scheme of samples arrangement in the autoclave

X-ray analysis of films was performed at the stationary installation of DRONE-3 with Cu-K $\alpha$  radiation directly from the metallic plates of anodized titanium.

The anodic photocurrent of titanium-oxide electrodes was conducted by a three-electrode scheme; a platinum wire served as the counter electrode, the comparison electrode was silver- chloride one. For iron oxide film illumination a xenon lamp without light filters was used. Illumination of the samples was measured with a light meter and accounted for xenon lamp as  $(160\text{--}180) \cdot 10^3$  Lux and for UV lamp — as  $12 \cdot 10^3$  Lux. The level of illumination on the sun in the latitude of Shymkent (South Kazakhstan) in June, measured at midday, was  $130 \cdot 10^3$  Lux. Current-voltage characteristic was double-checked for different synthesis conditions, the accuracy was confirmed by 3–4 parallel sample measurements, and the photocurrent dependence was constructed from their averaged values. Relative standard deviation from the average value is 0.5 %.

Micrographs and semi-quantitative analysis of the electrode surface were performed using scanning electron microscope JSM-6490LV (JEOL, Japan). Optical spectra of glasses were recorded on a Cary-50 spectrophotometer in a transmission mode.

### Results and Discussion

Simultaneous hydrothermal treatment of titanium and glasses in the autoclave allowed to form a layer of iron oxide film on the surface of the plates when changing iron trichloride solution concentration. This can be clearly seen from the cross-section of the glass plate (Fig. 2).

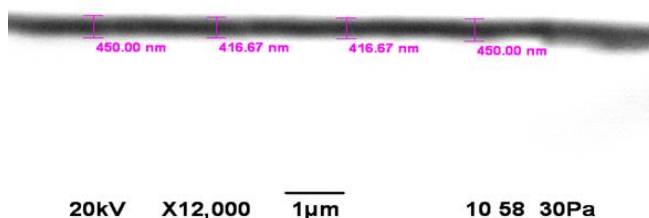


Figure 2. Micrograph of iron oxide film of on the glass plate (inverted image)

It is possible to determine the thickness of iron oxide layer in the limit of 416–450 nm, with the transmission spectrum (Fig. 3) identified as a layer of iron oxide. For example, it is in good agreement with the spectra of iron oxide in [5] in the limit of 350–800 nm. We can see the absorption limit which is in line with approximately 400 nm.

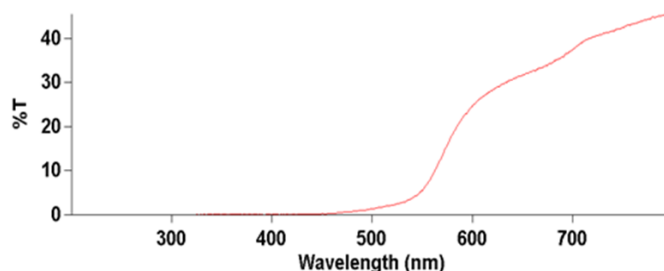


Figure 3. Transmission spectra of glass after glass treatment with iron trichloride in an autoclave

The presence of iron oxide film on titanium is also recorded on metal plate X-ray diffraction pattern (Fig. 4). However, due to the hematite signal weakness, the main peak of metallic titanium outweighs the iron peak.

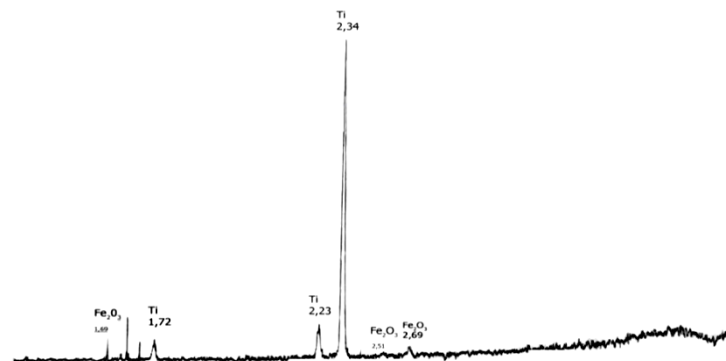


Figure 4. X-ray diffraction pattern of titanium plate with iron oxide layer

Figure 5 shows the current-voltage characteristic of the dark current for the electrode on titanium. It can be seen that there is no dark current within the potentials up to 800 mV.

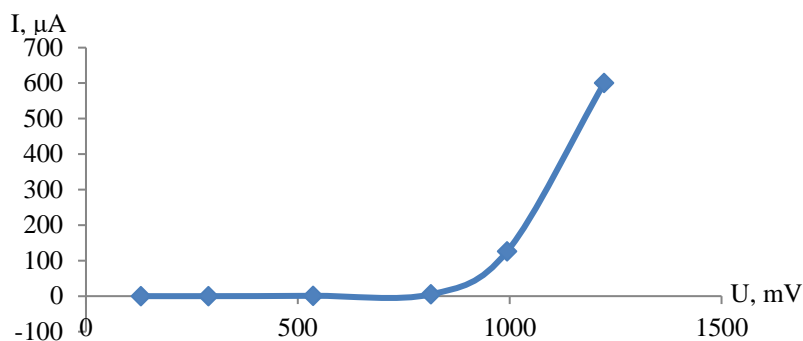


Figure 5. Current-voltage characteristic of a titanium electrode without lighting

An interesting current characteristic for titanium after titanium annealing in the air at 500 °C is given in Figure 6 (blue line). Annealing of titanium in the air leads to the formation of titanium dioxide film, and its current characteristics are insignificant — 15–20 μA (blue line), but increased current characteristics for iron oxide after hydrothermal synthesis and subsequent annealing of such a sample at 500 °C for 1 hour (red line) are obvious.

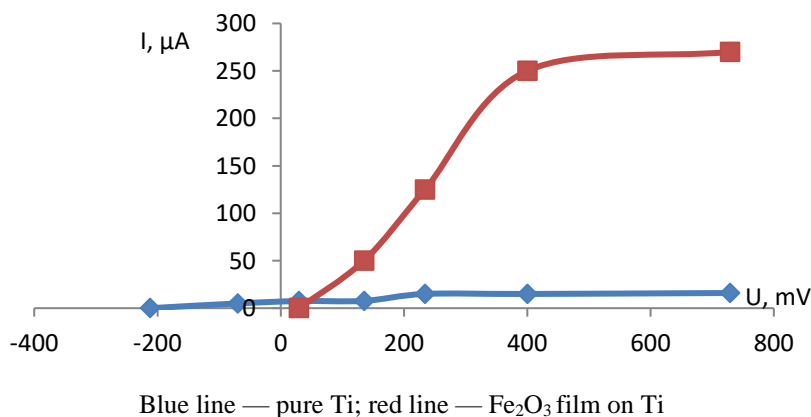


Figure 6. Current-voltage characteristic of pure titanium after annealing titanium dioxide film (blue line) and iron oxide film on titanium after annealing at 500 °C (red line)

Current characteristics for hematite on glass are almost identical (Fig. 7). Since the synthesis conditions for pairs of  $\text{Ti}/\text{Fe}_2\text{O}_3$  and  $\text{glass}/\text{Fe}_2\text{O}_3$  were identical (Fig. 1), we associate such a difference of current characteristics with the formation of the hematite boundary with the substrate, where in the case of glass the current characteristics are minimal, and when the titanium — hematite boundary is formed, the current characteristics are much higher. Perhaps it is precisely the recombination processes at the substrate, because hematite interface is significantly reduced in the case of  $\text{Ti}/\text{Fe}_2\text{O}_3$  pair as compared with the  $\text{glass}/\text{Fe}_2\text{O}_3$  pair.

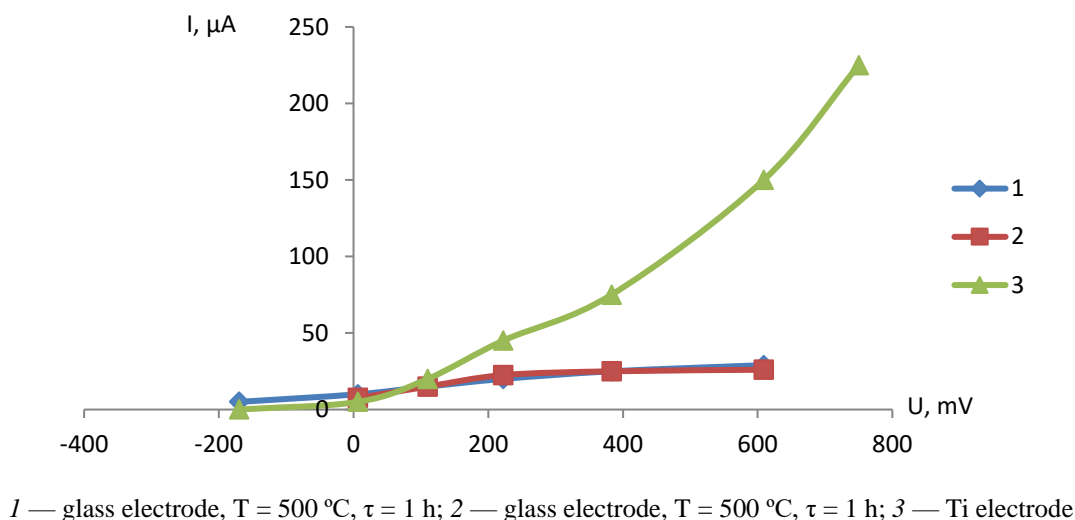


Figure 7. Anodic photo current of iron oxide films on glass and titanium

Figure 7 clearly shows the growth of current characteristics up to  $250\text{ }\mu\text{A}$ . Photo current on glass electrodes is insignificant and does not exceed  $30\text{ }\mu\text{A}$  (blue line — photo current during annealing at  $500\text{ }^{\circ}\text{C}$  for 1 hour and red line — photo current during annealing glass at  $700\text{ }^{\circ}\text{C}$  for 10 minutes). It can be seen at Figure 7 that the glass annealing does not lead to significant change of current characteristics of hematite on the glass. At the same time, a sharp (more than 5 times) increase of photo current on titanium electrodes is observed (green line). We assume that such a significant increase of photo current is associated with the formation of the  $\text{Ti}/\text{Fe}_2\text{O}_3$  heterojunction. We suppose that the conductivity incompleteness at the boundary is significantly reduced compared to the same transition at the  $\text{glass}/\text{Fe}_2\text{O}_3$  boundary, so the conductivity of the «titanium» electrode is significantly higher than that of the «glass» electrode.

We have attempted to introduce other ions (for example, Ni, Co, Ag, Cu as well as a number of other cations) into the process of synthesis of iron oxide films and thereby to change film conductivity. To do this, 20 to  $100\text{ g/l}$  of the corresponding cation was introduced into the initial electrolyte containing  $2\text{--}2.5\text{ g/l}$   $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ . The Figure 8 shows the spectrogram of the film, to which we tried to introduce a solution  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Then this solution was also autoclaved like for the initial iron oxide electrolyte and the preparation was carried out similarly.

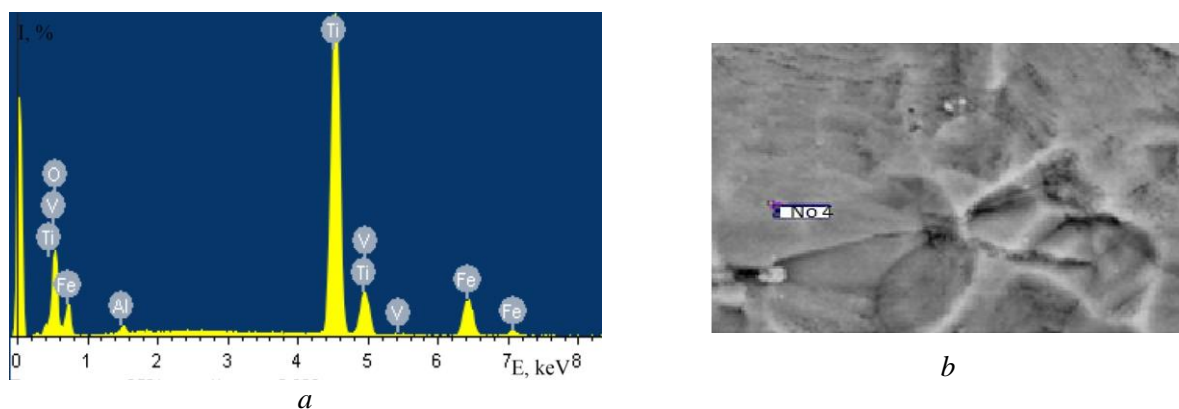


Figure 8. Spectrogram (a) and micrograph (b) of the iron oxide film with another cation introduction

We couldn't find any traces of the cation injected in the titanium film; only Fe and Ti elements and traces of Al and V elements are found on the spectrogram (Figure 8). Thus, hydrothermal conditions do not allow to introduce the accompanying cations into the synthesized film and the iron oxide film is formed on the surface in pure form. Thus, we did not find any improvement or degradation of the iron oxide layer on the current characteristics of the synthesized films (Fig. 8).

Current-voltage characteristic is peculiar as well in this case (Fig. 9). The current values fluctuate (red line) at approximately the same values as for the original iron oxide (blue line). Such insignificant fluctuations fit into the general paradigm of current-voltage characteristic dependence. Thus, we did not detect the improvement or degradation of the iron oxide layer in synthesized films with a cation.

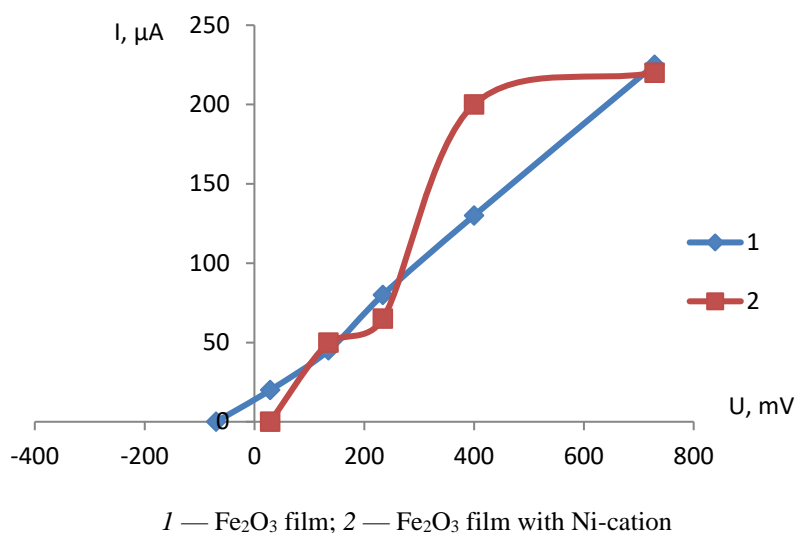


Figure 9. Current-voltage characteristics of iron oxide films (blue line) and films obtained in the presence of much nickel cations in a solution (red line)

We suppose that under hydrothermal conditions, an iron oxide film was formed on titanium, the electro-physical properties of which are very dependent on the properties of the substrate, i.e. titanium (Fig. 10).

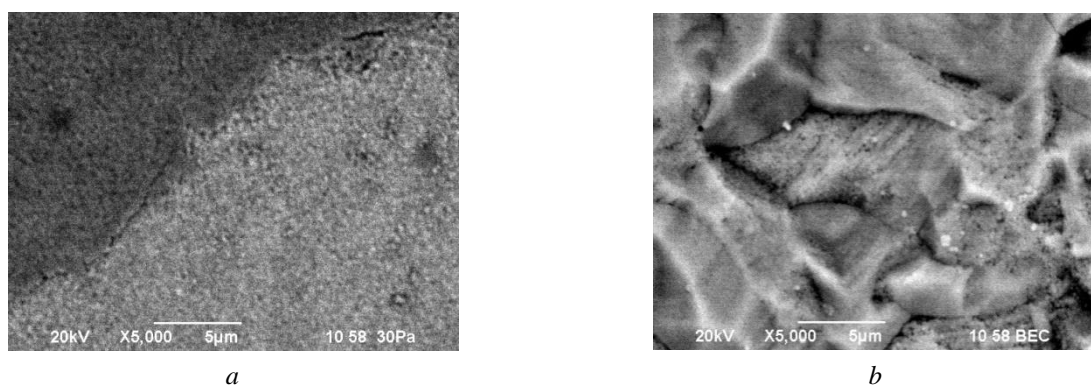


Figure 10. Micrographs of iron films on glass (*a*) and titanium (*b*)

In this case, we assume that the Ti/Fe<sub>2</sub>O<sub>3</sub> heterojunction, as well as the Ti/Fe<sub>2</sub>O<sub>3</sub>–NaOH electrolyte system itself, is a system that significantly reduces regeneration processes in the semiconductor layer and this sharply raises current characteristics of photoelectrodes. From these positions, perhaps, similar processes are described by authors of the publication [7], who obtained current characteristics three times the best of ours, i.e. 1.1 mA/cm<sup>2</sup>.

### Conclusion

Iron oxide films were formed and obtained under hydrothermal conditions on metallic titanium and conductive glasses. It was shown that the current characteristics of the metallic substrate are more than an order

of magnitude better than for glass. It is obvious that under identical synthesis conditions (hydrothermal growth, conducting basis) the formation of heterojunction largely depends on the substrate nature. A significant difference in current characteristics for different substrates is associated with the formation of a semiconductor layer, where the regeneration processes are very reduced for metallic titanium than for conductive glass.

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### **Титан және өткізүші шынылар бетіндегі гидротермалды өсірілген темір оксидінің қабықшалары және олардың су фотолизіндегі тоқтық сипаттамалары**

Фуджишима мен Хонданың алғашқы жұмыстарынан бастап жартылай өткізгіш электродтардағы фотолиздің өзектілігі жаңа материалдарды игерудің мүмкіндіктеріне байланысты өткірлігін жоғалтпайды, атап айтқанда өткізгіш шынылар олар үшін жартылай өткізгіштің жартылай мөлдір қабаты бар фотолизді ұяшықтар жасалуы мүмкін. Темір оксиді синтезінің гидротермалдық жағдайлары үшін осы шынылардың металмен салыстырғандағы қасиеттері салыстырылған. Сондай-ақ жартылай өткізгіш жүйелерді модификациялау үшін (Fe<sub>2</sub>O<sub>3</sub>) бірнеше катиондар енгізіп, темір оксидінің қабықшалары алынды. Төсеніштің табиғаты қалыптасатын өткізгіш қабықшаның қасиеттеріне елеулі әсер ететіні анықталды, бұл соңында темір оксидті жартылай өткізгіштің қабатында анодты фототоктар деңгейін қалыптастырды. Авторлар қабықшалардың ток сипаттамаларын зерттеген, олардың нәтижелері металл титанда өткізүші шынылармен салыстырғанда зарядтау процестері жақсы жүретінін көрсетті. Біз металл төсеніш жартылай өткізгіштің қабатындағы және фазалар шекарасында регенерациялық процестерді айтарлықтай төмендетеді деп есептейміз. Осылайша, қалыптасатын Ti/Fe<sub>2</sub>O<sub>3</sub> әртекті өткізу «өткізүші шыны/Fe<sub>2</sub>O<sub>3</sub>–электролит» жүйесіне қарағанда тиімдірек. Дегенмен, шынылардың фотолиздік жүйелер үшін болашағы жоқ деп айтуға болмайды. Жартылай өткізгіш материалдарды синтездеудің қолайлы жағдайларына қол жеткізу қажет.

*Кілт сөздер:* темір оксиді, өткізгіштік, спектр, вольтамперлік сипаттама, анодты фототок, тыйым салынған аймақтың ені, жартылай өткізгіш, допирлеу.

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### **Гидротермально выращенные пленки оксида железа на поверхности титана и проводящих стекол и их токовые характеристики при фотолизе воды**

Актуальность фотолиза на полупроводниковых электродах со времен пионерской работы Фуджишима и Хонды на металлическом титане не теряет остроты ввиду новых возможностей освоения новых материалов, таких как проводящие стекла, для которых могут быть созданы фотолизные ячейки с

полупрозрачным слоем полупроводника. Нами сопоставлены свойства таких стекол по сравнению с металлом для гидротермальных условий синтеза оксида железа. Также получены пленки оксида железа при введении ряда катионов для модификации полупроводниковых систем ( $\text{Fe}_2\text{O}_3$ ). Как оказалось, природа подложки существенным образом влияет на свойства формируемой проводящей пленки, что, в конечном итоге, формирует уровень анодных фототоков в слое железоксидного полупроводника. Авторами исследованы токовые характеристики таких пленок и показано, что на металлическом титане лучше происходят зарядные процессы, чем на проводящих стеклах. Мы считаем, что металлическая подложка существенно снижает регенерационные процессы как в слое полупроводника, так и на границе фаз. Таким образом, формируемый гетеропереход  $\text{Ti}/\text{Fe}_2\text{O}_3$ –электролит более эффективен, чем система «проводящее стекло/ $\text{Fe}_2\text{O}_3$ –электролит». Однако это не свидетельствует о том, что стекла менее перспективны для фотолизных систем. Необходимо добиваться более приемлемых условий синтеза полупроводникового материала.

**Ключевые слова:** оксид железа, проводимость, спектр, вольтамперная характеристика, анодный фототок, ширина запрещенной зоны, полупроводник, допирование.

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### **Obtaining of nanocatalyzers for low-temperature conversion of oxide carbon (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>) with reduced copper content**

The main goal of the work was to reduce the content of copper (in terms of copper (II) oxide) in the composition of the conversion catalyst, and to preserve high catalytic and physico-mechanical characteristics. As an alternative to the known technology for producing oxide catalysts from precursors of metal hydroxocarbonates, there have been selected a manner in which the precursor is copper/zinc hydroxocarbonate. It has been shown that of the many salts obtained from precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with an aurichalcite structure is most effective. The decomposition of these compounds results in the formation of nanosized metal copper clusters, which have a high specific surface area and high activity in the redox reaction of carbon monoxide conversion with water vapor to produce hydrogen. The coprecipitation conditions and the structure of copper/zinc hydroxocarbonate determine the subsequent activity of the oxide catalyst. A technology for producing nanocatalysts for low-temperature conversion of carbon monoxide with a low (up to 20 % — from 54 to 34 wt.%) copper content was proposed and the conditions for obtaining a precursor and catalyst were optimized.

**Keywords:** Aurichalcite, catalysts, conversion, copper content, low temperature, metal hydroxocarbonates.

#### *Introduction*

In recent years, the need for catalysts used in the production of hydrogen and hydrogen-containing gases by the method of hydrocarbon conversion has increased.

Existing methods for the preparation of copper-containing catalysts are based on the use of deposition processes and ammonia-carbonate technology. These preparation methods of copper-containing low-temperature catalysts are characterized by a complex, multi-stage and expensive main production scheme, which necessitates the improvement of existing technologies of catalysts' producing for the cost of low-temperature catalysts.

In the course of this work, a significant amount of sources on this issue was analyzed [1–3]. It has been established that the main condition for solving this problem is the formation of a certain structure of the corresponding metal hydroxides obtained by decomposition of ammonia-carbonate complexes of copper and zinc, followed by separation of the precipitate and heat treatment of the mass pressing.

As shown in [3], increased catalyst activity was achieved by chemical interaction of the catalyst components at an early stage of preparation, as well as by decomposition of ammonia-carbonate complexes. The completeness of the interaction was achieved by the processes in the kinetic mode (i.e., with intensive mixing of 150–500 rpm) at the solid — liquid interface.

Under these conditions, the aurichalcite phase (CuZn)<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> was detected in the obtained precursor. According to the differential thermal and x-ray phase analysis, the decomposition of the obtained precursor

is accompanied by the formation of highly dispersed oxides of copper and zinc (6–7 nm and 8–10 nm, respectively).

It is shown that of the many salts obtained from precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with an aurichalcite structure, which has a high specific surface area and activity, is the most effective.

Based on this, the main attention is paid to the conditions for the formation of copper/zinc hydroxycarbonate with the structure of aurichalcite as a precursor of the oxide solid catalyst solution, as well as the conditions for the formation of the oxide catalyst itself.

In this regard, the main goal of the work is to improve the existing technologies by optimizing the conditions for their production and cheapening low-temperature catalysts by reducing the copper component in the catalyst, by creating a nanostructured morphology of a solid solution of copper/zinc oxides while maintaining its high catalytic and physicochemical characteristics.

### *Experimental*

The copper/zinc hydroxocarbonate with an aurichalcite structure was prepared by precipitation from copper (II) nitrates and zinc, and sodium bicarbonate. It is shown that of copper/zinc hydroxocarbonate with the aurichalcite structure is formed both at a Cu:Zn ratio of 70:30 mol.% And at a ratio of 30:70 mol.%.

The wet weight of copper / zinc hydroxocarbonate after filtering the suspension and thoroughly washing from the concomitant salt of sodium nitrate was 271.00 g (of which 68.34 % moisture). The mass of dried (at 100 °C, for 2.5 days, and then at 120–125 °C, for 1 day) of copper/zinc hydroxocarbonate was 85.81 g (sample III.3).

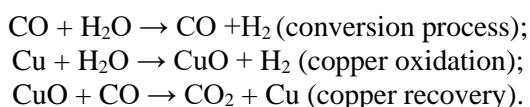
Three compositions of copper/zinc hydroxocarbonate were obtained, which differ in color. The pronounced light blue color is expressed for the sample — II.2; bluish-green for the sample — I.1 and dark blue — for the sample of copper/zinc hydroxocarbonate No. III.3, and during the drying process at a temperature of 100 °C it darkens, which indicates that a certain proportion of malachite is formed, decaying at temperatures of 80–100 °C. It was also noted that the sample of copper/zinc hydroxocarbonate — III.3 is characterized by a rather large size of well crystallized particles of a flat shape, in comparison with the two previous samples of copper/zinc hydroxocarbonate. The color of samples I.1 and II.2 after drying in the temperature range of 100–110 °C is stable.

### *Results and Discussion*

This study examined the industrial conditions for the preparation of the catalyst used in the process of low-temperature conversion of carbon monoxide with water vapor: CuO — 54 %, Cr<sub>2</sub>O<sub>3</sub> — 24 %, ZnO — 11 %, Al<sub>2</sub>O<sub>3</sub> — 19.5 % by weight.

The main role of the catalyst is the conversion of CO to CO<sub>2</sub> in the presence of water vapor at 270 °C with the formation of hydrogen for the synthesis of ammonia.

We present the probable redox reactions of CO conversion on a copper-zinc-chromium catalyst:



It has been shown that under industrial conditions occurs a formation of a catalyst with a zinc-malachite structure, which has low thermal stability.

In this regard, the main solution to the problem is to search for conditions for the formation of a specific structure of catalyst precursors — copper/zinc hydroxocarbonate; obtained by co-precipitation of nitrates of the corresponding metals in a precipitating medium, the preparation of which is shown in Figure 1.

The mixture contains various amorphous compounds, the structure of which depends on the dosage rate, the concentration of the base or precipitant. Depending on the change in conditions, precursors of various structures are formed. The reaction of the formation of hydrozincite (E) or aurichalcite (D) realizes by substitution from Na<sub>2</sub>Zn<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub>.

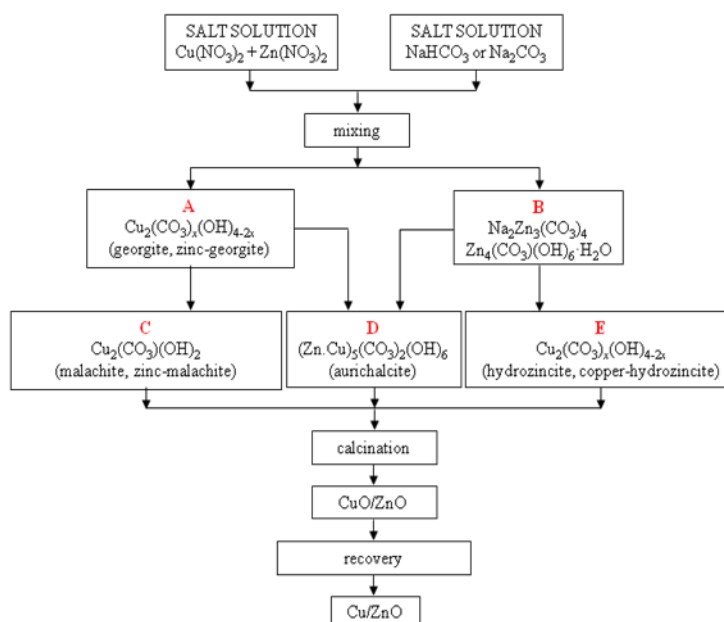


Figure 1. Formation of precursors and their structure

The catalytic activity of oxide catalysts was studied with varying the content of components in it (Tables 1 and 2). It has been shown that both the alumina content and the mass ratio of copper (II) oxide to zinc oxide (obtained under various conditions for the synthesis of copper/zinc hydroxocarbonate), as well as the total fraction of the latter in the composition of the catalyst, determine its properties (Table 1).

Table 1

**Activity, specific surface area and chemical composition of four-component oxide catalysts for low temperature conversion CO/H<sub>2</sub>O**

Catalyst	$A_{mean}$ , %	$S_{unit}$ , m <sup>2</sup> /g	$w[\text{CuO}]$ , mass. %	$w[\text{ZnO}]$ , mass. %	$w[\text{Cr}_2\text{O}_3]$ , mass. %	$w[\text{Al}_2\text{O}_3]$ , mass. %
Normative (Technical specifications of Rep. of Uzb. 6.3–57–95)	80 (no less)	–	54.0	11.0	14.0	19.5
CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	84.00	43.16	42.7	44.5	–	8.8
	91.00	68.50	41.3	39.2	–	17.8
	86.31	105.38	35.0	35.4	–	27.4
	76.54	123.93	30.6	29.7	–	38.0

As can be seen from the Table 1, the alumina content, as well as the mass ratio of copper (II) oxide to zinc oxide (obtained under various conditions for the synthesis of copper/zinc hydroxocarbonate), as well as the total fraction of the latter in the composition of the catalyst, determine its properties.

Table 2

**The activity, specific surface area and chemical composition of three-component oxide catalysts for low temperature conversion CO/H<sub>2</sub>O**

Catalyst	$w[\text{CuO}]$ , mass. %	$w[\text{ZnO}]$ , mass. %	$w[\text{Al}_2\text{O}_3]$ , mass. %	$S_{unit}$ , m <sup>2</sup> /g	$P_{unit} \times 10^{-2}$ , cm <sup>3</sup> /g	$A_{mean}$ , %
CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	36.80	58.60	2.80	147.89	6.40	92.22
	34.20	56.10	8.80	145.15	6.30	81.30
	31.70	49.90	17.10	160.38	6.90	76.00

As shown in the Table 2, copper/zinc hydroxocarbonate with an aurichalcite structure is formed both at a Cu:Zn ratio of 70:30 mol.% and at a ratio of 30:70 mol.%. It is shown that copper/zinc hydroxocarbonate

with the aurichalcite structure was obtained by precipitation from copper (II) nitrates and zinc, and sodium bicarbonate.

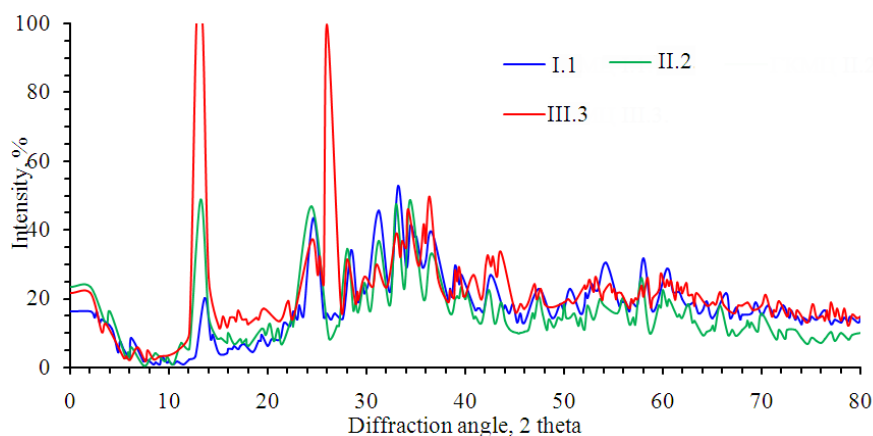


Figure 2. X-ray diffraction patterns of hydroxocarbonate samples copper/zinc obtained in three syntheses

The diffraction patterns of three samples of copper/zinc hydroxocarbonate, similar to the structure of aurichalcite are depicted in the Figure 2. According to the presented curves, three samples of copper/zinc hydroxocarbonate-HC Cu/Zn are characterized by the intensity of reflexes. The position of reflexes in all three samples remains almost constant.

In the spectrum of sample No. III.3, an intense reflection is observed in the range of  $27^\circ$ , the prevalence of the individual phase of copper (II) oxide in which, apparently, affects the structure and properties of the catalyst as a whole.

It has been revealed that the content of composing catalysts, the main part occupied a solution based on a zinc oxide lattice with copper (II) oxide clusters embedded in it during calcination of copper/zinc hydroxocarbonate with an aurichalcite structure.

All three catalysts obtained by varying the ratio Cu:Zn from copper/zinc hydroxocarbonate with the structure of aurichalcite have different properties, because a continuous series of solid solutions of copper/zinc hydroxocarbonate with the structure of aurichalcite is formed.

It has been noted that for an oxide low-temperature catalyst, the ratio Cu:Zn = 30:70 mol% is optimal. Violation of stoichiometry in the composition of copper/zinc hydroxocarbonate inevitably affects the structure and properties of the oxide catalyst. The coprecipitation conditions and the structure of copper/zinc hydroxocarbonate determine the subsequent activity of the oxide catalyst.

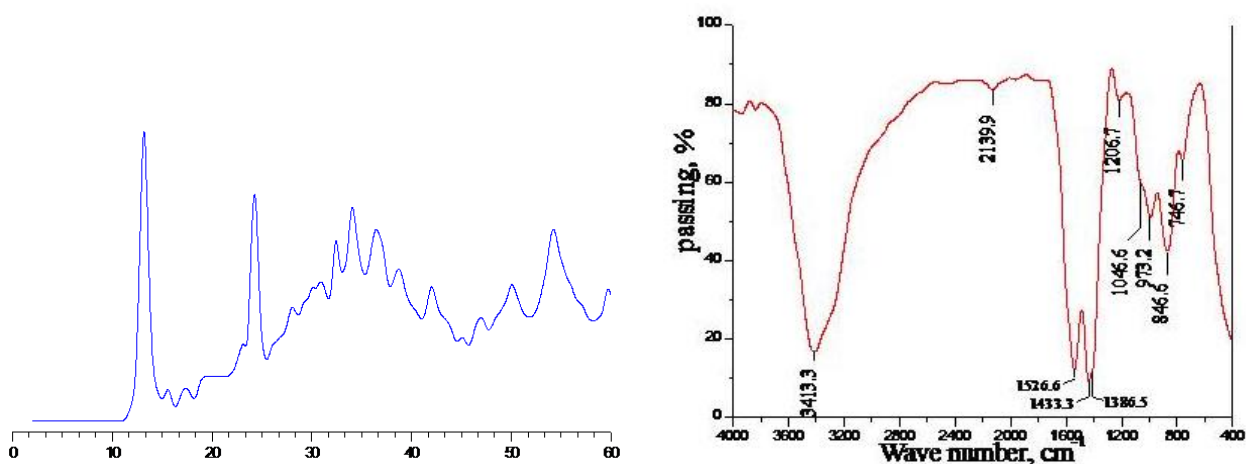


Figure 3. X-ray diffraction pattern and IR-spectrum of copper/zinc hydroxocarbonate {aurichalcite  $(\text{Cu}_{5-5x}\text{Zn}_{5x})(\text{CO}_3)_2(\text{OH})_6$ }

During the calcination of copper/zinc hydroxocarbonate with the aurichalcite structure  $(\text{Zn}_x\text{Cu}_{1-x})_5(\text{CO}_3)_2(\text{OH})_6$  (Fig. 3), a solid solution of copper/zinc oxides is formed with a maximum distortion

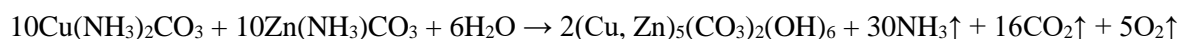
of the crystal lattice of copper (II) oxide. After preliminary activation of the catalyst (hydrogen reduction), there were formed the clusters of metallic copper with a high active surface area.

The aurichalcite spectra are characterized by: strong absorption vibrations at 1415 and 1340  $\text{cm}^{-1}$  of nitrate groups in gerhardtite; georgite is characterized by weak absorption vibrations below 1350  $\text{cm}^{-1}$ , except for carbonate groups at 838  $\text{cm}^{-1}$ ; hydroxyl groups at 3407, 3317  $\text{cm}^{-1}$  for malachite. Also, a slight difference is observed in the spectra of hydrozincite and aurichalcite, which makes impossible to distinguish which was monophase.

DSC can also be used as a method of identifying a mixture of phases and allows to determine the degree of homogeneity of zinc/copper. It is important that hydrozincite and aurichalcite have different destruction maxima of 241 °C and 325 °C, respectively, which makes it quite easy to identify hydrozincite present in the aurichalcite sample or vice versa. Thus, the optimal conditions for obtaining a catalyst with aurichalcite structure are established.

*The formation of catalyst precursors — hydroxocarbonate salt of copper and zinc with the structure of aurichalcite*

Under the action of mechanochemical activation of metals in a gaseous environment, copper and zinc ammonia are formed, which subsequently form a double hydroxocarbonate salt of copper and zinc with the structure of aurichalcite in the next stage of steam treatment:



The decomposition of such a precursor allows one to obtain copper and zinc oxides, the crystal lattices of which are distorted as much as possible, while after hydrogen reduction of such a solid solution, nanosized metal copper clusters are formed that have a high specific surface and high activity in the redox reaction of carbon monoxide conversion with water steam to produce hydrogen.

This technology is of significant interest as catalysts in the production of hydrogen and hydrogen-containing gases by the conversion of hydrocarbons, in the production of ammonia, methyl alcohol, etc.

### Conclusions

It was shown that of the many salts obtained from the precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with the aurichalcite structure is the most effective as a catalyst for the low-temperature conversion of carbon monoxide with water vapor.

The technology of producing nanocatalysts of low-temperature conversion of carbon monoxide with the aurichalcite structure was proposed, and the conditions for producing a precursor and catalyst with a reduced copper content of up to 20 % (from 54 to 34 wt.%) were optimized.

The conditions for obtaining a solid solution of copper/zinc oxides with an aurichalcite structure with a maximum distortion of the crystal lattice of copper oxide and the formation of nanoscale clusters of metallic copper with a high specific surface and activity in the redox reaction of carbon monoxide conversion with water vapor were determined.

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### Мыс құрамы төмендеген ( $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ ) көміртегі оксидінің төмен температуралы конверсиясында нанокатализаторларды алу

Жұмыстың негізгі мақсаты конверсиялық катализатор құрамындағы мыс құрамын төмендету ((II) мыс оксидіне қайта есептегенде) және жоғары каталитикалық және физика-механикалық сипаттамаларды сақтау болды. Металдардың гидроксокарбонаттарынан оксидті катализаторларды алудың белгілі технологиясына балама ретінде мыс/мырыш гидроксокарбонаты болып табылатын әдіс таңдалды. Түзілуден алынған көптеген тұздардың — метал гидроксокарбонаттары, аурихальцит құрылымы бар мыс/мырыш қос гидроксокарбонаты ең тиімді болып табылады, олардың ыдырауынан кейін металл мен мыстың наноөлшемді кластерлері пайда болады, үстіңгі беті бар және көміртегі оксидінің су буында сутекке айналу конверсиясының тотығу — калпына келтіру реакциясында белсенділікке ие. Мыс/мырыш гидроксокарбонатының тұндыру жағдайлары мен құрылымы, оксидті катализатордың келесі белсенділігін анықтайды. Төмен температуралы конверсиясының нанокатализаторын алу технологиясы ұсынылды (20 %-ға дейін 54-тен, 34-ші массаға дейін) және прекурсор мен катализаторды алу шарттары оңтайландырылған.

*Кілт сөздер:* төмен температуралы, катализаторлар, металдардың гидроксокарбонаттары, көміртегі оксиді конверсиясы, аурихальцит, мыс құрамы.

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### Получение нанокатализаторов низкотемпературной конверсии оксида углерода ( $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ ) с пониженным содержанием меди

Основной целью работы ставилось снижение содержания меди (в пересчете на оксид меди (II)) в составе катализатора конверсии и сохранение высоких каталитических и физико-механические характеристик. В качестве альтернативы известной технологии получения оксидных катализаторов из предшественников гидроксокарбонатов металлов был выбран способ, в котором предшественник представлял собой гидроксокарбонат меди/цинка. Показано, что из многих солей, полученных из предшественников — гидроксокарбонатов металлов, двойной гидроксокарбонат меди/цинка со структурой аурихальцита является наиболее эффективным, после разложения которого образуются наноразмерные кластеры металла и меди, которые имеют высокую удельную поверхность и активность в окислительно-восстановительной реакции конверсии оксида углерода водяным паром с образованием водорода. Показано, что условия соосаждения и структура гидроксокарбоната меди/цинка определяют последующую активность оксидного катализатора. Предложена технология получения нанокатализаторов низкотемпературной конверсии оксида углерода с пониженным (до 20 % — с 54 до 34 масс.%) содержанием меди и оптимизированы условия получения прекурсора и катализатора.

*Ключевые слова:* низкотемпературный, катализатор, гидроксокарбонаты металлов, конверсия оксида углерода, аурихальцит, содержание меди.

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(E-mail: gulmarzhan.94@mail.ru)***Thermodynamic analysis of oxidized copper minerals interaction with modified reagent**

Practicality of preliminary sulphidization of oxidized copper minerals for the purpose of oxidized ore concentration is shown in the paper. For the first time the thermodynamic analysis was carried out for interaction of modified sulphidizing reagent with major components of oxidized copper ore — malachite, azurite and chrysocolla. Ammonium polysulfide formed in the solution of sodium polysulfide and ammonium sulfate was used as modified sulphidizing reagent. Temperature dependence of standard Gibbs energy for the reaction of ammonium polysulfide with oxidized copper minerals was determined. It was noted that standard Gibbs energy for malachite and azurite interaction with modified reagent has negative values in the temperature range of 298,15–373 K, thus showing high probability of interaction, which grows together with temperature. Interaction with chrysocolla is less active than with malachite and azurite but is still possible at mentioned temperature, with interaction probability again proportional to temperature. Thus, the possibility of oxidized copper minerals sulphidization with modified sulphidizing reagent is determined in the research.

**Keywords:** oxidized minerals, chrysocolla, malachite, azurite, modified sulphidizing reagent, sulphidization, thermodynamic analysis, Gibbs energy.

*Introduction*

Cheap flotation enrichment methods, conventional for sulfide ore, are less effective for oxidized ore due to natural hydrophilicity of oxidized copper minerals surface [1–3].

One of feasible solutions is chemical modification of minerals via sulphidization resulting in transformation of oxidized minerals into sulfidized ones, which can improve the flotation enrichment efficiency [4–9].

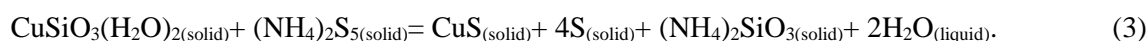
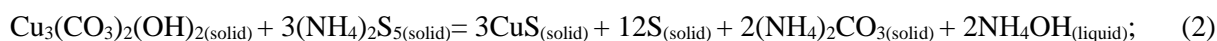
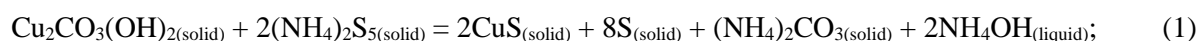
The thermodynamic analysis of possible reactions with determination temperature dependence of standard Gibbs energy has been carried out in order to assess the possibility of sulphidization with modified reagent.

Ammonium polysulfide formed in the solution of sodium polysulfide and ammonium sulfate was used as modified sulphidizing reagent.

The objective of work was to find the temperature dependence of ammonium polysulfide interaction with major components of oxidized copper ore, such as malachite, azurite and chrysocolla.

*Experimental*

Three types of interaction of modified reagent with copper compounds — malachite, azurite and chrysocolla have been studied:



Probability of reactions was estimated by alteration of standard Gibbs energy.

Calculation of temperature dependence of standard Gibbs energy is based on Hess law [10] and was made using the formula

$$\Delta_r G_T^0 = \sum \Delta_r G_T^0 (\text{products}) + \sum \Delta_r G_T^0 (\text{init.}), \quad (4)$$

where  $\Delta_r G_T^0$  — standard Gibbs energy at temperature (T),  $\sum \Delta_r G_T^0 (\text{products})$  — sum of standard Gibbs energy of reactions products formation at temperature (T),  $\sum \Delta_r G_T^0 (\text{init.})$  — sum of standard Gibbs energy of initial components formation at temperature (T).

Temperature dependence of reaction velocity constant was calculated using the next formula:

$$\lg K_{P(T)} = -\Delta_f G^0_T / (2.303RT), \quad (5)$$

where  $R$  is the universal gas constant.

Temperature dependence of standard Gibbs energy of reactions products formation was determined by approximated method of Temkin-Schwartzman [11, 12], taking  $\Delta C_p^0 = \text{const}$ , by the formula

$$\Delta_f G^0_T = \Delta_f H^0_{298.15} - T\Delta_f S^0_{298.15} - TM\Delta_f C_p^0_{298.15}, \quad (6)$$

where  $\Delta_f H^0_{298.15}$  is the standard enthalpy of compound formation at 298.15 K;  $\Delta_f S^0_{298.15}$  is the standard entropy of compound formation at 298.15 K;  $\Delta_f C_p^0_{298.15}$  is the standard heat of compound formation at 298.15 K;  $M$  is the coefficient, equal to

$$M = 298.15/T - 1 + \ln(T/298.15). \quad (7)$$

Standard entropy was determined by formula

$$\Delta_f S^0_{298.15} = S^0_{298.15} - \sum S^0_{298.15}(\text{elementary substance}), \quad (8)$$

where  $S^0_{298.15}$  is the standard entropy of compound at 298.15 K;  $\sum S^0_{298.15}(\text{elementary substance})$  is the sum of standard entropies of substances forming the compound at 298.15 K.

Standard heat capacity of compound formation was determined by the formula:

$$\Delta_f C_p^0_{298.15} = C_p^0_{298.15} - \sum C_p^0_{298.15}(\text{elementary substance}), \quad (9)$$

where  $C_p^0_{298.15}$  is the standard heat capacity of compound at 298.15 K;  $\sum C_p^0_{298.15}(\text{elementary substance})$  is the sum of standard heat capacities of substances forming the compound, at 298.15 K.

In case of insufficiency of the available literature data, the necessary values have been determined by proximate methods.

Standard heat capacity was estimated by the Kumok method [13] based on heat capacity increments system:

$$C_p^0_{298.15}(A_m B_n) = mC_p^i_{298.15}(A^{n+}) + nC_p^i_{298.15}(B^{m-}), \quad (10)$$

where  $C_p^i_{298.15}(A^{n+})$  is the increment of cation heat capacity;  $C_p^i_{298.15}(B^{m-})$  is the increment of anion heat capacity.

### Results and Discussion

The standard enthalpy values of compound formation at 298.15 K are given in the Table 1. Values for  $H_2O(\text{liquid})$ ,  $NH_4OH(\text{liquid})$ ,  $(NH_4)_2CO_3(\text{solid})$ ,  $CuS(\text{solid})$ ,  $Cu_2CO_3[OH]_2(\text{solid})$ ,  $Cu_3[CO_3]_2[OH]_2(\text{solid})$  compounds are from [6–8].  $S(\text{solid})$  equals to  $S_{8(g)}$  with enthalpy data by [14]. Standard enthalpy for  $(NH_4)_2S_5(\text{solid})$ ,  $(NH_4)_2CO_3(\text{solid})$  and  $(NH_4)_2SiO_3(\text{solid})$  was calculated by Kassenov method from ionic increments [12]. Lacking data on increment of  $S_5^{2-}$ ,  $SiO_3^{2-}$  ions were found by evaluation method using standard enthalpy of sodium pentasulfide and silicates of First Group metals [16]. Data for  $CuSiO_3 \cdot nH_2O(\text{solid})$  are from [18].

Table 1

Standard enthalpy of compound formation

Substance	$-\Delta_f H^0_{298.15}, \text{ kJ} \cdot \text{mol}^{-1}$
$H_2O(\text{liquid})$	285.829
$NH_4OH(\text{liquid})$	361.271
$S(\text{solid})$	12.735
$(NH_4)_2S_5(\text{solid})$	94.9
$(NH_4)_2CO_3(\text{solid})$	821.1
$CuS(\text{solid})$	53.136
$(NH_4)_2SiO_3(\text{solid})$	1251.6
$Cu_2CO_3[OH]_2(\text{solid})$	1051.020
$Cu_3[CO_3]_2[OH]_2(\text{solid})$	1631.341
$CuSiO_3 \cdot nH_2O(\text{solid})$	1747.3

There are standard entropy values of compound formation at 298.15 K in the Table 2.

Data for  $H_2O(\text{liquid})$ ,  $NH_4OH(\text{liquid})$ ,  $S(\text{solid})$ ,  $CuS(\text{solid})$ ,  $Cu_2CO_3[OH]_2(\text{solid})$ ,  $Cu_3[CO_3]_2[OH]_2(\text{solid})$ ,  $CuSiO_3 \cdot nH_2O(\text{solid})$  were calculated by formula (8) based on [14–17]. For chrysocolla accepted  $n = 2$ . Standard



entropy at 298.15 K for  $(\text{NH}_4)_2\text{S}_{5(\text{solid})}$ ,  $(\text{NH}_4)_2\text{CO}_{3(\text{solid})}$ ,  $(\text{NH}_4)_2\text{SiO}_{3(\text{solid})}$  was determined using entropy data found by Kumok method [13].

Table 2

### Standard entropy of compound formation

Substance	$\Delta_f S^0_{298,15}, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\text{H}_2\text{O}_{(\text{liquid})}$	-162.955
$\text{NH}_4\text{OH}_{(\text{liquid})}$	-359.004
$\text{S}_{(\text{solid})}$	23.567
$(\text{NH}_4)_2\text{S}_{5(\text{solid})}$	-579.1
$(\text{NH}_4)_2\text{CO}_{3(\text{solid})}$	-841.3
$\text{CuS}_{(\text{solid})}$	1.453
$(\text{NH}_4)_2\text{SiO}_{3(\text{solid})}$	-857.5
$\text{Cu}_2\text{CO}_3[\text{OH}]_{2(\text{solid})}$	-503.504
$\text{Cu}_3[\text{CO}_3]_2[\text{OH}]_{2(\text{solid})}$	-671.479
$\text{CuSiO}_3 \cdot n\text{H}_2\text{O}_{(\text{solid})}$	-629.305

Standard heat capacity of compounds formation at 298,15 K is shown in the Table 3.

For  $\text{H}_2\text{O}_{(\text{liquid})}$ ,  $\text{NH}_4\text{OH}_{(\text{liquid})}$ ,  $\text{S}_{(\text{solid})}$ ,  $\text{CuS}_{(\text{solid})}$ ,  $\text{Cu}_2\text{CO}_3[\text{OH}]_{2(\text{solid})}$  compounds the data were taken from [14–17]. Values for  $(\text{NH}_4)_2\text{S}_{5(\text{solid})}$ ,  $(\text{NH}_4)_2\text{CO}_{3(\text{solid})}$ ,  $(\text{NH}_4)_2\text{SiO}_{3(\text{solid})}$  compounds were found using Kumok method [13], those for  $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}_{(\text{solid})}$  are from [19].

Table 3

### Standard heat capacity of compounds formation

Substance	$\Delta_f C_p^0_{298,15}, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\text{H}_2\text{O}_{(\text{liquid})}$	31.793
$\text{NH}_4\text{OH}_{(\text{liquid})}$	53.576
$\text{S}_{(\text{solid})}$	-2.594
$(\text{NH}_4)_2\text{S}_{5(\text{solid})}$	-17.633
$(\text{NH}_4)_2\text{CO}_{3(\text{solid})}$	-14.3
$\text{CuS}_{(\text{solid})}$	0.712
$(\text{NH}_4)_2\text{SiO}_{3(\text{solid})}$	-18.8
$\text{Cu}_2\text{CO}_3[\text{OH}]_{2(\text{solid})}$	-5.309
$\text{Cu}_3[\text{CO}_3]_2[\text{OH}]_{2(\text{solid})}$	4.203
$\text{CuSiO}_3 \cdot n\text{H}_2\text{O}_{(\text{solid})}$	45.288

By means of the equation 6 the temperature dependence of standard Gibbs energy for every interacting compound have been calculated. The results are given in the Table 4.

Table 4

### Temperature dependence of standard Gibbs energy of compounds formation

Substance	T, K					
	298.15	313	328	343	358	373
	$\Delta_f G^0_T, \text{kJ} \cdot \text{mol}^{-1}$					
$\text{H}_2\text{O}_{(\text{liquid})}$	-237.244	-234.836	-232.426	-230.038	-227.67	-225.323
$\text{NH}_4\text{OH}_{(\text{liquid})}$	-254.234	-248.922	-243.595	-238.305	-233.05	-227.828
$\text{S}_{(\text{solid})}$	5.708	5.359	5.009	4.660	4.313	3.967
$(\text{NH}_4)_2\text{S}_{5(\text{solid})}$	77.759	86.365	95.070	103.788	112.517	121.258
$(\text{NH}_4)_2\text{CO}_{3(\text{solid})}$	-570.266	-557.768	-545.133	-532.488	-519.834	-507.171
$\text{CuS}_{(\text{solid})}$	-53.569	-53.591	-53.614	-53.637	-53.66	-53.684
$(\text{NH}_4)_2\text{SiO}_{3(\text{solid})}$	-995.936	-983.196	-970.313	-957.417	-944.509	-931.589
$\text{Cu}_2\text{CO}_3[\text{OH}]_{2(\text{solid})}$	-900.9	-893.423	-885.869	-878.301	-870.736	-863.167
$\text{Cu}_3[\text{CO}_3]_2[\text{OH}]_{2(\text{solid})}$	-1431.139	-1421.166	-1411.09	-1401.01	-1390.928	-1380.843
$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}_{(\text{solid})}$	-1559.673	-1550.344	-1540.953	-1531.594	-1522.264	-1512.963

Using respective data from Table 4 in the equation (4) the temperature dependence of standard Gibbs energy for the reactions (1–3) was determined. Formula (5) was used to calculate temperature dependence of equilibrium constant for the reaction (Table 5).

Table 5

Temperature dependence of standard Gibbs energy and equilibrium constant

Reaction	T, K	298.15	313	328	343	358	373
10	$-\Delta_r G^0_T, \text{kJ} \cdot \text{mol}^{-1}$	394.826	399.229	403.75	408.367	413.048	417.808
	Equation	$\Delta_r G^0_T = -0.307T - 303.1$					
	$\lg K_p$	69.25	66.70	64.37	62.26	60.34	58.58
11	$-\Delta_r G^0_T, \text{kJ} \cdot \text{mol}^{-1}$	543.349	547.774	552.31	556.931	561.615	566.377
	Equation	$\Delta_r G^0_T = -0.307T - 451.5$					
	$\lg K_p$	95.30	91.52	88.06	84.91	82.04	79.41
12	$-\Delta_r G^0_T, \text{kJ} \cdot \text{mol}^{-1}$	19.247	21.044	22.86	24.684	26.51	28.346
	Equation	$\Delta_r G^0_T = -0.121T + 16.99$					
	$\lg K_p$	3.38	3.52	3.64	3.76	3.87	3.97

Based on Table 5 data, the temperature dependence diagrams were built for interaction of malachite, azurite and chrysocolla with modified reagent (Fig. 1).

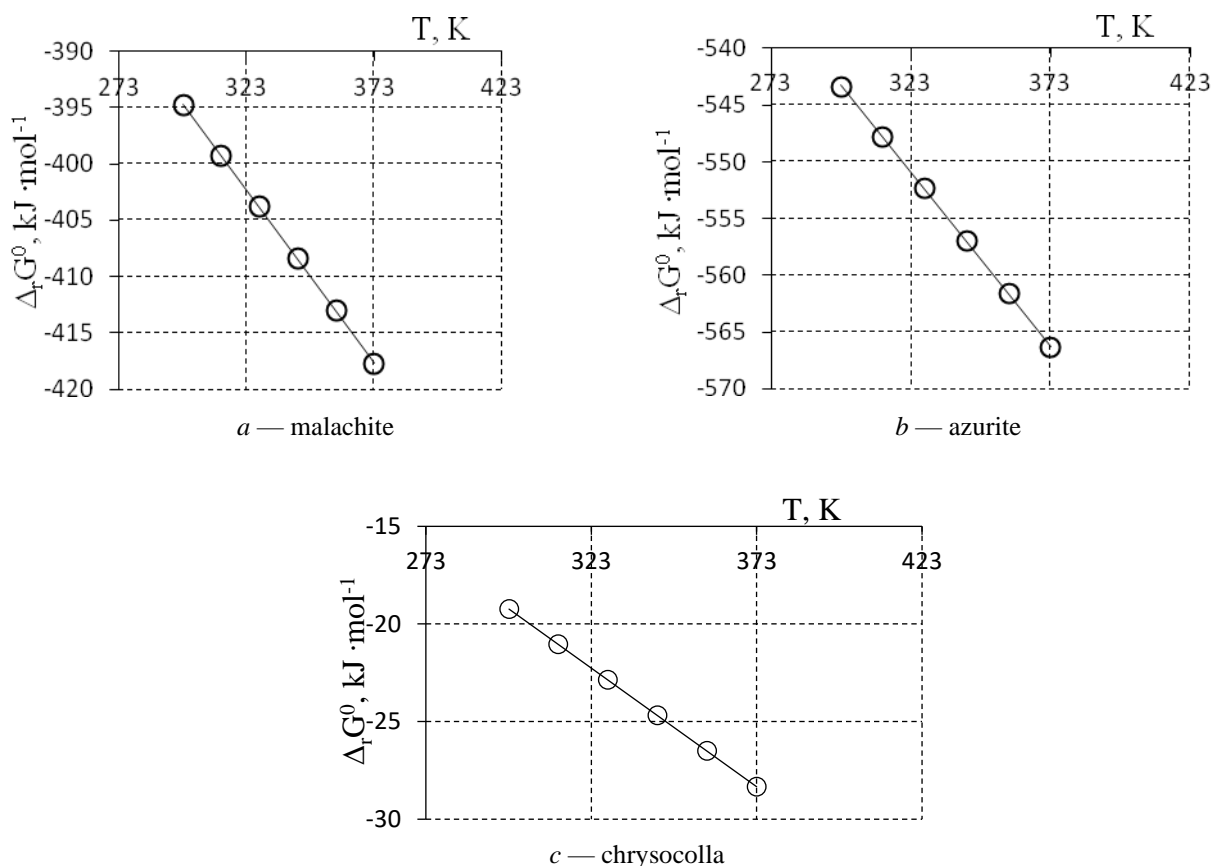


Figure 1. Temperature dependence of standard Gibbs energy for interaction of copper minerals with modified reagent

As follows from Figure 1, standard Gibbs energy for malachite and azurite is negative in the whole temperature range, indicating high probability of interaction, growing with temperature. Interaction with chrysocolla is less active than with malachite and azurite but is still possible at mentioned temperature, with interaction probability again proportional to temperature growth.

Interaction of a modified reagent with chrysocolla in interval of 298.15–373 K is lower than for malachite and azurite. But also it can proceed in this temperature interval. Raise of temperature also is able to increase the probability of interaction.

### Conclusions

Based on the results of thermodynamic analysis the modified reagent is recommended as oxidized copper minerals sulphidizer for flotation enrichment of oxidized copper ore. In particular, the possibility of sulphidizing the ore containing malachite, azurite and chrysocolla as major components, is demonstrated in the study.

*Financial support of scientific research was carried out under the project AP 05130454 «Development of an effective technology for the processing of oxidized copper ores using a modified reagent» of the Ministry of education and sciences of the Republic of Kazakhstan.*

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### Тотыққан мыс минералдарының модификацияланған реагентпен әрекеттесуінің термодинамикалық талдауы

Тотыққан мыс кендерін байыту кезінде тотыққан мыс минералдарын алдын ала сульфидтеу керектігі көрсетілген. Алғаш рет тотыққан мыс кендерінің негізін құраушы — малахит, азурит және хризоколланың модификацияланған сульфидтеуші реагентпен әрекеттесуінің термодинамикалық талдауы жүргізілді. Модификацияланған сульфидтеуші реагент ретінде натрий полисульфиді мен аммоний сульфатының ерітіндісінде пайда болған аммоний полисульфиді қолданылды. Аммоний полисульфидінің тотыққан мыс минералдарымен реакциясының стандартты Гиббс энергиясының температуралық тәуелділігі айқындалды. Малахит пен азурит үшін 298,15–373 К аралығында модификацияланған реагентпен реакциясы кезінде стандартты Гиббс энергиясы теріс әсер көрсететіндігі анықталды. Сондықтан модификацияланған реагенттің малахит және азуритпен әрекеттесу ықтималдығы жоғары. Температураның

жоғарылауы өзара әсер ету ықтималдығын арттырады. Модификацияланған реагенттің хризоколмен әрекеттесуі малахит пен азуритке қарағанда әлсіз көрсетілген. Алайда осы температура интервалында ағып кетуі мүмкін. Температураның жоғарылауы сонымен қатар өзара әсер ету ықтималдылығын арттырады. Осыған байланысты, тотыққан мыс минералдарының модификацияланған сульфидтеуші реагенті — аммоний полисульфидімен сульфидтенуінің мүмкіндігі көрсетілген.

*Кілт сөздері:* тотыққан минералдар, хризокола, малахит, азурит, сульфидтеуші модификацияланған реагент, сульфидтеу, термодинамикалық талдау, Гиббс энергиясы.

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## Термодинамический анализ взаимодействия окисленных минералов меди с модифицированным реагентом

Показана необходимость предварительной сульфидизации окисленных минералов меди при обогащении окисленной медной руды. Впервые проведен термодинамический анализ взаимодействия модифицированного сульфидирующего реагента с основными составляющими окисленной медной руды — малахитом, азуритом и хризоколлой. В качестве модифицированного сульфидирующего реагента применен полисульфид аммония, образованный в растворе полисульфида натрия и сульфата аммония. Определена температурная зависимость стандартной энергии Гиббса реакции полисульфида аммония с окисленными медными минералами. Показано, что изменение стандартной энергии Гиббса реакции для малахита и азурита с модифицированным реагентом в интервале 298,15–373 К принимает отрицательные значения. Следовательно, высока вероятность взаимодействия модифицированного реагента с малахитом и азуритом. Повышение температуры способствует увеличению вероятности взаимодействия. Связь модифицированного реагента с хризоколлой выражена слабее, чем малахита и азурита. Однако она может протекать в данном температурном интервале. Повышение температуры также способствует увеличению вероятности взаимодействия. Таким образом, установлена принципиальная возможность сульфидизации окисленных медных минералов модифицированным сульфидирующим реагентом — полисульфидом аммония.

*Ключевые слова:* окисленные минералы, хризокола, малахит, азурит, модифицированный сульфидирующий реагент, сульфидизация, термодинамический анализ, энергия Гиббса.

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## Possibility of enrichment of ore processing waste from Karagaily and Zheskazgan mining plants by dry separation method

This study aims at review of the effects of dry separation method on the ore flotation efficiency and thoroughly discusses the possibility of waste enrichment by sieving through fine-mesh sieves with sizes ( $d > 0.4$ ;  $0.16 < d < 0.4$ ;  $0.08 < d < 0.16$ ;  $d < 0.08$  mm). A granulometric analysis of four samples waste production, was carried out and the copper content in each fraction was determined. According to the results of the study, the following was established: 1) the largest proportion has a grain size fraction over the range 0.16–0.08 mm in the «current tails» of the Karagaily ore-processing plant, in this fraction turned out to be the highest copper content; 2) a larger amount of copper is contained in coarse fraction of «stored tails» and «current tails» of Zheskazgan ore-processing plant 1–2, therefore, it is possible to sift out a finely dispersed fraction; 3) the largest fraction by grain size is over the range of 0.16–0.08 mm in «aged tails» of Zheskazgan PP 3, but the largest weight percentage of copper is over the range  $0.08 < d < 0.16$ . As a result of the studies, it was found that «current tails» and «stored tails» are applicable for the ore enrichment by dry separation method. The «Current tails» of the KPP are not suitable for enrichment by dry separation.

**Keywords:** concentration plant, tailings samples, analysis, fraction, grain sizes, screening, copper content, dry separation.

### Introduction

The problem of handling solid waste is the most urgent component of ensuring national security for our country, since the volumes of accumulated waste are considered as one of the factors of the progressive environmental crisis. The sphere of secondary use of resources in Kazakhstan is at the stage of active formation. The purpose of this research was to study the possibility of using dry separation method for enrichment of ore processing waste from mining plants.

Today, special attention is paid to the problem of utilization of mining waste, as the use of technogenic mineral resources is not only one of the reserves of mineral raw materials for the mining industry, but also an important part of the state policy of resource saving and environmental protection.

Around the world, the process of mining and processing metal ores forms a large amount of waste of various aggregation state. At present, they contain billions of tons of ore that has undergone certain processing. Further accumulation of mining complex waste causes a serious problems of the environmental situation on the planet. The urgent issue is the creation of new environmentally friendly technologies for mining, focused on their maximum use [1].

Recent years, there is an increase in waste accumulation, therefore the environmental factor significantly impacts to the economy. According to the estimates of specialists from German metallurgical companies, the items of taxes and environmental costs of production have begun to gain the most weight recently. Therefore, progressive technologies for the production of metals from recycled materials are increasingly being introduced abroad. The sources of such raw materials are solid waste storage facilities of mining and metallurgical industries, the so-called technogenic deposits [2].

### Experimental

The difficulty in separating of contaminants is caused mainly due to the moisture of the mass: with its increase, the stickiness of the impurities grows. In addition to moisture, the degree of stickiness is influenced by the grain and mineralogical compositions: the greatest stickiness is observed in clay and loamy soils, and less — in sandy loam, sand and stone dust formed during crushing. With the dry enrichment method, it is advisable to use cyclones for screening small fractions, since the use of vibrosieve with small mesh sizes is impossible due to the constant contamination of the holes [3, 4].

Therefore, for the enrichment of granules with a diameter of less than 1 mm by dry separation method, vibration systems are used. They are supplied with the platform and a separation plate with air blowing, which are inclined at certain angle to the horizontal. In this case it is possible to separate the mineral in accordance with their size under the influence of the vibration friction force.

The dry separation and enrichment unit includes a second vibration platform, which is installed on the second one-navigation separation. The angle of inclination and the direction of vibration force is approximately 20–60°. At least one gutter is installed on the indicated vibration platform, which is placed under the material inlet, a grating part is installed inside the gutter, the angle of the grating part and the vibration of the second platform is 2–20°. The sealed chamber is closed by the grating part, on the side wall of the gutter there is a gas inlet, at least one outlet for deposition and one more for the upper drain, a first, second, third, fourth partitions are installed around the side wall of the gutter. The above mentioned output for deposition is installed in the direction of low end of the sieve piece.

A useful effect is achieved by means of the vibration platform and a strainer, which are inclined to the vibration force. Enrichment and separation can be carried out in accordance with the mineral density. Moreover, due to the outlet for the upper discharge, the lighter material can be separated by the pouring method, which allows to achieve a good separation effect [5].

Four samples of the following grades have been taken for the experiment: 1) «current tails» of the Karagaily processing plant (KPP); 2) «stored tails» of the Zhezkazgan processing plant (ZHPP) No. 1, 2; 3) «current tails» of ZHPP; 4) «stored tails» of ZHPP No. 3 (grain sizes in samples are 0.01–0.5 mm). These samples have been subjected to study in terms of the possibility of enrichment with sieve methods.

Dispersion of the samples was determined by sieve analysis. It has been taken 250 grams of powder from the processing plants. This samples were passed through sieves with sizes 0.4, 0.16, and 0.08. Before sifting large lumps of the sample were grinded in the mortar. Each fraction was weighed and the copper content was determined on the atomic absorption spectrometer «Varian AA-140».

### Results and Discussion

The aim of our research work was to determine the feasibility of enriching these wastes by sieving through fine mesh sieves with sizes ( $d > 0.4$ ;  $0.16 < d < 0.4$ ;  $0.08 < d < 0.16$ ;  $d < 0.08$  mm). In order to achieve this purpose has been conducted a particle size analysis of mentioned above samples.

Assuming the dividing out of the number of grains by size to be the normal distribution, using the approximation and the Gauss function, it was determined the position of the distribution maximum and other statistical characteristics such as, the mathematical expectation and variance (Fig. 1).

For KPP «current tails», the distribution is described by a Gaussian curve with the following parameters: expectation is 0.11 mm, variance = 0.05, which confirms the normal distribution, i.e. uniform distribution in all fractions.

Based on the results of the mineralogical analysis, the granulometric analysis of the «Karagaily current tails» sample has been carried out. According to the results copper was in the form of chalcopyrite, due to its hardness that is contained in large fractions. Granulometric analysis of the remaining samples was also performed.

The results of this work are presented in the tables and depicted in the graphs below. As a result of conducted experiments the next data have been obtained. According to this values the sieves sizes, namely diameter impacts to the composition and copper content of considered samples. A maximum amount of mass fraction and copper content corresponds to the sieves with diameter between 0.08 and 0.16 mm.

Table 1

Results of particle size analysis of the sample «Current tails» (KPP)

Sieve diameter, mm	Mass fraction		Average copper content, %
	g	%	
$d > 0.4$	0	0	0
$0.16 < d < 0.4$	71.18	28.47	0.02
$0.08 < d < 0.16$	145.12	58.05	0.18
$d < 0.08$	33.7	13.48	0.01
For all fractions	250.0	100	0.11

The average copper content for all fractions was calculated by the formula

$$A = \sum_i p_i x_i \quad A = \sum_i p_i x_i = 0.0 \cdot 0 + 0.2847 \cdot 0.02 + 0.5805 \cdot 0.18 + 0.1348 \cdot 0.01 = 0.11$$

As a result of the analysis (Table 1) it has been determined that the largest fraction of the grain size is in the range of 0.16–0.08 mm, therefore, there is the highest copper content in this fraction.

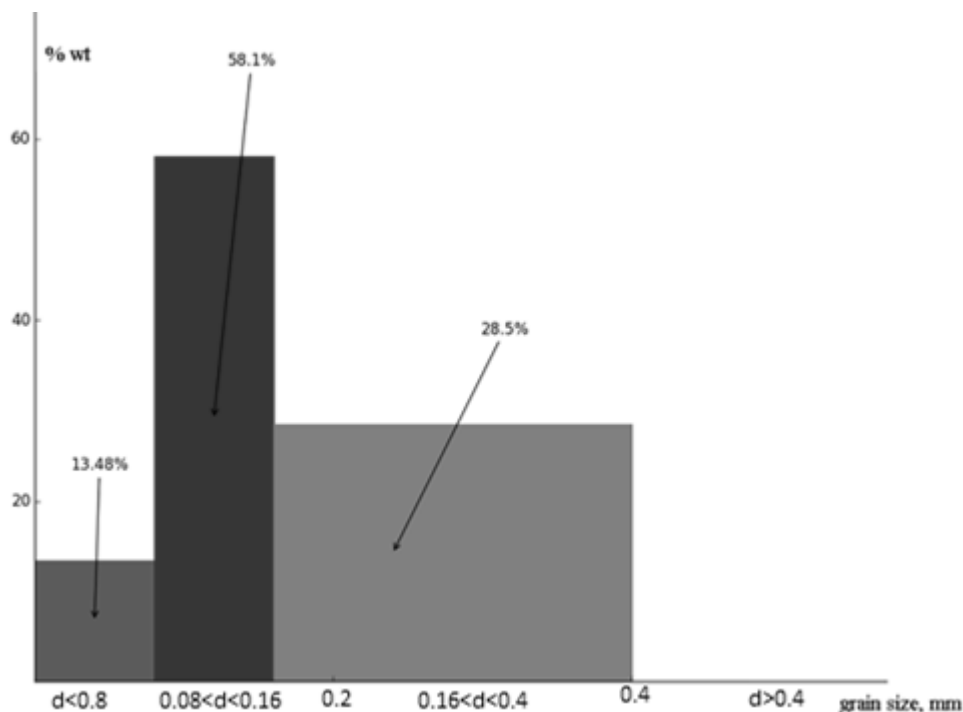


Figure 1. Distribution of the sample «current tails» of KPP by grain sizes

Based on the analysis, it was shown that division into fractions for enrichment is not feasible for the «current tailings» of KPP, since after sieving the percentage of waste will be much higher than in other samples. This fact makes the dry separation method ineffective for the mentioned above sample.

According to the results of the analysis of the «stored tailings» sample of ZHPP 1, 2 (Table 2) more copper is contained in the larger fractions of the sample therefore, it is possible to sift out the finely dispersed fraction and enrich the copper content of the tailings (Fig. 2).

Table 2

**Results of the granulometric analysis of the sample «Stored tails» of ZHPP 1,2**

Sieve diameter, mm	Mass fraction,		Average copper content, %
	g	%	
d > 0.4	0	0	0
0.16 < d < 0.4	97.14	38.86	0.11
0.08 < d < 0.16	124.54	49.82	0.08
d < 0.08	28.32	11.32	0.01
For all fractions	250.0	100	0.08

According to the analysis results of the sample «current tailings» of ZHPP 1, 2 (Table 3) it is clear that, as well as the previous one, more copper is contained in the larger fractions of the sample, and in the diapason of  $0.16 < d < 0.4$  the largest amount (0.09 %), therefore, it is possible to sift out the finely dispersed fraction and enrich the copper content (Fig. 3).

As a result of the analysis of the «stored tails» of ZHPP 3, it was determined that the largest fraction of the grain size is in the range of 0.4–0.16 mm, but the largest percentage of the mass fraction of copper is in the fraction of  $0.08 < d < 0.16$ . In this case, it is advisable to sift out the coarse fraction  $d > 0.4$  (Fig. 4).



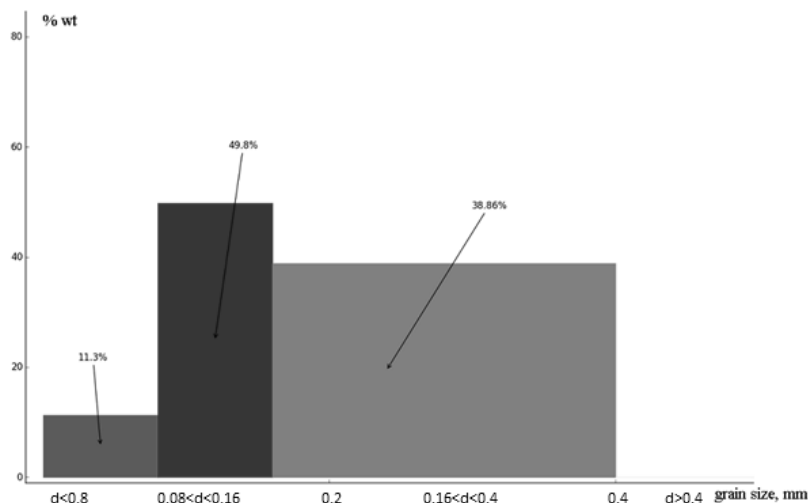


Figure 2. Distribution of the «stored tails» sample of ZHPP 1, 2 by grain size

Table 3

**Results of the granulometric analysis of the sample «Current tails» of ZHPP 1, 2**

Sieve diameter, mm	Mass fraction,		Average copper content, %
	g	%	
$d > 0.4$	0	0	0
$0.16 < d < 0.4$	128.01	51.20	0.09
$0.08 < d < 0.16$	91.71	36.68	0.08
$d < 0.08$	30.28	12.12	0.01
For all fractions	250.0	100	0.07

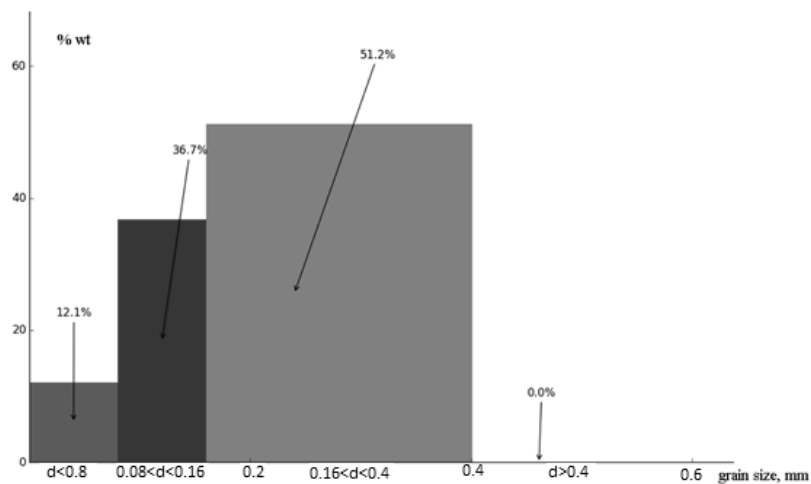


Figure 3. Distribution of current tailings sample by grain size 1, 2

Table 4

**Results of the particle size analysis of the sample «Stored tails» ZHPP 3**

Sieves diameter, mm	Mass fraction,		Average copper content, %
	g	%	
$d > 0.4$	11.88	4.75	0.02
$0.16 < d < 0.4$	120.08	48.03	0.06
$0.08 < d < 0.16$	59.67	23.87	0.09
$d < 0.08$	58.37	23.35	0.01
For all fractions	250.0	100	0.06

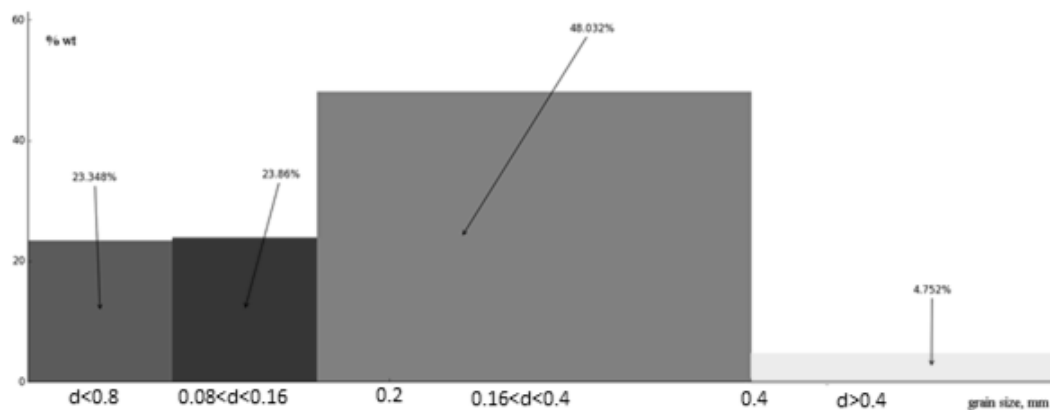


Figure 4. Distribution of the «stored tails» sample of the ZHPP 3 by grain size

The results obtained in this study indicate that the both «Current tails» and «Stored tails» of Zhezkazgan ore plant processing 1, 2, and «Stored tails» of third sample KPP are suitable for the dry separation enrichment method. However the current tails of Karagaily plant have a Gaussian normal distribution of all fractions and the copper content is appropriate, so these samples are not suitable for enrichment by dry separation. The application of the dry separation method for this sample forms a large amount of waste, therefore, for this fraction, dry separation is ineffective.

The dry separation method allows to use the units with double vibrating platforms and sieve components located one above the other. The material for enrichment must be dried to a moisture content of 5 %.

The difficulty of separation of contaminants is mainly due to the humidity: the wetter is the sample, the stickier impurities are. The degree of stickiness, in addition to moisture, is influenced by grain and mineralogical compositions. The greatest stickiness is observed in clay and loamy soils, smaller one in sandy, sand and stone dust formed during crushing.

Therefore, to enrich granules with a diameter of less than 1 mm by the method of dry separation, vibration systems are used with the help of a platform and separation plate with a blow-by air, which are inclined at an angle to the horizon, then under the influence of vibration friction force it is possible to separate the mineral according to the size.

### Conclusions

As a result of the research, it is established that the «current tails» of the ZHPP 1, 2 are suitable for enrichment by means of dry separation method; «stored tails» of the ZHPP 1, 2 and «stored tails» of the KPP 3 are applicable too.

Thus, dry separation plants with double vibration platforms and sieves located one above the other can be used to enrich the concentration plants tails by the dry separation method. The material for enrichment must be entirely dried to a humidity of 1.5–5.0 %.

The dry separation process is required to enrich maximum ore and obtain copper from sample materials, which is advantageous for the copper separation in subsequent processes.

The validation of the dry separation method allowed to demonstrate that the presence of copper in the ore tailings can be determined by means of simple methods of analysis. The pretreatment of the ore tailings is established under technical considerations, environmental pollution, capital costs and operational risks.

The advantages of dry separation method are the low capital and energy costs, in addition to the great flexibility to be environmental friendly. When used in the removal of soil contaminants, it reduces disposal costs and allows the recovery of precious metals.

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### **Қарағайлы және Жезқазған кен-байыту фабрикаларының қалдықтарын құрғақ бөлу әдісімен байыту мүмкіндігі**

Мақала құрғақ бөлу әдісінің кенді байыту тиімділігіне әсерін талдауға бағытталған. Сонымен қатар, өлшемдері ұсак електерді ( $d > 0,4$ ;  $0,16 < d < 0,4$ ;  $0,08 < d < 0,16$ ,  $d < 0,08$  мм) елеуіштер арқылы өткізіп, қалдықтарды байыту мүмкіндігі қарастырылған. Төрт қалдық үлгілерінің гранулометриялық сарапта-масы жүргізіліп, олардың әрбір фракцияларындағы мыстың құрамдық мөлшері анықталған. Зерттеу нә-тижелері бойынша: 1. Қарағайлы байыту фабрикасының «ағымдық қалдықтарының»  $0,16-0,08$  мм ара-лығындағы фракцияларында бөлшектердің өлшемі ең жоғары болатыны және осы фракцияларда мыс-тың ең жоғары мөлшері табылған; 2. Жезқазған байыту фабрикасының 1–2 үлгілерінің «ағымдық» және «жинақталған» қалдықтарында да мыстың мөлшері жоғары болады; 3. Бөлшектер мөлшерінің өлшемі бойынша ең үлкен фракция Жезқазған байыту комбинатының 3-үлгісіндегі  $0,16-0,08$  мм аралығындағы «жинақталған» қалдықтарда кездеседі. Зерттеулер нәтижесінде «ағымдық» және «жинақталған» қал-дықтарды құрғақ бөлу әдісі арқылы байытуға болатыны анықталды. Қарағайлы байыту комбинатының «ағымдық» қалдықтары құрғақ бөлу әдісімен байытуға жарамайды.

*Кілт сөздер:* байыту фабрикасы, қалдық үлгілері, сараптама, фракция, түйіршік өлшемдері, елеу, мыс-тың құрамы, құрғақ бөлу.

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### **Возможность обогащения отходов Карагайлинской и Жезказганской горно-обогатительных фабрик методом сухого разделения**

Статья направлена на анализ влияния метода сухого разделения на эффективность обогащения руды. Кроме того, обсуждены возможности обогащения отходов путем просеивания через мелкие сита с раз-мерами ( $d > 0,4$ ;  $0,16 < d < 0,4$ ;  $0,08 < d < 0,16$ ,  $d < 0,08$  мм). Был проведен гранулометрический анализ четырех образцов и определено содержание меди в каждой фракции. По результатам исследования было установлено: 1) наибольший размер зерна имеют фракции в диапазоне  $0,16-0,08$  мм в «текущих хвостах» Карагайлинского обогатительного комбината, в этой же фракции оказалось самое высокое содержание меди; 2) большое количество меди также обнаружено в крупной фракции «лежалых хво-стов» и «текущих хвостов» Жезказганского обогатительного комбината 1–2, поэтому здесь можно от-фильтровать мелкодисперсную фракцию; 3) самая большая фракция по размеру зерна находится в диа-пазоне  $0,16-0,08$  мм в «лежалых хвостах» Жезказганского обогатительного комбината 3, но наиболь-ший весовой процент меди находится в диапазоне  $0,08 < d < 0,16$ . В результате исследований было уста-новлено, что «текущие хвосты» и «лежалые хвосты» применимы для обогащения руды методом сухого разделения. «Текущие хвосты» Карагайлинского обогатительного комбината не подходят для обогаще-ния путем сухого разделения.

*Ключевые слова:* обогатительная фабрика, образцы хвостов, анализ, фракция, размеры зерна, просеива-ние, содержание меди, сухая сепарация.

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