

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



№ 4(96)/2019

ХИМИЯ сериясы

Серия ХИМИЯ

CHEMISTRY Series

**ҚАРАҒАНДЫ
УНИВЕРСИТЕТІНІҢ
ХАБАРШЫСЫ**

**ВЕСТНИК
КАРАГАНДИНСКОГО
УНИВЕРСИТЕТА**

**BULLETIN
OF THE KARAGANDA
UNIVERSITY**

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

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Қазан–қараша–желтоқсан
30 желтоқсан 2019 ж.

Октябрь–ноябрь–декабрь
30 декабря 2019 г.

October–November–December
December, 30, 2019

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, 2019
Караганда, 2019
Karaganda, 2019

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Тел.: (7212) 77-03-69 (ішкі 1026); факс: (7212) 77-03-84.

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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 28.12.2019 ж. қол қойылды. Пішімі 60×84 1/8. Қағазы офсеттік. Көлемі 15,87 б.т. Таралымы 300 дана. Бағасы келісім бойынша. Тапсырыс № 146.

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

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Тел.: (7212) 77-03-69 (внутр. 1026); факс: (7212) 77-03-84.
E-mail: vestnick_kargu@ksu.kz; ipustolaikina@gmail.com (*отв. секретарь*)
Сайт: <http://chemistry-vestnik.ksu.kz>

Редакторы

Ж.Т. Нурмуханова, С.С. Балкеева

Компьютерная верстка

В.В. Бутяйкин

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 28.12.2019 г. Формат 60×84 1/8. Бумага офсетная. Объем 15,87 п.л. Тираж 300 экз.
Цена договорная. Заказ № 146.

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

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E-mail: vestnick_kargu@ksu.kz; ipustolaikina@gmail.com (*secretary*)

Web-site: <http://chemistry-vestnik.ksu.kz>

Editors

Zh.T. Nurmukhanova, S.S. Balkeyeva

Computer layout

V.V. Butyaikin

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 28.12.2019. Format 60×84 1/8. Offset paper. Volume 15,87 p.sh. Circulation 300 copies. Price upon request. Order № 146.

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

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Указатель статей, опубликованных в «Вестнике Карагандинского университета» в 2019 году. Серия «Химия».....	119
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G.Ya. Guba¹, A.O. Gusar¹, E.A. Mamaeva¹, V.A. Popova¹,
I.R. Dolgov¹, A.A. Bakibayev², R.R. Ahmedjanov³

¹Tomsk Polytechnic University, Russia;

²National Research Tomsk State University, Russia

³Tomsk State Pedagogical University, Russia

(E-mail: anngsa@mail.ru)

Polymerization of lactic acid oligomers under microwave irradiation

The kinetics of the polymerization of lactic acid oligomers (LAO) was studied for the first time at various microwave irradiation powers (MW) in the presence of Sn(Oct)₂/benzyl alcohol (C₆H₅CH₂OH) catalyst and toluenesulfonic acid (TSA). LAO was polymerized in a multimodal reactor in a vacuum while sparging with nitrogen at powers of 130, 280, 360 W. The optimal concentrations of catalysts and initiator were determined, which represent 0.03 % Sn(Oct)₂/C₆H₅CH₂OH and 0.3–0.4 % TSA by weight of LAO. It was established that the polymerization of LAO in the presence of TSA proceeds already at 130 W. As the MW power increases, the rate of LAO polymerization increases. When Sn(Oct)₂/C₆H₅CH₂OH was used as a catalyst, the LAO polymerization process proceeds at a noticeable rate at 280 W, and after 25 min the molecular weight was about 20,000 Da. During the polymerization of LAO in the presence of catalysts at 360 W, lactide forms along with the formation of polylactic acid (PLA). Using the methods of IR and NMR spectroscopy, the structure of the obtained substances was studied. The synthesized PLA samples are optically pure; the optical rotation angle is 156–158 degrees×ml/dm×g. It has been suggested that during LAO polymerization under MW conditions, the so-called «non-thermal microwave effect» is observed, that is, at the same temperature (215 °C), but at different powers (280 W and 360 W), the LAO polymerization proceeds at different rates.

Keywords: microwave irradiation, lactic acid, polylactic acid, lactic acid oligomers, NMR spectroscopy, IR spectroscopy, specific optical rotation, catalyst.

Introduction

PLA is one of the most promising biodegradable polymers used for various biomedical applications because of its biocompatibility and biodegradation in the human body into non-toxic metabolites [1–5].

Tin octanoate is recognized as the most effective catalyst for the synthesis of PLA. In this case, compounds containing hydroxyl groups, such as alcohols [2, 6, 7], initiate the ring opening polymerization process.

With traditional methods for the synthesis of PLA stringent conditions are necessary: high vacuum, long polymerization time and the consumption of large amounts of energy.

MW is able to accelerate chemical reactions 10–100 times. The wide possibilities offered by MW in chemistry are of great interest in the study and application of the effects of exposure to microwave radiation. It is believed that MW has firstly, the ability to cause rapid and significant heating of organic compounds and secondly, to activate reagent molecules and especially, cause their dissociation into ions and free radicals. The MW photon at a frequency of 2.45 GHz has the energy equal to 9.6×10^{-4} eV. This is not enough even to break the hydrogen bond [8, 9].

To date considerable experience has been accumulated on the use of MW to accelerate the synthesis of PLA [10–19].

The works [3, 6, 17–18, 20–23] show the results of studies of the synthesis of PLA under MW conditions by polymerization of lactides. The rate of polycondensation of lactic acid (LA) under MW conditions depends on the volume of reacting substances [24], pressure [19–20], and the monomer/catalyst ratio [25].

The polymerization of PLA with the opening of the lactide ring was successfully carried out using the conventional and microwave methods in [26]. The lactide polymerization reaction time under MW conditions was reduced from 6 hours to 20 minutes, the molecular weight (Mw) of the PLA was 11000 Da and under ordinary conditions the Mw of the PLA was 2000 Da.

The processes of direct polymerization of LA under MW conditions are attractive as energy-saving processes, since they avoid the labor-consuming and energy-consuming stage of lactide synthesis [3, 12, 14, 26, 27].

Direct condensation of LA is carried out in three stages: removal of free water, polycondensation with the formation of oligomers and condensation of oligomers to high molecular weight polymers in the melt. On the first and third stages, water removal is critical to the reaction rate. For the second stage, the rate is determined by the chemical reaction [12, 28].

The authors of [12, 26] studied the polycondensation of 85 % LA in the presence of a SnCl₂/TSA binary catalyst under MW conditions in a monomode reactor. MW with Mw 16000 Da was obtained by carrying out the reaction for 30 min at a pressure of 30 mmHg. When only TSA is used as a catalyst, LAO with Mw less than 1000 Da is formed. This polymer can also be converted to high molecular weight PLA by melt polycondensation [12].

The effect of MW is currently debatable [6, 11, 25, 27, 29–31]. No data were found on increasing the reaction rate due to an increase in activation energy in the MW field in the literature.

The authors of [25], while studying the polymerization of lactide in a toluene solution, expressed the opinion that microwave irradiation did not cause any changes in the polymerization kinetics, which made it possible to consider the absence of a specific «non-thermal» effect during microwave synthesis.

Authors [30] studied the kinetics of caprolactam polymerization under MW conditions. As a result, a specific «non-thermal» effect was suggested.

Authors [31] investigated the polycondensation of LA under MW conditions in xylene in the presence of catalysts at a power of 100–400 W and pointed to the existence of a specific «non-thermal» effect induced by an electric field.

In [32], a lactide-pullulan copolymer was synthesized in a monomode microwave reactor and it was found that at the same reaction temperature (80 °C) with increasing irradiation power from 50 to 200 W, the yield of the final product increased. The authors suggested the existence of a specific «non-thermal» effect.

An analysis of the literature data showed that, despite the large number of publications on the synthesis of PLA under MW conditions, the results obtained are disparate, performed under different conditions and in various microwave reactors [29]. Although it can be said unequivocally that under MW conditions, the time for the synthesis of PLA decreases by 10–15 times.

In this work, the influence of the MW power, the time and nature of the catalysts on the polymerization of LAO under the MW conditions in a multimode reactor was investigated.

Experimental

LAO obtained according to the method described in [33] by evacuation for 25 min at 280 W of an 80 % aqueous solution of D(+)-acid of the PURAK 80 brand (country of origin is the Netherlands) was used as the object of study. Sn(Oct)₂, TSA applied qualifications chemically pure, C₆H₅CH₂OH analytical grade was used as initiator.

The IR spectra of the starting compounds and reaction products were recorded on an Agilent Resolutions Pro IR spectrometer.

The ¹H NMR spectra of the synthesized LAO and PLA were recorded using a Bruker AVANCE AV 300 Fourier spectrometer (Germany), an operating frequency of 300 MHz, and a deuterated CDCl₃ solvent.

The molecular weights of the obtained samples were determined by the viscometric method using a Ubbelode viscometer. Chloroform was used as a solvent. The molecular weights of PLA were also determined by gel permeation chromatography on an Agilent 1200 instrument. Chloroform was used as a solvent, the eluent velocity was 1 ml/s.

To determine the angle of optical rotation (degrees×ml/dm×g), an AR-300 polarimeter was used, the tube length was 1 dm, and the solvent was chloroform, λ = 589 nm.

Thermal studies of PLA samples were performed on an SDT Q600 V20.9 Build 20 instrument. LAO was polymerized under microwave irradiation according to the general scheme shown in Figure 1.

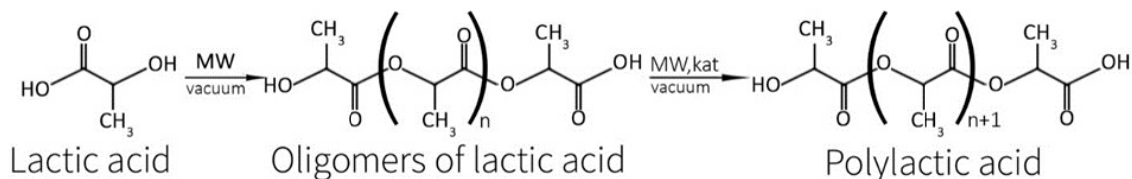


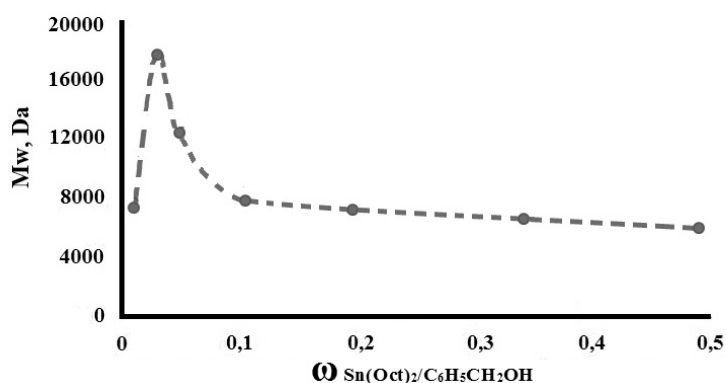
Figure 1. Scheme for the synthesis of PLA (catalyst — $\text{Sn}(\text{Oct})_2$, TSA)

The resulting 10 g LAO was loaded into a 100 ml glass heat-resistant flask and catalysts ($\text{Sn}(\text{Oct})_2$, TSA) were added in an amount of 0.03–0.3 %, together with the initiator ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, in the ratio of catalyst/initiator 1:1). They were placed in a microwave reactor and sparged with nitrogen at a pressure of 200 mmHg at various powers 130–360 W.

Results and Discussion

It is known that Mw of PLA depends on a number of factors: the nature and amount of the catalyst, the ratio of catalyst:cocatalyst, temperature and polymerization time. Figure 2 shows the curves of the dependence of the molecular weight of PLA on the concentration of the catalyst. The polymerization was carried out at 280 W for 25 min. The highest Mw of PLA was achieved at a catalyst concentration (ω) of 0.03 mass.%.

The increasing of catalyst concentration to $\omega = 0.03$ mass.% leads to molecular weight growth. However, further catalyst concentration increase provokes the reverse process of molecular weight decreasing. Moreover, samples changed the color to darker one. Taking into account these facts, it could be suggested that catalyst concentration increase stimulates polymer destruction process.



$\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH} = 1:1$; Power = 280 W; $\tau = 25$ min

Figure 2. Dependence of Mw PLA on ω of the catalyst during LAO polymerization under MW

$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ is an effective initiator of $\text{Sn}(\text{Oct})_2$ in the synthesis of PLA. Upon addition of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ Mw to $\text{Sn}(\text{Oct})_2$, the PLA increases and reaches a maximum at a ratio of 1:1, and then decreases (Fig. 3). In the absence of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, the polymerization process is practically not observed. When the ratio of catalyst: initiator is 1:2 and the reaction takes more than 15 minutes, the polymer is degraded and the reaction mass becomes black-brown. The mechanism of PLA at $\text{Sn}(\text{Oct})_2$ and alcohols are described in [15, 17]. It is known that alcohols presence increases the reaction rate of cyclic LAO polymerization at the presence of $\text{Sn}(\text{Oct})_2$.

It could be suggested that $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ forms intermediate complex. The optimal ratio is 1:1.

The kinetic curves of LAO polymerization in the presence of $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ are shown in Figure 4. The dependence of Mw at an irradiation power of 130 W (205 °C), Mw LAO slowly increases. So, during the course of the reaction for 30 min, the Mw LAO is only 1500 Da.

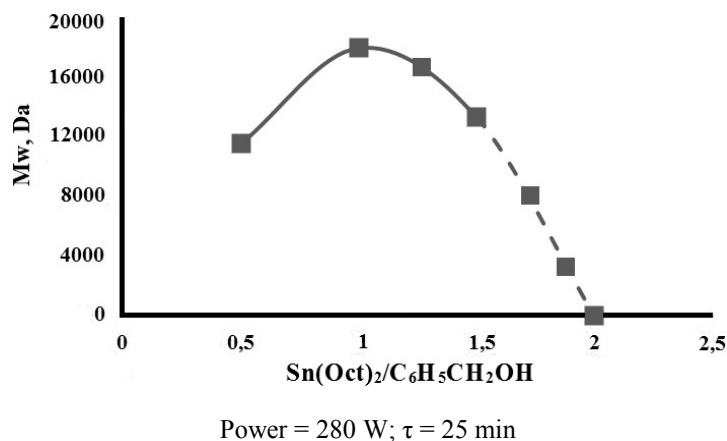
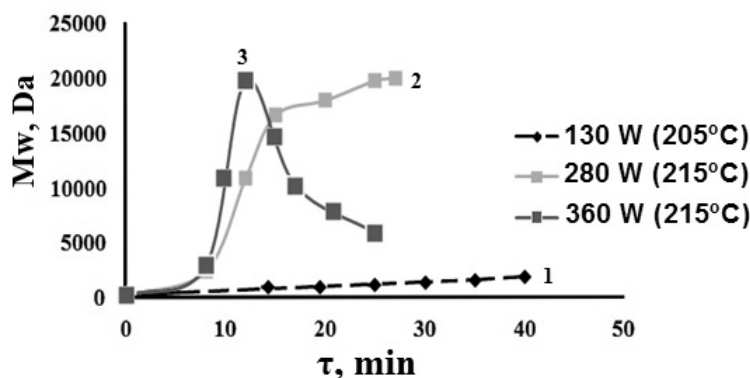


Figure 3. Dependence of Mw of PLA on the molar ratio of Sn(Oct)₂/C₆H₅CH₂OH during LAO polymerization under MW conditions



Catalyst — Sn(Oct)₂/C₆H₅CH₂OH; Power: 1 — 130 W; 2 — 280 W; 3 — 360 W
Ratio catalyst/initiator/LAO = 3/3/10000 (mass.%)

Figure 4. Kinetic curves of LAO polymerization in the presence of a catalyst

At an MW power of 280 W, the sample heats up during the first 10 minutes and the process of polycondensation of low molecular weight LAO occurs with the removal of water. With an increase in the process time, the molecular weight of LAO sharply increases. Presumably, at this period of the process, the LAO polymerization stage is limiting with the opening of the cycle after 15 minutes the polymerization process slows down, which is apparently due to the fact that the diffusion stage of the process becomes limiting.

It should be noted separately that the temperature of the LAO reaction mass reaches 215 °C both at 280 W and 360 W [33].

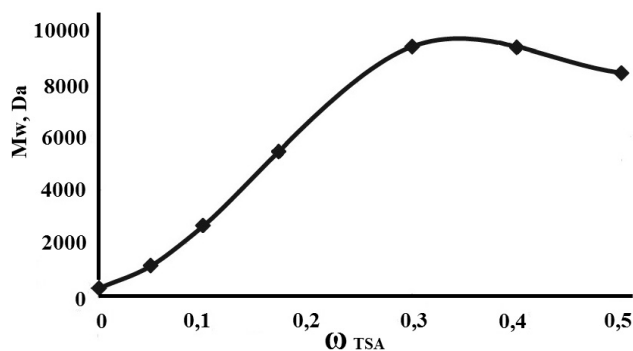
At a power of 360 W, the molecular weight of the polymer increases sharply and reaches its maximum value of about 20000 Da in 12 minutes.

With an increase in the process time, the resulting polymer is degraded and Mw LAO sharply decreases, and a white crystalline compound is formed at the outlet of the reactor, which was identified as lactide using IR spectroscopy.

Thus, we can assume that in this case the so-called «non-thermal microwave effect» is observed, that is, under the same conditions at the same temperature (215 °C), but with different capacities (280 W and 360 W), the LAO polymerization proceeds at different rates.

LAO polymerization in the presence of TSA was performed at powers of 130 W, 280 W, and 360 W. The dependence of Mw of PLA on ω TSA is presented in Figure 5.

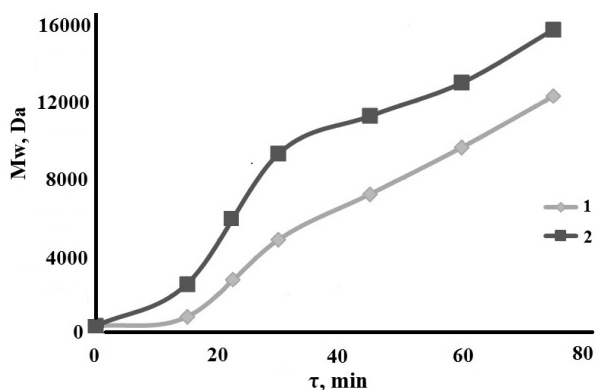
This dependence shows that with an increase in the catalyst concentration from 0.05 to 0.3 %, an increase in Mw is observed. The optimal ω TSA is in the range of 0.3–0.4 mass.%.



Power = 280 W; τ = 30 min

Figure 5. Dependence of Mw of PLA on ω TSA upon polymerization of LAO under MW conditions

The kinetic curves of LAO polymerization in the presence of TSA are presented in Figure 6. With an increase in reaction time, an increase in Mw of LAO is observed. However, Mw PLA grows unevenly at 280 W. When carrying out the reaction up to 15 minutes, a weak growth of the LAO chain is observed, low molecular weight oligomers are formed. In the range from 15 to 30 minutes, a sharp increase in the Mw of the polymer occurs, and then the chain grows in a linear relationship.



1 — 130 W; 2 — 280 W (ω TSA 0.3 mass.%)

Figure 6. Dependence of Mw of the PLA sample on time in the conditions of MW

During the polymerization of LAO at a power of 360 W, volatile cyclic lactides are formed in parallel with the formation of PLA, which are white crystals deposited on the walls of the flask and the condenser. Physicochemical properties of the synthesized samples and experimental conditions are presented in Table.

Table

Synthesis conditions and physicochemical properties of synthesized LAO samples

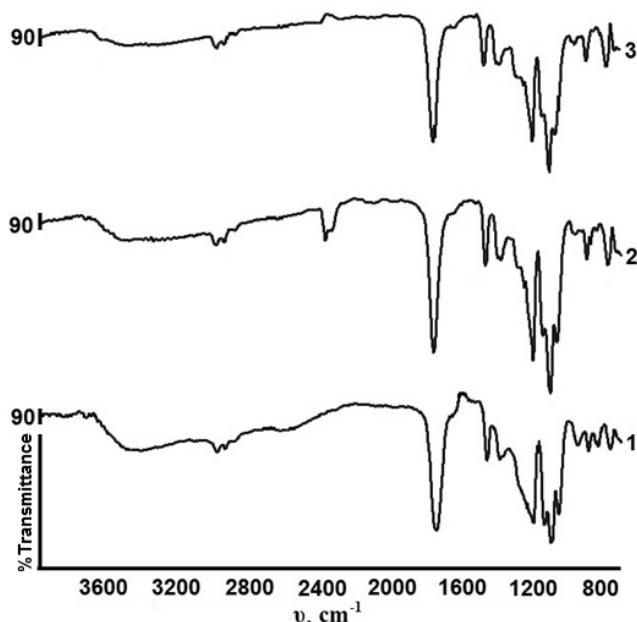
Catalyst	Power, W	t , °C	τ , min	Mw ^a , Da	Mw ^b , Da	Mn ^b , Da	PD	$[\alpha]_{589}^{25}$ degrees×ml/dm×g
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	130	205	35	1700	—	—	—	—
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	280	215	25	19900	19230	12820	1,50	-156
TSA	280	215	35	9350	9940	5402	1,84	-157
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	360	215	8	3000				—
			12	19500				-158
			17	10300				-152
			25	6000	The sample darkened, lactide formed			
TSA	360	215	10	Lactide formed				

Note. t , °C — temperature; τ — reaction time, min; Mw^a, Da — calculated using a viscometric method; Mw^b, Da — determined by NMR spectroscopy; Mn^b, Da — determined by gel permeation chromatography; $[\alpha]_{589}^{25}$ — optical rotation angle.

Therefore, it could be suggested that MW power determines the kinetics of LAO polymerization in the presence of TSA.

The data obtained confirm the presence of a «non-thermal microwave effect» during LAO polymerization under MW conditions, since at the same temperature but diverse capacities, LAO polymerization proceeds at different rates by various mechanisms at 280 W and 360 W.

The optical rotation angle of the synthesized samples is 156–158 degrees \times ml/dm \times g, i.e., the synthesized samples are optically pure. Figure 7 shows the IR spectra of PLA samples synthesized under MW conditions.



1 — $\tau = 20$ min after polymerization;
 2 — $\tau = 30$ min at 280 W in the presence of 0.3 mass.% TSA;
 3 — $\tau = 30$ min at 280 W in the presence of 0.03 mass.% $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

Figure 7. IR spectra of LAO obtained at a power of 280 W

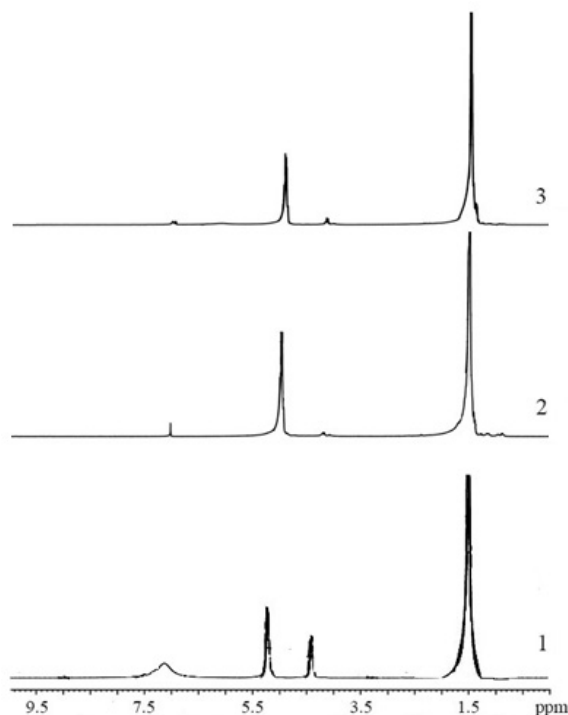
The interpretation of the absorption bands of the IR spectra is given below: 3500–3300 (νOH), 2997 ($\nu_{\text{as}}\text{CH}_3$), 2947 ($\nu_{\text{s}}\text{CH}_3$), 2882 (νCH), 1760–1727 ($\nu\text{C}=\text{O}$), 1452 ($\delta_{\text{as}}\text{CH}_3$), 1388–1348 ($\delta_{\text{s}}\text{CH}_3$), 1368–1360 ($\delta_{1\text{CH}}+\delta_{\text{s}}\text{CH}_3$), 1315–1300 ($\delta_{2\text{CH}}$), 1270 (νCOC), 1215–1185 ($\nu_{\text{as}}\text{COC}$), 1130 ($\nu_{\text{as}}\text{CH}_3$), 1100–1090 ($\nu_{\text{s}}\text{COC}$), 1045 ($\nu\text{C}-\text{CH}_3$), 960–950 ($\nu\text{CH}_3 + \nu\text{CC}$), 875–860 ($\nu\text{C}-\text{COO}$), 760–740 ($\delta\text{C}=\text{O}$).

In the IR spectra, intense absorption bands of carbonyl groups $\text{C}=\text{O}$ (1757 cm^{-1}) and absorption bands of $\text{C}-\text{O}-\text{C}$ bonds of 1188 cm^{-1} , PLA characteristic are observed.

On curves 2 and 3 (Fig. 7), belonging to the samples of synthesized PLA, the intensity of the absorption bands in the region of $3600\text{--}3500\text{ cm}^{-1}$, characterizing the vibrations of the OH groups, significantly decreased. The peaks in the region of 1759 cm^{-1} , which belong to the stretching vibrations of the $\text{C}=\text{O}$ bond, become more symmetrical. The band in the region of 1188 cm^{-1} , related to the stretching vibrations of the $-\text{C}-\text{O}-$ bond, becomes more pronounced. Figure 8 shows the ^1H NMR data of PLA samples synthesized under MW conditions.

Chemical shifts ^1H NMR LAO and PLA are presented below:

Chemical shift in ppm	Structural assignments
5.2	1H, m, $-\underline{\text{CH}}(\text{CH}_3)-$
4.4	1H, m, $-\underline{\text{CH}}(\text{CH}_3)\text{OH}$, end group)
1.6	(3H, d, $-\underline{\text{CH}}_3$)



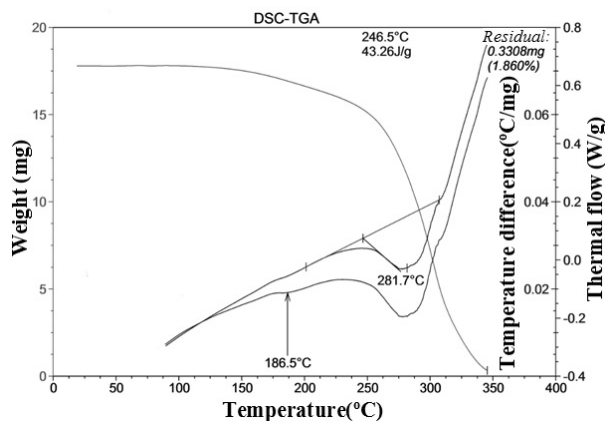
- 1 — OLA obtained by irradiating MW in vacuum for 20 minutes;
 2 — PLA, obtained from OLA in the presence of TSA for 30 minutes at a power of 280 W;
 3 — PLA obtained from OLA in the presence of $\text{Sn}(\text{Oct})_2$ for 25 minutes at a power of 280 W

Figure 8. ^1H NMR spectra

The proton signal of the multiplet of the methine group of the terminal group $-\text{CH}(\text{CH}_3)\text{OH}$ LAO is 4.4 ppm, the chemical shift of the proton of the multiplet of the methylene group of the PLA is 5.2 ppm. By the ratio of signal intensities of methine groups in the region of 4.4 and 5.2 ppm we can judge the depth of the polymerization process of LAO to PLA.

Intensive chemical shifts of 4.4 ppm are observed on curve 1 (Fig. 8), which suggests the presence of a significant number of terminal hydroxyl (and, accordingly, carboxyl) groups in LAO. In the spectra of PLA samples obtained by the polymerization of LAO in the presence of TSA and $\text{Sn}(\text{Oct})_2$ (see Fig. 8). Chemical shifts at 4.4 ppm are observed. Other shifts are absent.

Figure 9 shows the DSC thermogram of a PLA sample synthesized at 280 W for 25 min in the presence of 0.09 mass.% $\text{Sn}(\text{Oct})_2$. The absence of a pronounced melting peak at 180–190°C suggests that the polymer mainly has an amorphous structure.



$\tau = 20$ min in the presence of $\text{Sn}(\text{Oct})_2$

Figure 9. DSC-TGA spectra of PLA synthesized under MW conditions

Conclusions

The optimal concentrations of catalysts and initiator for the synthesis of PLA were determined, which are 0.03 % Sn (Oct)₂/C₆H₅CH₂OH and 0.3–0.4 % TSA by weight of LAO.

It was found that with an increase in the power of MW, the rate of LAO polymerization in the presence of catalysts increases. When Sn(Oct)₂/C₆H₅CH₂OH is used as a catalyst, the LAO polymerization process proceeds at a noticeable rate at 280 W, and after 25 min Mw is about 20000 Da. The synthesized PLA samples are optically pure; the optical rotation angle of the synthesized samples is 156–158 degrees×ml/dm×g. It has been suggested that during LAO polymerization under MW conditions, the so-called «non-thermal microwave effect» is observed, that is, at the same temperature (215 °C), but with various capacities (280 W and 360 W), the LAO polymerization proceeds at different rates by diverse mechanisms. During the polymerization of LAO in the presence of catalysts at 360 W, a small amount of lactide is formed along with the formation of PLA.

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Г.Я. Губа, А.О. Гусар, Е.А. Мамаева, В.А. Попова,
И.Р. Долгов, А.А. Бакибаев, Р.Р. Ахмеджанов

Қысқа толқынды сәулелендіру жағдайында сүт қышқылы олигомерлерін полимерлеу

Сүт қышқылының олигомерлерінің (СҚО) полимерленуінің кинетикасы алғаш рет микротолқынды сәулеленудің (МТС) әртүрлі қуаттарында, Sn(Oct)₂ / бензил спирті (C₆H₅CH₂OH) катализаторы және толуолсульфоқышқылы (ТСК) қатысуымен зерттелді. СҚО полимеризациясы мультимодальды реактордағы вакуумда азотпен барботаждау және 130, 280, 360 Вт қуаттылықтарда жүргізілді. 0.03 % Sn(Oct)₂/C₆H₅CH₂OH және СҚО салмағы бойынша 0,3–0,4 % ТСК болатын катализаторлар мен сокатализаторлардың оңтайлы концентрациясы анықталды. СҚО салмағынан 0,03 % Sn(Oct)₂/C₆H₅CH₂OH және 0,3–0,4 % ТСК тұратын катализаторлар мен сокатализаторлардың оптималды концентрациясы табылды. ТСК қатысуымен СҚО-ны полимерлеу 130 Вт-тан басталатындығы анықталды. МТС қуатының жоғарылауымен СҚО полимерлену жылдамдығы артады. Sn(Oct)₂/C₆H₅CH₂OH катализатор ретінде қолданғанда, СҚО полимеризациясы 280 Вт жылдамдықпен жүреді, ал 25 минуттан кейін молекулалық массасы шамамен 20000 Да болды. СҚО полимерлеу процесі кезінде катализаторлардың қатысуымен 360 Вт қуаттылықта полисүт қышқылдың (ПСК) түзілуімен бірге лактид түзіледі. ИҚ және ЯМР спектроскопия әдістерінің көмегімен алынған полимерлердің құрылымы зерттелді. Синтезделген ПСК үлгілері оптикалық таза, оптикалық бұрылу бұрышы 156–158 градус×мл/дм×г тең. Болжам бойынша, МТС жағдайында СҚО полимеризациясы кезінде «жылусыз микротолқынды эффект» деп аталатын, яғни бірдей жағдайларда, бірдей температурада (215 °C), бірақ әртүрлі қуаттылықта (280 және 360 Вт) СҚО полимерленуі әр түрлі жылдамдықпен жүреді.

Кілт сөздер: микротолқынды сәулелендіру, сүт қышқылы, полисүт қышқылы, сүт қышқылы олигомерлері, ЯМР спектроскопиясы, ИҚ спектроскопиясы, меншікті оптикалық айналу, катализатор.

Г.Я. Губа, А.О. Гусар, Е.А. Мамаева, В.А. Попова,
И.Р. Долгов, А.А. Бакибаев, Р.Р. Ахмеджанов

Полимеризация олигомеров молочной кислоты в условиях микроволнового облучения

Впервые изучена кинетика полимеризации олигомеров молочной кислоты (ОМК) при различных мощностях микроволнового облучения (МВО) в присутствии катализатора/сокатализатора Sn(Oct)₂/бензиловый спирт (C₆H₅CH₂OH) и толуолсульфокислоты (ТСК). Полимеризацию ОМК проводили в мультимодальном реакторе в вакууме при барботировании азотом при мощностях 130, 280,

360 Вт. Определены оптимальные концентрации катализаторов и сокатализаторов, которые составляют 0,03 % $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ и 0,3–0,4 % ТСК от массы ОМК. Установлено, что полимеризация ОМК в присутствии ТСК протекает уже при 130 Вт. С повышением мощности МВО скорость процесса полимеризации ОМК увеличивается. При использовании в качестве катализатора $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ процесс полимеризации ОМК с заметной скоростью протекает при 280 Вт, и через 25 мин молекулярный вес составлял около 20000 Да. При проведении процесса полимеризации ОМК в присутствии катализаторов при 360 Вт, наряду с образованием полимолочной кислоты (ПМК), происходит образование лактида. С применением методов ИК- и ЯМР-спектроскопии изучено строение полученных полимеров. Синтезированные образцы ПМК являются оптически чистыми, угол оптического вращения равен 156–158 градусам \times мл/дм \times г. Высказано предположение, что при полимеризации ОМК в условиях МВО наблюдается так называемый «нетепловой микроволновой эффект», т.е. в одинаковых условиях при одинаковой температуре (215 °С), но разных мощностях (280 и 360 Вт) процесс полимеризации ОМК протекает с различной скоростью.

Ключевые слова: микроволновое облучение, молочная кислота, полимолочная кислота, олигомеры молочной кислоты, ЯМР-спектроскопия, ИК-спектроскопия, удельное оптическое вращение, катализатор.

O.S. Lebed¹, Yu.A. Chertikhina¹, B.Zh. Mutaliyeva², D.E. Kudasova², A.V. Prosyani¹

¹Ukrainian State University of Chemical Technology, Dnipro, Ukraine;

²M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
(E-mail: dariha_uko@mail.ru)

Amidation of amino ethylene-1,2-dicarboxylic acid diesters: a theoretical consideration

The amidation features of the Z- and E-isomers of aminoethylene-1,2-dicarboxylic acid diesters $\text{MeO}_2\text{CCN}=\text{C}(\text{NRR}^1)\text{CO}_2\text{Me}$, where $\text{R} = \text{H}$; $\text{R}^1 = \text{H, Me, } t\text{-Bu}$; $\text{R} = \text{R}^1 = \text{Me}$, have been considered based on the data of quantum chemical calculations in the PBE/def2-TZVPP approximation in the framework of Natural Bond Orbital (NBO). Amino-fumaric acid derivatives were chosen as objects for analysis since activated enamines containing conjugated enamine and carbonyl groups in their structure are one of the promising classes of regulators. It was shown by the calculations that for enamines I-IV, regardless of their configuration, conformers with α -s-trans, β -s-cis-arrangement of C=C and C=O bonds are most beneficial. These findings are consistent with experimental data on the relative configurational stability of the Z- and E-isomers of N-alkylaminoethylene-1,2-dicarboxylic acid diesters. The direction of the amidation reactions depends critically on the structure of the reactant and the reaction conditions. It was established that the amidation of amino acid-1,2-dicarboxylic acid diesters obeys to orbital control of the reaction. The observed regioselectivity of non-catalytic amidation on the α -ester group was explained by the joint influence of a decrease in the electrophilicity (increase in the energy of the loosening π -orbital) of the β -carbonyl group due to effective conjugation with the π -system of the C=C-NHR and an increase in the electrophilicity of the α -carbonyl group with an increase in its conjugation with the rest part of the molecule. The inertness of N,N-dimethylaminomaleate to reactions with amines is caused by the increased energy of $\pi^*_{\text{C=O}}$ -orbitals of ester groups. Bis-amidation of amino-ethylene-1,2-dicarboxylic acid diesters is possible only in the presence of catalysts.

Keywords: amidation, quantum chemical calculations, activated enamines, regioselectivity, conformers, cisoid arrangement of bonds, transoidal arrangement of bonds, isomers, orbital control.

Introduction

In modern agricultural technologies most important attention is paid to use of plant promoters, because they, unlike other chemicals, usually require small doses for use, do not affect the environment and have contribution to the production of environmentally friendly agricultural products.

One of the promising classes of promoters are activated enamines, containing in their structure conjugated enamine and carbonyl groups, including derivatives of aminofumaric acid [1–3]. Thereby, the amidation of amino ethylene-1,2-dicarboxylic acid diesters has particular interest. It is known [4] that the direction of amidation reactions depends strictly on the structure of the reactant and the reaction conditions. The amino-fumaric acid diesters with unsubstituted nitrogen atom, at interaction with ammonia, primary and secondary aliphatic amines in absolute alcohols, produce monoamides of Z-2-amino-3-alkoxycarbonylacrylate acid, and in aqueous methanol — mostly or exclusively 1-alkyl-3-alkylaminopyrrole-2,5-diones (with the exception of reactions with ammonia and tert-butylamine, leading only to the corresponding monoamides).

The amino fumarates and monoamides of Z-2-amino-3-alkoxycarbonylacrylic acid in similar reactions under conditions of basic catalysis ($\text{MeOH}_{\text{abc}}/\text{MeONa}$) produce bisamides of aminofumaric acid. N-alkylaminofumarates and N-tert-butylaminomaleate at interaction with primary amines in any conditions produce 1-alkyl-3-alkylaminopyrrol-2,5-dione, and N,N-dialkylaminomaleates are inert in all cases.

Experimental

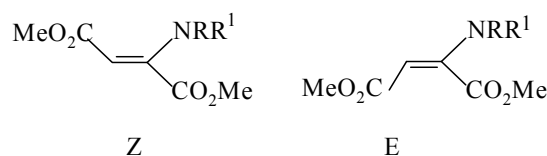
Quantum chemical calculations of the ground states of key compounds were carried out in the PBE/def2-TZVPP approximation [5, 6] in order to analyze and explain the observed experimental regularity. Quantum chemical calculations were carried out within the framework of the density functional theory [7, 8] using the PBE96 functional [9] and the basic set of atomic functions def2-TZVPP [10] using the Firefly 7.1 software complex [11], which fully satisfy to the decision of the tasks. Chemcraft 1.7 program was used to visualize the spatial structure and construct imine molecules [12].

Geometry optimization was performed for all systems. There are several stable conformations for all studied compounds, so the search of the most stable geometry (having the least energy) was carried out by optimizing the structures of possible conformers.

The belonging of the found points to the minima and saddle points of the potential energy surfaces was confirmed by calculations of the second derivatives with respect to coordinates (Hessian calculation). The absence of imaginary frequency values in the vibrational spectrum testified that the optimized structures correspond to minimum.

The atomic populations, charges, and energies of intramolecular interactions were obtained using the natural orbitals of bonds (NBO) [13–15] with the help of NBO 5.G program [16] introduced in the Firefly 7.1 package. The NBO method allows to analyze nonempirical wave functions within one- and two-center localized orbitals, thus making it convenient to thoroughly analyze intra- and intermolecular interactions. The calculation was carried out for optimized geometries of the studied enamines. The NPA (Natural Population Analysis) scheme was used to obtain the values of atomic populations and charges. Earlier it was shown that of the charges that can be estimated by quantum chemical methods (Mulliken, AIM-, CHELPG-, MK-charges) the best correlation with the experimental and calculated values of chemical shifts ^{13}C NMR observed for NPA-charges [17]. By calculations it was established that obtained data will correspond to the location of the molecules in the gas phase or, at least, in solution of a non-polar aprotic solvent. In reality, almost all reactions were carried out in polar protic solvents — in absolute or aqueous methanol with specific solvating effect. Nevertheless, from our point of view, the use of calculated data to a sufficient degree is authentic and useful for analysis due to comparable impact of solvation on the properties of the considered related compounds — derivatives of aminoethylene-1,2-dicarboxylic acid.

N-derivatives of dimethyl ester amine-fumaric and amino-maleic acids I-IV were selected as objects for analysis:



R = H; R¹ = H (I), Me (II), *t*-Bu (III); R = R¹ = Me (IV)

Results and Discussion

Calculations identified that for enamines I-IV, despite their configuration, the conformers with α -s-trans, β -s-cis-arrangement of C=C and C=O bonds are the most favorable (Table 1). Wherein, for Z-II, Z-III N-alkyl derivatives of aminofumaric acid the transoidal arrangement of the substituent at the nitrogen atom and C=C bond is the most beneficial, while for aminomaleic acid — their cisoidal arrangement.

Table 1

Internal energies (E_{int}) and dihedral angles ($\Theta_{\text{NC}2\text{C}1=\text{O}(\alpha), \circ}$) of preferred conformers of Z- and E-isomers of enamines I-IV

Enamine	E_{int} , a. u. ¹	$\Theta_{\text{NC}2\text{C}1=\text{O}(\alpha), \circ}$	Enamine	E_{int} , a. u. ¹	$\Theta_{\text{NC}2\text{C}1=\text{O}(\alpha), \circ}$	ΔE_{int}^4 , kJ/mol
Z-I	-589.3090	0	E-I	-589.2909	58.8	-47.5
Z-IIa	-628.5595 ²	0	E-IIa	-628.5555 ²	54.8	-10.5
Z-IIb	-628.5642 ³	21.7	E-IIb	-628.5512 ³	73.9	-34.1
Z-IIIa	-746.3755 ³	0.5	E-IIIa	-746.3697 ²	59.1	-15.2
Z-IIIb	-746.3776 ³	42.0	E-IIIb	-746.3658 ³	74.9	-31.0
Z-IV	-667.8108	21.3	E-IV	-667.8148	71.5	10.5

Note. ¹ — 1 a.u. = 1 Hartree = 2625,5 kJ/mol; ² — cisoidal arrangement of bonds R¹-N and C=C; ³ — transoidal arrangement of bonds R¹-N and C=C; ⁴ — the difference between the total internal energies of the preferred conformers of the Z- and E-isomers. Conformer a — cisoidal arrangement of bonds R¹-N and C=C; Conformer b — transoidal arrangement of bonds R¹-N and C=C. All conformers have α -s-trans- β -s-cis-arrangement of bonds C=O and C=C.

For enamines I-III, aminofumaric acid diesters (Z-isomers) are energetically preferable, thermodynamic preference of which are decreasing with increasing of volume of substituents at nitrogen atom. In the case of

enamine IV which has the most voluminous substituent, derivative of aminomaleic acid (E-isomer) is energetically most favorable. These conclusions approve experimental data on the relative configuration stability of Z- and E-isomers of diesters of N-alkylamino-ethylene-1,2-dicarboxylic acid [4].

The calculated data were used to explain the regiospecificity of the amidation reaction of amino ethylene-1,2-dicarboxylic acid derivatives. Theoretically, the amidation reaction can be carried out under conditions of charge control, in which the unshared electron pair of the amine nitrogen atom attacks the most electropositive carbon atom of the investigated molecule, or in the conditions of orbital control, in which the highest occupied molecular orbital (HOMO) of the nucleophile (the unshared electron pairs of amine) interacts with the lowest free molecular orbital (LFMO) of the electrophile.

Analysis of the data in Table 2 reveals that the maximum and almost identical partial positive charges ($q_{C_1(\alpha)}-q_{C_4(\beta)} = 0.022-0.038 \bar{e}$) are localized on the carbon atoms of the carbonyl groups, which should provide almost equally probable amidation with a small preference on α -ester groups. This contradicts the experimental data [4], according to which regio-specific amidation on α -alkoxycarbonyl group is observed for aminofumarates, and N,N-dimethylamino-maleate E-IV, for which the maximum q_C value is observed is generally inert in this reaction. Thus, the amidation of diesters of amine-ethylene-1,2-dicarboxylic acid does not obey the charge control of the reaction.

According to the perturbation theory of molecular orbitals (MO) [18], the orbital control of reaction is determined by the efficiency of the interaction between employed and vacant MOs, inversely proportional to the energy gap (ΔE) between them [19]. Respectively, regiospecificity of amidation of aminofumarates should depend on the ΔE value between interacting orbitals, that is MO $\pi^*_{C=O}$ of ester group and unshared pair of electrons of nitrogen atom of amine (nN). Then, independently on substituent at nitrogen atom, α -methoxycarbonyl group in Z-isomers of enamines I-IV should be more reactive because of significantly less energy of π^* -MO of α -carbonyl group ($E\pi^*_{C_1=O} = -135.5 \div -101.6$ kJ/mol) in comparison with energy of π^* -MO of β -carbonyl group ($E\pi^*_{C_4=O} = -83.5 \div -41.7$ kJ/mol) and, correspondingly, lower value ΔE between interacting MOs. This fact corresponds to observed regiospecificity of amidation of aminofumarates I, II in absolute methanol in the presence of basic catalysis. In the case of Z-III N-tert-butylaminofumarate two the most favorable conformers are observed that have practically equal energies ($\Delta E_{BH} = 5.5$ kJ/mol), but far different dihedral angles $\Theta_{NC_2C_1=O(\alpha)}$ (Table 1) and energies of $\pi^*_{C_1=O}$ MOs (Table 2). Obviously, amidation of Z-III enamine is only possible in the case of effective conjugation of α -ester group with C=C bond, leading to decrease of $\pi^*_{C_1=O}$ orbital energy and formation of an appropriate Z-IIIa conformer. Thereby, non-reactive with amines Z-IV N,N-dimethylaminofumarate deserves special attention, although dihedral angle $\Theta_{NC_2C_1=O(\alpha)}$ (Table 1), summary energy of conjugation of α -carbonyl group with double bond and energy of $\pi^*_{C_1=O}$ MO are close to those for Z-II N-methylaminofumarate (Table 2), that enters in reaction of amidation. The explanation of this fact can't be connected with spatial difficulties for attack by nucleophile of ester group, because they are practically identical for considered enamines. The higher energy of $\pi^*_{C_1=O}$ MO in Z-IV enamine could be exceptional reason.

Table 2

Calculation of the quantum chemical analysis data for preferred conformers of Z- and E-isomers of enamines I-IV

No.	Bond length, l , Å				Partial charges, e					The energy of interactions, kJ/mol				Energy of π^* -orbital, kJ/mol		
	N-C ₂	C ₂ =C ₃	C ₁ -C ₂	C ₃ -C ₄	$q_{C_1(\alpha)}$	q_{C_2}	q_{C_3}	$q_{C_4(\beta)}$	q_N	Conjugation ¹	HB ²	nN→ π^*	C2=C3	C1=O	C4=O	
Z-I	1.348	1.375	1.505	1.446	0.674	0.117	-0.395	0.652	0.709	81.6 ^a	102.6 ^b	30.6	205.6	-47.5	-135.5	-83.5
Z-II	1.351	1.385	1.505	1.440	0.673	0.122	-0.399	0.648	0.493	75.7 ^a	107.2 ^b	48.8	210.2	-43.3	-114.7	-81.1
Z-III	1.356	1.390	1.510	1.439	0.682	0.125	-0.393	0.645	0.514	56.3 ^a	107.1 ^b	61.2	209.7	-45.4	-126.7	-81.5
	1.351	1.386	1.508	1.440	0.683	0.135	-0.403	0.649	0.514	85.2 ^a	108.3 ^b	50.8	203.7	-33.1	-65.6	-75.9
Z-IV	1.365	1.377	1.515	1.455	0.671	0.114	-0.378	0.644	0.300	68.9 ^a	89.8 ^b	—	136.9	-33.1	-101.6	-41.7
E-I	1.371	1.360	1.514	1.458	0.690	0.142	-0.398	0.662	0.721	20.4 ^a	90.6 ^b	<2.1	126.5	-37.1	-67.5	-54.7
E-II	1.363	1.365	1.514	1.457	0.695	0.135	-0.419	0.662	0.500	25.0 ^a	91.0 ^b	<2.1	161.7	-28.4	-80.1	-44.1
E-III	1.363	1.367	1.520	1.455	0.698	0.151	-0.424	0.662	0.516	10.6 ^a	94.3 ^b	<2.1	179.9	-17.6	-71.2	-39.6
E-IV	1.367	1.370	1.520	1.453	0.701	0.143	-0.421	0.660	0.307	6.4 ^a	95.8 ^b	—	166.5	-21.0	-58.3	-42.0

Note. ¹ — summary energy of interactions a) $\pi_{C_2=C_3} \rightarrow \pi^*_{C_1=O}$, $\pi_{C_1=O} \rightarrow \pi^*_{C_2=C_3}$; b) $\pi_{C_2=C_3} \rightarrow \pi^*_{C_4=O}$, $\pi_{C_4=O} \rightarrow \pi^*_{C_2=C_3}$; ² — sum of energies interactions $nO \rightarrow \sigma^*_{H-N}$; ³ — Interaction energy $nN \rightarrow \pi^*_{C_2=C_3}$. HB-intramolecular hydrogen bond.

Taking into account that in the condition of amidation reaction the β -ester groups of I-IV aminofumarates and α -ester group of Z-IV enamine are inert, conditionally the energy of Z-IV enamine $\pi^*_{C1=O}$ MO can be taken as a high limit of $\pi^*_{C=O}$ energy, at which non-catalytic amidation of ester groups is impossible. In this case all considered aminomaleates in which the energy of α - and β - $\pi^*_{C=O}$ make up from -80.1 till -39.6 kJ/mol, should be inert in the reaction of amidation of any of ester groups. Unfortunately, this assumption impossible to check experimentally, first of all, on other aminomaleates. Respectively, formation of bis-amides of aminoethylene-1,2-dicarboxylic acid is possible only at decrease of energetic gaps between interacting orbitals, that possible to be reached by amidation in absolute alcohol in the presence of sodium methylate at intermediate formation of corresponding amide-anions, that have more high energy of nitrogen atom's unshared pair of electrons. Really, fumarates and monoamides of Z-2-amino-3-alkoxyl-carbonylacrylic acid in the condition of basic catalysis ($\text{MeOH}_{\text{abs.}}/\text{MeONa}$) form bisamides of aminofumaric acid [4].

Thus, although quantum-chemical calculations were carried out for molecules in gas phase, they let us explain experimental data on amidation of esters of N-derivatives of aminoethylene-1,2-dicarboxylic acid.

It should be noted that according calculation data (Table 2) energy of $\pi^*_{C1=O}$ MO is directly connected with efficiency of its conjugation with π -system of other part of molecule — removal of α -carbonyl group from molecule plane leads to increase of its MO. For example, change of digedral angle $\Theta_{\text{NC2C1=O}(\omega)}$ in Z-III enamine from 0.5 to 42° increases energy of $\pi^*_{C1=O}$ MO for 61 kJ/mol, in energetically preferable Z- or E-isomers of I-IV enamines energy of $\pi^*_{C1=O}$ MO is increased generally symbatically to increasing of $\Theta_{\text{NC2C1=O}(\omega)}$ values. Energy of conjugation of unshared electron pair (UEP) of nitrogen with π -bond of C=C (interaction of $n\text{N} \rightarrow \pi^*_{C2=C3}$) in I-IV E-isomers increased with increasing of energy of UEP (-729.6 , -651.9 , -618.9 and -627.1 kJ/mol, respectively); in the case of Z-isomers the corresponding pattern is not observed (-598.5 , -577.5 , -559.9 , -566.9 and -581.8 kJ/mol, respectively), possibly because of concomitant impact of intramolecular hydrogen bond $\text{N-H} \dots \text{O}=\text{C}_4$ (interaction $n\text{O} \rightarrow \sigma^*_{\text{H-N}}$). Summary energy of conjugation (sum of interaction energies, Table 2) in Z-isomers of I-IV enamines significantly high than in E-isomers, which explains the increased thermodynamical stability of Z-I-Z-III isomers; decreasing of relative stability of Z-isomer of IV enamine is caused by steric interaction between voluminous ester and dimethylamine groups. On other hand, observed change in bond length (elongation of $\text{C}_2=\text{C}_3$ and shortening of N-C_2 , C_1-C_2 , C_3-C_4 in Z-isomers relatively to E-isomers) is also stipulated by more high energies of conjugation in Z-isomers.

Conclusions

Thus, the amidation of amino ethylene-1,2-dicarboxylic acidsdiesters is obey to orbital control of the reaction. The observed regiospecificity of non-catalytic amidation on the α -complex ester group is due to the combined effect of decreasing electrophilicity (increasing the energy of loosening π -orbitals) of the β -carbonyl group due to effective conjugation with the π -system $\text{C}=\text{C}-\text{NHR}$ and increasing the electrophilic α -carbonyl group with increasing its conjugation with the rest molecules. The inertness of N,N-dimethylamino maleate to reactions with amines is caused by the increased energy of the $\pi^*_{\text{C=O}}$ -orbitals of the complex ester groups. Bis-amidation of amino-ethylene-1,2-dicarboxylic acidsdiesters is possible only in the presence of catalysts.

Acknowledgments

Financial support of scientific research was carried out under the project AP 05132810 «Scientific-practical bases of microencapsulation of bioactive substances and principally new stimulators of plant development with the purpose of agricultural production intensification» of the Ministry of education and sciences of the Republic of Kazakhstan.

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O.C. Лебедь, Ю.А. Чертихина, Б.Ж. Муталиева, Д.Е. Кудасова, А.В. Просьяник

Аминоэтилен-1,2-дикарбон қышқылының диэфирлерін амидирлеу: теориялық тұрғыдан қарастыру

Табиғи байланыс орбитальдарының (Natural Bond Orbital, NBO) формализмі шеңберінде PBE/def2-TZVPP жуықтауында кванттық-химиялық есептеулер деректерінің негізінде Z- және E-изомерлердің аминоэтилен-1,2-дикарбон қышқылы диэфирлерінің $\text{MeO}_2\text{CCH}=\text{C}(\text{NRR}^1)\text{CO}_2\text{Me}$ амидирлеу ерекшеліктері қарастырылды, мұнда $\text{R} = \text{H}$; $\text{R}^1 = \text{H}, \text{Me}, t\text{-Bu}$; $\text{R} = \text{R}^1 = \text{Me}$. Реттеушілердің перспективалы класстарының бірі белсенді түрдегі құрылысында байланысқан енамин және карбонил топтары бар эмальдар болып табылады, талдау жасау нысандар ретінде аминифумар қышқылы туындылары таңдалады, сондықтан, амино-этилен-1,2-дикарбон қышқылының диэфирін амидирлеу реакциялары жүргізілді. Есептеулер көрсеткендей, I-IV енаминдер үшін олардың конфигурациясына қарамастан, $\text{C}=\text{C}$ және $\text{C}=\text{O}$ байланыстарының орналасуында α -s-trans, β -s-циске ие конформерлер тиімді болып табылады. Бұл қорытындылар N-алкиламиноэтилен-1,2-дикарбондық қышқылдар диэфирлерінің Z- және E-изомерлерінің салыстырмалы конфигурациялық тұрақтылығы туралы тәжірибелік деректерге сәйкес келеді. Амидирлеу реакцияларының бағыты реагент құрылымына және реакция жағдайына критикалық жағынан байланысты болады. $\text{MeO}_2\text{CCH}=\text{C}(\text{NRR}^1)\text{CO}_2\text{Me}$, мұнда $\text{R} = \text{H}$; $\text{R}^1 = \text{H}, \text{Me}, t\text{-Bu}$; $\text{R} = \text{R}^1 = \text{Me}$ амино-этилен-1,2-дикарбон қышқылы диэфирлерінің Z- және E-изомерлерінің амидирлеу ерекшеліктері қарастырылған. Анықталғандай, амино-этилен-1,2-дикарбон қышқылы диэфирлерін амидирлеу реакциясының орбиталдық бақылауына бағынады. α -күрделі эфирлер топтары бойынша каталикалық емес амидирлеудің байқалған аймаққа тән болуының байқалуы π -жүйесімен $\text{C}=\text{C}-\text{NHR}$ -мен тиімді байланысына β -карбонил тобын төмендететін электрофильдіктің (π -орбиталдың көпсіту энергиясын жоғарылату) және қалған молекула бөлігімен байланысу артумен α -карбонил тобының электрофильділігін жоғарылатумен байланысты. Амидермен N,N-диметиламиноацетіл реакцияларға инерттілігі $\pi^*_{\text{C}=\text{O}}$ -күрделі эфирлер топтарының орбиталдары энергиясының артуымен байланысты болып келеді. Амино-этилен-1,2-дикарбон қышқылының диэфирлерін бис-амидирлеу тек ғана катализаторлардың қатысуымен мүмкін болады.

Кілт сөздер: амидирлеу, квантты-химиялық есептеулер, белсенді енаминдер, аймаққа тән, конформерлер, байланыстардың цисоидты орналасуы, трансиды байланыстың орналасуы, изомерлер, орбиталдық бақылау.

О.С. Лебедь, Ю.А. Чертихина, Б.Ж. Муталиева, Д.Е. Кудасова, А.В. Присяник

Амидирование диэфиров аминоэтилен-1,2-дикарбоновой кислоты: теоретическое рассмотрение

На основании данных квантово-химических расчетов в приближении PBE/def2-TZVPP в рамках формализма натуральных связевых орбиталей (Natural Bond Orbital, NBO) рассмотрены особенности амидирования Z- и E-изомеров диэфиров аминоэтилен-1,2-дикарбоновой кислоты $\text{MeO}_2\text{CCH}=\text{C}(\text{NRR}^1)\text{CO}_2\text{Me}$, где $\text{R} = \text{H}$; $\text{R}^1 = \text{H}, \text{Me}, t\text{-Bu}$; $\text{R} = \text{R}^1 = \text{Me}$. Так как одним из перспективных классов регуляторов являются активированные енамины, содержащие в своей структуре сопряженные енаминную и карбонильную группы, в качестве объектов для анализа выбраны производные аминифумаровой кислоты. Расчёты показали, что для енаминов I-IV, независимо от их конфигурации, наиболее выгодными являются конформеры, обладающие α -s-транс, β -s-цис-расположением связей C=C и C=O. Эти выводы согласуются с экспериментальными данными по относительной конфигурационной устойчивости Z- и E-изомеров диэфиров N-алкиламиноэтилен-1,2-дикарбоновой кислоты. Направление реакций амидирования критическим образом зависит от строения реактанта и реакционных условий. Установлено, что амидирование диэфиров аминоэтилен-1,2-дикарбоновой кислоты подчиняется орбитальному контролю реакции. Наблюдающаяся региоспецифичность некаталитического амидирования по α -сложноэфирной группе обусловлена совместным влиянием снижения электрофильности (повышением энергии разрыхляющей π -орбитали) β -карбонильной группы вследствие эффективного сопряжения с π -системой C=C-NHR и повышением электрофильности α -карбонильной группы с ростом ее сопряжения с остальной частью молекулы. Инертность N,N-диметиламиноацетата к реакциям с аминами вызвана повышенной энергией $\pi_{\text{C=O}}^*$ -орбиталей сложноэфирных групп. Бисамидирование диэфиров аминоэтилен-1,2-дикарбоновой кислоты возможно лишь в присутствии катализаторов.

Ключевые слова: амидирование, квантово-химические расчеты, активированные енамины, региоспецифичность, конформеры, цисоидное расположение связей, трансидное расположение связей, изомеры, орбитальный контроль.

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M.S. Sagyndykova¹, A.A. Imanbayeva¹, Ye.M. Suleimen², M.Yu. Ishmuratova^{1,3}

¹Mangyshlak Experiment Botanical Garden, Aktau, Kazakhstan;

²Institute of Applied Chemistry at L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan;

³Ye.A. Buketov Karaganda State University, Kazakhstan

(E-mail: m.sagyndykova@mail.ru)

Chemical composition and properties of essential oil of *Ferula foetida* (Bunge) Regel growing on Mangyshlak peninsula

The medicinal plant, *Ferula foetida*, has been studied, which has a wide range of pharmacological properties. Since ancient times, ferules have been used in folk medicine in various countries (Central Asia, Iran, China, India) for treatment of scabies, wounds, tumors, syphilis, tuberculosis, seizures, hysteria, the gastrointestinal tract, and as an antiparasitic remedy. Chemical composition of *Ferula foetida* essential oil has been analyzed. The samples were taken from two different populations on Mangyshlak peninsula — on loamy and sandy massifs. Use of GC-MS analyses helped identifying 47 compounds comprising 91.5 % of the total components in the oil. Components of essential oil of two populations — Tuyesu sands and Tynymbay Shoky hills — differ through growing phase. 2,5-Diethylthiophene, 3,4-diethylthiophene, bulnesol, guaiol, myristicine, α -pinene, caryophyllene oxide, 2,5-dipropylthiophene, elemicine, 1-heptatriacontanol, β -*trans*-caryophyllene, β -*cis*-caryophyllene, α -caryophyllene, β -pinene, dimethyl trisulfide, α -eudesmol, β -eudesmol; β -eudesmene, 2-methylthieno[3.2-b]thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxa-spiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl) are common for both populations. These components have acaricide, antitussive, expectorate effect, as well as anxiolytic, antidepressant, antioxidant, growth stimulating properties. Concentration of major components is higher in plants growing in harsher edaphic conditions. Comparative analysis of essential oil of *Ferula foetida* growing in Iran, Turkey and Kazakhstan shows differences in the composition. The differences are caused by the climatic conditions. The results of the studies may further be used for standardization of the raw materials.

Keywords: essential oil, *Ferula foetida*, herbs, Mangyshlak, GC-MS, climate, arid zone, latex.

Introduction

Aromatic plants and essential oils were used for millennia in medicine, cosmetics and perfumery. It is believed that therapeutic properties of essential oils as treatment-and-prophylactic drugs are not fully studied. However, huge experience of using separate essential oils as inhalator and antifungal remedy, was accumulated in literature and applied medicine. Many oils are capable of reducing arterial pressure. They are effective at treatment of hypostases, rheumatism, inflammations, skin and other diseases.

Synthesis and accumulation of separate classes of biologically active agents in wild-growing herbs are mostly defined by climatic conditions in the respective growth areas [1].

Therefore, comprehensive study of separate groups of plants, including composition of essential oils, is critical for definition of main spheres for their use as treatment-and-prophylactic drugs. It may as well include a number of scientific tasks like studying of mechanism of synthesis of separate compounds in the raw materials in different phases of growth and development, metabolism of separate compounds, developing methods for their identification and allocation. Widespread use of phytogenic products is caused by their biological activity, mild effect and less side effects compared to synthetic products [2].

The greatest number of essential oil plants leads to *Apiacea* families. *Ferula* L. genus is the largest genus of *Apiacea* family and contains more than 170 species, the majority of which is herbs. One of these plants is *Ferula foetida* (Bunge) Regel, which is used in traditional medicine in Central Asia, China, Iran and India since ancient time.

Ferula foetida is a very polymorphic species. The plant has a specific, unpleasant smell. It grows up to 2 m high, has a massive stalk of 5–8 cm in diameter at the basis. The leaves are 30–40 cm long, ternate-pinnate. The flowers are yellow and form a spherical inflorescence [3].

The main medical component of *Ferula foetida* is rhizome latex [4]. Solidified latex of *Ferula foetida* consists of resin (40–65 %), gum (12–25 %) and essential oil (5–20 %). Generally, the essential oil contains organic sulfides, which give onion-garlic smell [5], and α -pinene, umbelliferone, coumarin and other compounds [6, 7].

Antioxidative, antimicrobial, antifungal, anti-diabetic effects have been revealed as a result of pharmacological studies of this species [8, 9]. Therapeutic effect of medications based on the herbal raw materials is defined by a combination of all compounds contained in the plants: tannins, flavonoids, saponins, terpenoids, vitamins, sesquiterpenes, coumarins and essential oil [8]. Therefore, assessment of essential oil composition of useful plants is a vital and practical task at this time.

The purpose of the research is to assess the quantitative and qualitative composition of essential oil obtained from the roots of *Ferula foetida* (Bunge) Regel growing on Mangyshlak peninsula.

Methodology

The raw material has been collected from natural places of growth on Mangyshlak peninsula in arid zone. The samples were collected in spring of 2014 during vegetation and full blossoming phase. Collecting and preparation (air drying) of raw materials and obtaining of essential oil (hydro distillation) were carried out by the standard techniques. The studied samples are named by their geographical places near the place of collection of the raw materials. Characteristics of the collected samples are given in Table 1. The site map of *Ferula foetida* growth area is shown on Figure 1.

Table 1

Characteristics of the collected samples

No.	Local name	Ontogenesis phase	Identified compounds number
1	Tuyesy sands	Vegetation	42–47
		Blossoming	43
2	West Tynymbay Shoky hill	Vegetation	31–45
		Blossoming	44

Roots of the plants were ground, and a portion of 100 g sharp, has been measured for each sample. Essential oil has been separated by hydro distillation method with the use of Clevenger apparatus. Duration of hydro distillation was 2 hours. The compounds were identified by GC-MS method.

Definition of composition of the essential oil was carried out on Clarus-SQ 8 (Perkin Elmer) gas chromatograph with mass and spectrometer detector.

Preparation of essential oil sample: 25 mg of *Ferula foetida* essential oil was placed in a measuring flask with the capacity of 25 ml, dissolved in 15 ml of hexane, brought to the tag, and mixed.

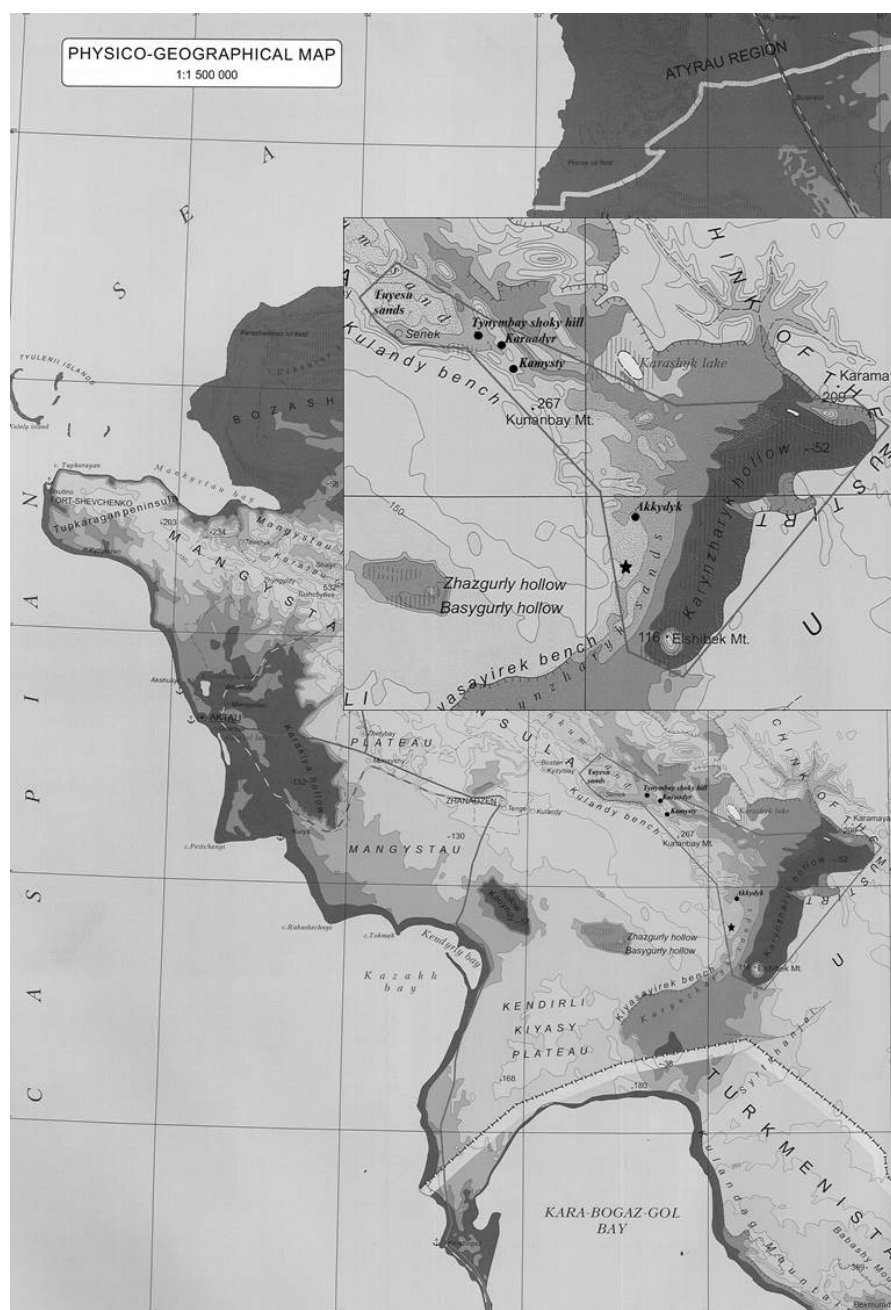
Chromatographic conditions: capillary column Restek Rxi®-1 ms of 0.25 mm × 30 m × 0.25 microns; sample volume: 1.0 µl; gas carrier He, gas carrier velocity is 1 ml/min., split ratio 1:25; column temperature: 40 °C, build-up — 2 °C/min. to 280 °C, evaporator temperature is 280 °C; the mass and spectrometer detector: t — 240 °C, EI+ = 70 eV; scanning time from 4 to 120 min; the mode of ions scanning: 39–500 m/z. Percentage of the components was calculated automatically, proceeding from the areas of peaks of the general ions chromatogram. The components were identified by the mass-spectrums and retention time, with the use of the National Institute of Standard and Technology Library.

Results and discussion

Results of the studies on composition of essential oil of *Ferula foetida* growing in two different ecological populations of Mangyshlak peninsula are reported in this article.

Natural populations of *Ferula foetida* are widespread as a part of the East Mangyshlak geobotanical district, in the southern part of the peninsula. They grow on the fixed and semi-fixed sands of the loamy plains of Middle and South deserts. Also, *Ferula* is spread in wormwood, saxaul, saltwort communities, often as a co-dominant of spring communities.

Tuyesu sands are located in the south of Mangyshlak peninsula, close to Senek village, where *Ferula* is involved in saxaul–ferula–sagebrush–psammophyte–shrubs associations. The relief has slides, hilly ridges, and wavy fixed sandy massifs. The soils are sandy and sabulous, mostly non-saline or sub-saline. Tuyesu sands have shallow fresh waters and potable top waters. Groundwater depth varies from 3–5 m to 41 m. The thickness of watered eolian sand massif is around 5 m to 33.3 m.

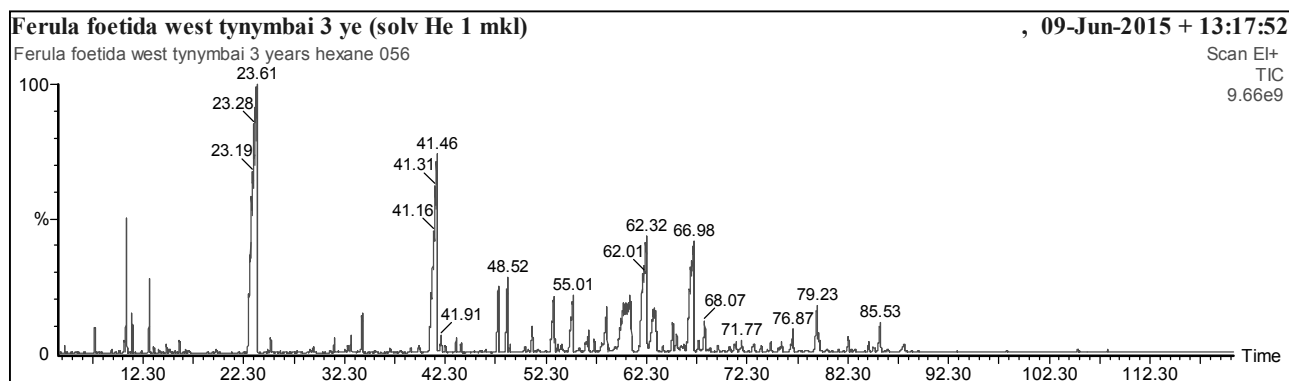


- Survey boundary;
●— Mass growth places

Figure 1. Site map of *Ferula foetida* growth area (Mangyshlak peninsula)

Tynymbay Shoky hill is located near Kunabay Mountain. *Ferula foetida* is observed in saxaul-ferula-santolina-mugwort, sedge-artemisia terrae-albae-ferula associations. The region is significantly different from the others both on mechanical makeup, and salinity of the soil. The sandy loam soil occurs at a depth of 30 cm, low loamy — from 30 to 50 cm and mid loamy — from 50 to 100 cm. Salinity level is low from the surface down to 50 cm, middle level — from 50 to 80 cm and high level — from 80 to 100 cm. Watering of the region is extremely low. The plants take up liquid from atmospheric precipitation and shallow ground waters with various salinity levels.

From 31 to 47 components were detected and identified in the examined samples, using the gas-chromato-mass-spectrometry (GC-MS), which constitute 88.2–92.5 % of the whole essential oil. Ether oil of *Ferula foetida* represents liquid of yellow color with specific garlic-onion-like odor which is caused by the presence of sulphide compounds. Chromatogram of essential oil of *Ferula foetida* roots is given in Figure 2.

Figure 2. Chromatogramm of essential oil of *Ferula foetida* roots

The main compounds of essential oil of Mangyshlak's *Ferula foetida* plants are: 2,5-diethylthiophene, 3,4-diethylthiophene, bulnesol, guaiol, caryophyllene oxide, myristicine, β -*trans*-caryophyllene, α -pinene, β -pinene, dimethyl trisulfide, β -*cis*-caryophyllene; β -*cis*-caryophyllene, α -caryophyllene, α -eudesmol, β -eudesmol, 1-heptatriacontanol, β -eudsmene, 2-methylthieno[3.2-b]thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxaspiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl), elemicine and 2,5-dipropylthiophene.

The composition of essential oil varies from sample to sample, except for the main components. The structure of the main components is almost constant throughout all the samples. The quantitative content of the main components is higher in West Tynymbai Shoky hill populations, i.e. in plants growing in harsher edaphic conditions. Presence of certain substances only in individual samples is caused by the fact that population, and even individual plants, occur with significantly different composition for this species or population [10].

Thus, the obtained data show that composition of essential oil from two populations of Mangyshlak peninsula differs by the content of the main components. Composition of essential oils can vary depending on the age, growth phase and habitat.

Comparison of essential oil components with species growing in various regions of Iran shows a significant difference in the qualitative and quantitative content of components both between species, growing in Iran, and between species growing in different countries. Comparison results of gum resin, aerial organs and essential oils composition in different populations are shown in the Tables 2–4.

Table 2

The main components of Iran and Pakistan *Ferula foetida* essential oil obtained from oleo-gum resin, %

Components	Location					
	Larestan, Iran	Yazd province, Iran	Kerman, Iran	Isfahan, Iran	Darab mountain, Iran	Pakistan
(E)-1-propenyl sec-butyl disulfide	20.3–23.9 [11]	40.1–44.4 [12]	58.9 [13]	22.1 [14]		
10- <i>epi</i> - γ -eudesmol	15.1 [11]					
(Z)-1-Propenyl sec-butyl disulfide	27.7 [11]	23.9–28 [12]		35.1 [14]		
Guaiol		3.1–5.5 [12]				
Carotol		1.6–5.1 [12]				
β -Pinene					1 [15]	
α -Pinene				12.2 [14]	21.4 [15]	
(Z)- β -Ocimene			11.9 [13]			
(E)- β -Ocimene			9 [13]			
Phelandrene						6.49 [16]
Propenyl sec-butyl disulfide						51.9 [16]
Undecylsulfonyl acetic acid						18.8 [16]

Table 3

The main components of Iran and Pakistan *Ferula foetida* essential oil obtained from root, %

Components	Location		
	Gonabad, Iran	Tabas, Iran	Mangyshlak peninsula, Kazakhstan
(<i>E</i>)-1-Propenyl sec-butyl disulfide	30.7 [17]	18.8 [17]	
10- <i>epi</i> - γ -Eudesmol	12.7 [17]	18.7 [17]	
(<i>Z</i>)-1-Propenyl sec-butyl disulfide	12.4 [17]	9.2 [17]	
β -Pinene			0.1–1.0
α -Pinene			0.3–3.1
2,5-Diethylthiophene			11.0–26.2
3,4-Diethylthiophene			8.5–35.3
Bulnesol			5.6–20.7
Guaiol			5.8–19.3
Caryophyllene oxide			0.9–4.7
Myristicine			0.6–7.6
1-Heptatriacontanol			0.3–3.2
2,5-Dipropylthiophene			0.5–5.6
Elemicine			0.5–6.1

Table 4

The main components of *Ferula foetida* aerial organs growing in Iran and Turkey, %

Components	Aerial organs				Fruits	Leaves	
	Location				Mount Telesm, Kerman-shah, Iran	Kashana region, Isfahan, Iran	No information
	Kerman, Iran	Turkey	Sari forest, Iran	Neishabour mountains, Iran			
1	2	3	4	5	6	7	8
1-Methylpropyl (1 <i>E</i>)-prop-1-en-1-yl disulfide	32.8 [18]						
α -Pinene	11.3 [18]	59.9 [19]		3.4 [21]	1.7 [22]	12.8 [23]	1.5 [24]
Germacrene B	5.5 [18]						
β -Pinene		13.5 [19]				6.2 [23]	
Limonene		3.2 [19]					
Bornyl acetate		2.1 [19]					
2-Methyl-5-(1-methylethyl)			18.2 [20]				
α -Bisabobol			10.4 [20]				
Arsinetriethyl			8.7 [20]				
Cyclopropa[a]naphthalene octahydrotetramethyl			6.6 [20]				
<i>trans</i> -2-Undecen-1-ol						17.3 [23]	
Thymol						10.9 [23]	
Dodecanal						9.7 [23]	
Spathulenol						8.5 [23]	
β -Eudesmol					1.9 [22]	6.8 [23]	
γ -Elemene						32.2 [23]	
Eremophilene							31.3 [24]
δ -Cadinene							22.0 [24]
Longiborneol							12.1 [24]
Dehydroaromadendrene							39.7 [24]
Isoledene							36.4 [24]
τ -Gurjunene							3.9 [24]
j -Guaiene							3.5 [24]
Ledenoxid							1 [24]

1	2	3	4	5	6	7	8
<i>trans</i> -Caryophyllene							1 [24]
α -Gurjumene							1 [24]
2-j-Pinene							0.2 [24]
(<i>E</i>)-1-Propenyl sec-butyl disulfide				53.8 [21]	1.1 [22]		
(<i>Z</i>)-1-propenyl sec-butyl disulfide				35.6 [21]	5.9 [22]		

Chemical composition of essential oils obtained from *Ferula foetida* oleo-gum resin of two different sites in the central part of Iran, Yazd and Tabas, were identified in 2008. 39 substances were identified in the essential oil, which included 77.7 % (Tabas) and 72.4 % (Yazd) of sulphur-containing compounds; monoterpene hydrocarbons (2.8 and 3.4 %), sesquiterpene hydrocarbons (4.6 and 7.3 %); oxylene hydrocarbons sesquiterpenes (6.3 % and 12.4 %)[12].

Sefidkon et al. assert that the main component of Iran *Ferula foetida* essential oil is (*E*)-1-propenyl sec-butyl disulfide (58.9 %) which might be responsible for the positive properties of the essential oil, such as insecticidal, repellent (scaring insects) effect [15, 5]. Meanwhile, this component was not detected in the samples of the populations growing in Mangyshlak peninsula. However, other components, which were not previously identified, have been revealed: 2,5-diethylthiophene (11.0–26.2 %) and 3,4-diethylthiophene (8.5–35.3 %), which feature acaricidal activity and are used for treatment of animal scab [25].

The following basic components were also identified in essential oil of *Ferula foetida* growing in Mangyshlak: bulnesol (5.6–20.7 %), guaialol (10.6–19.3 %). Concentration of the other components detected in all the samples was below 2 %.

Properties of the identified components are diverse; thus, bulnesol and guaialol feature anti-tussive activity, while bulnesol and α -cadinol (detected only in blooming samples of the plants growing westwards Tynymbay Shoky hill) feature expectorative activity.

β -Caryophyllene is effective in treatment of anxiety and depression since it possesses anxiolytic and antidepressant properties. This terpenoid is also contained in cannabis and is linked to one of the two cannabinoid receptors — CB₂ — the ones that are impacted by marijuana, and thus does not lead to euphoria [26]. Myristicine is responsible for psychoactive effects. During metabolism, the components are aminating, which turns them into the centralized active amphetamine derivatives. In the course of amination, Myristicine gives MMDA — a well-known entactogenic compound acting similar to ecstasy. Pinenes are used in perfumery, and more seldom — as lacquer and paint solvents. Pinenes are well sensed by insects and act as important regulator of their chemical communication. Eudesmol features antioxidant activity.

Dimethyl-trisulphide confers a specific garlic-onion-like odor upon the plant and is used as a flavoring agent and food supplements. Eudesmol features antioxidant activity. Triacontanol features high biological activity and influences plant growth by increasing assimilation of carbon dioxide and improving the photosynthesis. It allows a plant to acquire more nutritive agents from the environment, which leads to enhanced growth of the plant and increases the yield. Minimal concentrations manifest the maximum effect [27].

Moreover, in the studied samples we have identified such materials depicted in samples of the plants growing in other countries as: α -pinene, β -pinene, *epi*- γ -eudesmol, β -eudesmol, germacrene B, α -bisabolol, δ -cadinene, β -*trans*-caryophyllene, guaiane. Concentration of these materials in the root resin of *Ferula foetida* growing in Mangyshlak was lower by more than 10 % compared to plants growing in Iran.

Composition analysis of ether oil exuded from oleo-gum resin, roots and leaves of *Ferula foetida* from different areas of Iran and Turkey reveals differences both, in qualitative and quantitative indicators.

Thus, composition of *Ferula foetida* essential oil differs both, by number of determined components, and by their quantity within one population as well as between the populations. This can be caused by natural and climatic conditions and by other genetic factors [3, 24].

Conclusions

Two different populations of *Ferula foetida* collected from loamy and sandy massifs on Mangyshlak have been analyzed. 47 compounds out of 48, comprising 91.5 % of the total components, were identified in the oil by GC-MS. Essential oil components of two populations — Tuyesu sands and Tynymbay Shoky hill — differ through growing phase. 2,5-Diethylthiophene, 3,4-diethylthiophene, bulnesol, guaialol,

myristicine, α -pinene, caryophyllene oxide, 2,5-dipropylthiophene, elemicin, 1-heptatriacontanol, β -*trans*-caryophyllene, β -*cis*-caryophyllene, α -caryophyllene, β -pinene, dimethyl trisulfide, α -eudesmol; β -eudesmol, β -eudesmene, 2-methylthieno[3.2-b] thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxa-spiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl) are constant components for both Mangyshlak populations. These components have acaricide, antitussive, expectorate effect, as well as anxiolytic, antidepressant, antioxidant, growth stimulating properties.

Concentration of major components is higher in plants growing in harsher edaphic conditions. Comparative analysis of essential oil of *Ferula foetida* growing in Iran, Turkey and Kazakhstan shows differences in the composition. The differences are caused by the climatic conditions.

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М.С. Сагындыкова, А.А. Иманбаева, Е.М. Сулеймен, М.Ю. Ишмуратова

Маңғышлақ түбегінде өсетін *Ferula foetida* (Bunge) Regel эфир майының химиялық құрамы мен қасиеттері

Алуан түрлі фармакологиялық қасиеттері бар сасық курай (*Ferula foetida*) дәрілік өсімдігі зерттелген. Ежелгі дәуірден бастап ферула халық медицинасында әртүрлі елдерде (Орталық Азия, Иран, Қытай, Үндістан) қышыма, жара, ісік, мерез, туберкулез, құрысулар, есірік, асқазан-ішек жолдарын емдеу үшін, сондай-ақ паразитке қарсы құрал ретінде қолданылды. Маңғышлақ түбегінің екі түрлі сазды және құмды популяцияларында таралған сасық курайдың эфир майының құрамы анықталған. Газды-хромато-масс-спектрометрия әдісімен тұтас май қосындысының 91,5% құрайтын 47 компонент табылып, анықталған. Түйесу құмдары мен Тынымбай шоқы төбешігінің батыс бөлігіндегі популяциялардың эфир майы келесі компоненттердің құрамымен ерекшеленеді: Түйесу популяциясының барлық үлгілердің құрамында диметилтрисульфид, α -кариофиллен, β -эвдесмен, 2-метилтиено[3.2-b]-тиофен, 5,5-диметил-4-[(1E)-3-метил-1,3-бутадиенил]-1-оксапиро[2.5]октан, ал Тынымбай шоқының батыс бөлігіндегі барлық үлгілердің құрамында 2,5-дипропилтиофен и S-(9-тиабицикло[3.3.1]нон-6-ен-2-ил)этантоат болуы. Бірақ екі популяциялардың барлық үлгілерінің құрамында 2,5-диэтилтиофен, 3,4-диэтилтиофен, бульнезол, гвайол, кариофиллен оксид, миристицин, β -*trans*-кариофиллен бар. Олар кене жойғыш, жөтелге қарсы және қақырық түсіретін белсенділіктерімен, депрессияға және мазасыздыққа қарсы қолданылатын қасиеттерімен ерекшеленеді. Негізгі компоненттердің концентрациясы ызғарлы эдафикалық жағдайларда өсетін өсімдіктерден жоғары. Иран, Түркия және Қазақстанда өсетін сасық курайдың эфир майларының салыстырмалы талдауы климаттық жағдайларға байланысты эфир майларының құрамындағы айырмашылықтарды көрсетеді. Болашақта зерттеу нәтижелерін шикізатты стандарттау үшін қолдануға болады.

Кілт сөздер: эфир майы, сасық курай, дәрілік өсімдіктер, Маңғышлақ, ГХ-МС, ауа райы, құрғақ аймақ, шайыр.

М.С. Сагындыкова, А.А. Иманбаева, Е.М. Сулеймен, М.Ю. Ишмуратова

Химический состав и свойства эфирного масла *Ferula foetida* (Bunge) Regel, произрастающей на полуострове Мангышлак

Изучено лекарственное растение ферула вонючая, которая обладает широким спектром фармакологических свойств. С древнейших времен ферула применялась в народной медицине различных государств (Иране, Китае, Индии) и Средней Азии для лечения чесотки, заживления ран, опухолей, сифилиса, туберкулеза, судорог, истерии, желудочно-кишечного тракта, а также как противопаразитарное средство. Исследован состав эфирного масла ферулы, произрастающей в двух различных популяциях полуострова Мангышлак — на суглинистых и песчаных массивах. Методом газо-хромато-масс-спектрометрии идентифицировано 47 веществ, составляющих 91,5% от суммы цельного масла. Эфирное масло популяций песков Туйесу и западное возвышенности Тынымбай шоки отличаются по содержанию: диметилтрисульфид, α -кариофиллен, β -эвдесмен, 2-метилтиено[3.2-b]тиофен, 5,5-диметил-4-[(1E)-3-метил-1,3-бутадиенил]-1-оксапиро[2.5]октан во всех образцах популяции Туйесу и наличие 2,5-дипропилтиофена и S-(9-тиабицикло[3.3.1]нон-6-ен-2-ил)этантоата во всех образцах популяции западное возвышенности Тынымбай шоки. Однако для

них присуще наличие 2,5-диэтилтиофена, 3,4-диэтилтиофена, бульнезола, гвайола, кариофилленоксида, миристицина, β -*trans*-кариофиллена, обладающих акарицидной, противокашлевой и отхаркивающей активностью, а также анксиолитическими и антидепрессантными свойствами. Концентрация основных компонентов выше у растений, растущих в более суровых эдафических условиях. Сравнительный анализ эфирных масел ферулы вонючей, произрастающей в Иране, Турции и Казахстане, показывает различия в составе эфирных масел, которые вызваны климатическими условиями. Результаты исследований в дальнейшем могут быть использованы для стандартизации сырья.

Ключевые слова: эфирное масло, ферула вонючая, лекарственные растения, Мангышлак, ГХ-МС, климат, аридная зона, смола.

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G. Toleutay^{1,2}, E. Su³, S.E. Kudaibergenov^{1,2}¹*Institute of Polymer Materials and Technology, Almaty, Kazakhstan;*²*Satbayev University, Almaty, Kazakhstan;*³*Istanbul Technical University, Turkey**(E-mail: skudai@mail.ru)*

Swelling and mechanical properties of quenched polyampholyte hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and (3-acrylamidopropyl) trimethylammonium chloride (APTAC)

In our previous paper (Bulletin of the Karaganda University. Chemistry series, 2019, 2(94), P. 35–43) we considered the behavior of quenched (or strongly charged) polyampholytes based on fully charged anionic monomer — 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and cationic monomer — (3-acrylamidopropyl) trimethylammonium chloride (APTAC) in aqueous-salt solutions. In the present paper we report the mechanical properties of quenched polyampholyte hydrogels synthesized by free-radical copolymerization of the same monomers in the presence of N,N-methylenebisacrylamide (MBAA) as crosslinking agent. The hydrogel samples in dependence of the molar amount of AMPS were abbreviated as AMPS-75H, AMPS-50H and AMPS-25H. The swelling, rheological, and mechanical properties of quenched polyampholyte hydrogels were evaluated for different compositions of copolymers at fixed initial monomer concentration $C_0 = 0.5$ wt.% and constant amount of [MBAA] = 20 mol.%. The formation of hydrogels in the course of (co)polymerization of oppositely charged monomers in presence of MBAA was monitored by rheometric measurements using oscillatory deformation tests at an angular frequency $\omega = 6.3$ rad·s⁻¹ and strain amplitude $\gamma_0 = 0.01$. The strain-stress curves of as-prepared and swollen polyampholyte gels demonstrate that the highest values of Young's modulus E , fracture stress σ_f and elongation $\varepsilon\%$ are characteristic for as-prepared AMPS-75H and swollen AMPS-50H samples. These results are interpreted in terms of polyelectrolyte and polyampholyte effects.

Keywords: quenched polyampholyte hydrogels, swelling, rheological and mechanical properties, strain-stress, Young's modulus, ionic interactions.

Introduction

Three-dimensional quenched polyampholytes (QPA) can be divided into two categories: chemically and physically crosslinked hydrogels [1, 2]. The long-range Coulombic interactions between opposite charges along the backbone is a governing factor of conformational and volume-phase changes of QPA hydrogels. Swelling ratio at equilibrium Q_e for QPA gels prepared from 2-(methacryloyloxy)ethyltrimethylammonium chloride (MADQUAT) and AMPS was studied in pure water and 2 mol·L⁻¹ NaCl solution [3]. Similar to linear QPA, hydrogels of QPA are in swollen and collapsed states in dependence of the net charges expressed as $\Delta f = f^+ - f^-$ (where f^+ and f^- are the molar ratios of cationic and anionic monomers to the total monomer concentration, respectively). As the concentration of the anionic and cationic parts deviates from the equimolar ones $\Delta f \neq 0$ the swelling ratio increases rapidly. A reasonable explanation of these results are that the number of osmotically active ions in the hydrogel phase increases as the molar ratio of cationic to anionic groups diverges from unity according to Donnan equilibrium. While as the molar ratio of cationic to anionic groups approaches to unity the excess free counterions that are not needed to satisfy the electroneutrality of the chain are effectively «dialyzed» from the hydrogel interior. In 2 mol·L⁻¹ NaCl solution the electrostatic effects are screened and the swelling ratio at equilibrium Q_e levels off and gel behaves as a neutral system. At low ionic strength polyampholyte chains bearing net charges of opposite signs form intraionic complexes leading to a phase separation. At high ionic strength, the gel swells due to screening of electrostatic interactions and such microscale structure dissolves.

QPA hydrogels based on [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC) and 4-vinylbenzenesulfonate (NaSS) P(MAPTAC-co-NaSS) [4] and P(AMPS-APTAC) [5] were compared with polyionic complex (PIC) composed of P(MAPTAC) and P(NaSS) [4]. The main difference between P(MAPTAC-co-NaSS) and P(MAPTAC)-P(NaSS) hydrogels is that the former is composed of oppositely charged monomers, while the latter is the product of matrix polymerization of NaSS on the matrix of

P(MAPTAC). The conformation of P(MAPTAC-*co*-NaSS) can be stabilized by both inter- and intra-ionic interactions, while P(MAPTAC)-P(NaSS) chains are stabilized by interionic salt bonds. The effects of charge ratio and monomer concentrations, the molecular weight of polyelectrolytes on the swelling, toughness, self-healing, and viscoelasticity of QPA and PIC hydrogels were comparatively studied. It was demonstrated that the PIC hydrogels are much tougher than the QPA hydrogels and exhibit better mechanical properties. This is due to structural and morphological differences of two systems. The PIC hydrogel shows a more inhomogeneous, large segregated structure with large pore size ($d = 0.5\text{--}3.0\ \mu\text{m}$), while the QPA hydrogels show more homogeneous structure with diameter of pores $0.1\text{--}0.3\ \mu\text{m}$.

The swelling properties of AMPS-APTAC were evaluated by continuous monitoring of $60\ \mu\text{m}$ sized hydrogels with the help of instrument [6]. It was shown that the charge balanced P(AMPS-APTAC) hydrogel exponentially swells upon ionic strength increases from $5 \cdot 10^{-4}$ to $0.15\ \text{M}$ NaCl exhibiting antipolyelectrolyte effect [7] in response to added salts.

A new class of tough, viscoelastic and self-healing hydrogels was designed by authors [8–11] from supramolecular QPA prepared by random copolymerization of oppositely charged ionic monomers at high monomers concentration and equimolar monomers ratio (charge balance point). These physical gels contain the strong ionic bonds that play the role of permanent crosslink and weak ionic bonds that are responsible for elongation, deformation, twisting, fatigue resistance, internal friction, adhesion, self-healing, shape memory, anti-biofouling and other important functions. In spite of topological difference, the QPA hydrogels are similar to double-network hydrogels [12]. In both cases, the strong bonds form a primary network and the weak bonds — a sacrificial network. The effect of the charge fraction (f) on the swelling volume ratio ($Q_v = V/V_0$, where V and V_0 are the volumes of swollen and as-prepared hydrogels), Young's modulus E , and the compressive fracture stress σ_b of the hydrogels MAPTAC-*co*-NaS) was evaluated. The extremums of curves correspond to the vicinity of charge balance point ($f \approx 0.48\text{--}0.53$) where the Coulomb attraction prevails over the repulsion and polymer chain collapse to globular state. In imbalanced region ($f < 0.48$ and $f > 0.53$) the Coulomb repulsion prevails and polymer segments elongate. The shrinking of the gels near the charge balance point ($f \approx 0.505 \pm 0.025$) is accompanied by dramatic increase in the modulus E and fracture stress σ_b .

A series of experiments were carried out to clarify the effect of specific ions on mechanical and electrical properties of QPA hydrogels on the examples of P(MAPTAC-*co*-NaSS) and various salts [13]. A virgin sample is represented as inhomogeneous medium composed of strong ionic bonds that play the role of permanent crosslink like covalent cross linker and weak ionic bonds that can be ruptured and re-formed. The cut virgin sample contains the ruptured strong and weak ionic bonds. After contacting of the cut surfaces a large number of ionic contacts in the vicinity of surfaces are re-formed across the interface which leads to healing.

Earlier [14] we have studied the swelling properties of a series of QPA hydrogels based on P(AMPS-APTAC) in aqueous-salt solutions. The swelling behavior regardless of hydrogel composition, was followed by Fickian diffusion. The adsorption and desorption ability of QPA hydrogels was evaluated with respect to ionic dyes and surfactants.

In the present paper we report the mechanical properties of QPA hydrogel samples of P(AMPS-APTAC) in dependence of the molar amount of AMPS. The rheological, and mechanical properties of quenched polyampholyte hydrogels were evaluated for different compositions of copolymers at fixed initial monomer concentration $C_0 = 0.5\ \text{wt.}\%$ and constant amount of $[\text{MBAA}] = 20\ \text{mol.}\%$.

Experimental

Materials

Commercially available 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS, 50 wt. % in water), (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75 wt. % in water), N,N' -methylenebis(acrylamide) (MBAA) purchased from Sigma-Aldrich were used as received. Ammonium persulfate (APS) purchased from Changzhou Qi Di Chemical Co. was used without further purification.

Preparation of polyampholyte hydrogels

Polyampholyte hydrogels were prepared by solution polymerization of the monomers AMPS and APTAC at $60 \pm 2\ ^\circ\text{C}$ in the presence of MBAA as a cross-linker, and $10\ \text{mM}$ APS as an initiator respectively. The molar amount of AMPS in the comonomers feed was varied from 25 to 75 mol.% while initial monomer concentration C_0 and amount of MBAA were fixed at 5 wt.% and 20 mol.%. Further, the QPA hydrogels were coded as AMPS-75H, AMPS-50H and AMPS-25H (where 75, 50 and 25 are the mole percent of AMPS in initial monomer feed). For example, AMPS-50H was prepared from the mixture of 50 mol.%

AMPS and 50 mol.% APTAC in the presence of 20 mol.% MBAA. The synthetic protocol for preparation of AMPS-50H is the following: the mixture AMPS (0.4 g), APTAC (0.2 g), MBAA (0.06) was stirred at room temperature for 15 min to obtain a homogeneous solution. After the addition of APS (30 mg) and stirring for 1–2 min, nitrogen gas was bubbled through the homogeneous solution for 30 min to eliminate oxygen. The solution was then transferred into 1 mL volume syringes, placed into oven and polymerized at 60 °C during 24 h.

Methods

Rheological measurements

The rheological measurements were conducted on a Bohlin Gemini 150 rheometer system (Malvern Instruments, UK) equipped with a Peltier device for temperature control. Hydrogel samples were prepared between rheometer plates at 60 °C for monitoring gelation. The frequency sweep tests were carried out over the frequency range of 0.1 to 100 rad·s⁻¹ placing the gel samples between the cone and plates (diameter 40 mm) at the constant distance between them 150 μm. The frequency-sweep tests at strain amplitude $\gamma_0 = 0.01$ were carried out at 25 °C.

Swelling tests

Hydrogels taken out of the syringes after 24 h reaction time were cut into small pieces of about 1 cm in length, and immersed in an excess of water. After reaching an equilibrium degree of swelling, which was monitored by recording the mass and diameter of gel specimen, the samples were taken out of water and freeze-dried (Christ Alpha 2–4 LDplus). The fraction of the monomers converted into a water-insoluble polymer, that is, the gel fraction W_g was calculated by formula:

$$W_g = \frac{m_{dry}}{C_0 \times m_0}, \quad (1)$$

where m_{dry} and m_0 are the weights of the gel specimens in dried and as-prepared states, respectively, and C_0 is the monomer concentration (wt.%) in the initial reaction mixture.

The relative weight (m_{rel}) and volume (V_{rel}) swelling ratios of as-prepared gels were determined by formulas:

$$m_{rel} = \frac{m_{swl}}{m_0}; \quad (2)$$

$$V_{rel} = \left(\frac{d_{swl}}{d_0} \right)^3, \quad (3)$$

where d_0 and d_{swl} are the diameters of as-prepared and swollen specimen respectively, m_{swl} is the weight of swollen gel specimen.

Mechanical tests

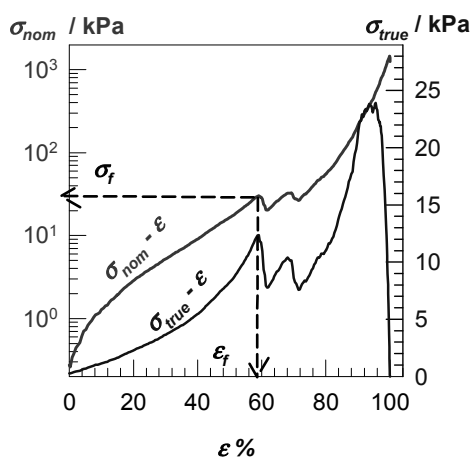


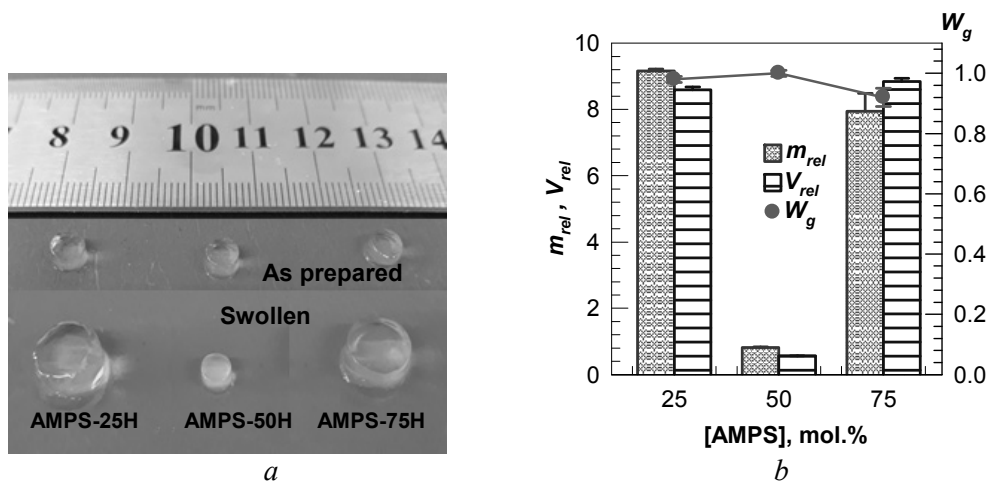
Figure 1. Typical stress-strain curves of under compression where the nominal stress σ_{nom} (red curve) and true stress σ_{true} (blue curve) are plotted against the compressive strain ε . Dashed lines represent calculations of the fracture stress σ_f and fracture strain ε_f from the maximum in the $\sigma_{true}-\varepsilon$ curve

The compression tests were performed at room temperature on Zwick Roell test machine using 500 N load cell. Initial compressive contact to 0.05 N was applied to ensure complete contact between the sample and the surface. Load and displacement data were collected during the experiments at a constant crosshead speed of 3 mm·min⁻¹. Compressive stress was presented by its nominal σ_{nom} and true values σ_{true} , which are the force per cross-sectional area of the undeformed and deformed specimen, respectively. Assuming the sample volume remains constant during deformation, the true stress σ_{true} was calculated as $\sigma_{true} = \lambda\sigma_{nom}$, where λ is the deformation ratio (deformed length/original length). The compressive strain is given by the compression ratio ε which is the change in the sample length relative to its initial length, i.e., $\varepsilon = 1 - \lambda$. Figure 1 shows the typical stress-strain curves of AMPS-50H, where the σ_{nom} and σ_{true} are plotted against the strain ε .

Results and Discussion

Swelling characteristics of QPA hydrogels

Photos of as-prepared and swollen (immersed into water and equilibrated) as well as the relative weight m_{rel} , volume V_{rel} , and gel fraction W_g of QPA hydrogels calculated by formulas 1–3 are shown in Figure 2. As prepared (or initial) hydrogel samples have the same size. After immersing and equilibration in aqueous solution the QPA hydrogels of AMPS-75H and AMPS-25H are transparent and in swollen state, while AMPS-50H is cloudy and in shrunken state. These results are explained by Donnan effect. In case AMPS-25H and AMPS-75H, due to excess of positive and negative charges in hydrogel network the number of osmotically active ions in the hydrogel phase increases leading to swelling of hydrogels. In case of AMPS-50H, the equimolar amount of cationic and anionic charges compensate each other and the excess free counterions (Na⁺ and Cl⁻) that are no more needed to satisfy the electroneutrality of the chains are effectively released from the hydrogel interior.

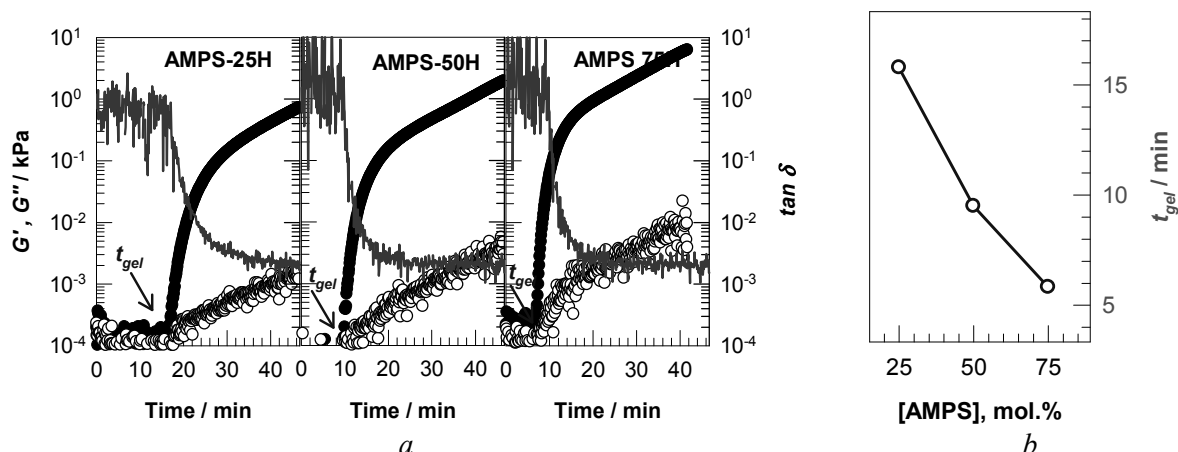


a — Images of as-prepared (top) and swollen (bottom) QPA hydrogels in water;
b — the relative weight m_{rel} (red bars), volume V_{rel} (blue bars), and gel fraction W_g (green symbol) of polyampholyte hydrogels as a function of AMPS in the feed

Figure 2

Gelation

The dynamics of gel formation was monitored by rheometric measurement using the oscillatory deformation tests at an angular frequency ω of 6.3 rad·s⁻¹ and strain amplitude γ_0 of 0.01. Figures 3a, b show the loss G'' and storage modulus G' of the reaction solutions plotted vs the reaction time together with the loss factor $\tan\delta$ (G''/G') of the reaction system. As seen from Figure 3b the gelation time decreases with increasing of AMPS content in reaction mixture. This is probably accounted for higher reactivity of AMPS ($r_{AMPS} = 0.62$) in comparison with APTAC ($r_{APTAC} = 0.36$) that is responsible for decreasing of gelation time [15–17].



a — Storage G' (filled symbols), loss modulus G'' (open symbols) and loss factor $\tan \delta$ (red lines) of the reaction mixture as a function of reaction time. $\omega = 6.3 \text{ rad}\cdot\text{s}^{-1}$. $T = 60 \text{ }^\circ\text{C}$. Blue arrows show the gelation point of the system;
b — Gel points t_{gel} ($\tan \delta = 1$, open symbols) are plotted as a function of AMPS content in reaction mixture.
 Error bars are smaller than the symbols where the bars are not shown

Figure 3

Mechanical and rheological properties

Table represents the mechanical characteristics of QPA hydrogels with different AMPS content. With increasing of AMPS content the mechanical strength (E_c) increases 3 times and fracture stress (σ_f) increases 2 times.

Table

Swelling and compressive mechanical properties of QPA hydrogels. [MBAA] = 20 mol. %, [APS] = 10 mM

Code	m_{rel}	$\text{H}_2\text{O wt.}\%$	W_g	As-prepared gel		Swollen gel	
				E/kPa	σ_f/kPa	E/kPa	σ_f/kPa
AMPS-25H	9.2 ± 0.1	99.4	0.98	5.2 (0.4)	24 (1)	11.2 (0.7)	6.0 (0.8)
AMPS-50H	0.82 ± 0.02	99.5	1.00	12 (1)	30 (2)	23 (2)	147 (12)
AMPS-75H	7.9 ± 0.5	93.8	0.92	19 (4)	55 (3)	33 (1)	27 (3)

Figure 4 shows the results of rheological measurements: storage G' , loss modulus G'' and loss factor $\tan \delta$ of as-prepared QPA hydrogels. It is seen that APMS-75H demonstrates stronger mechanical properties but exhibits the brittleness (lines on the third graph are approximated). These results are in good agreement with the loss factor $\tan \delta$ (G''/G') of the reaction system.

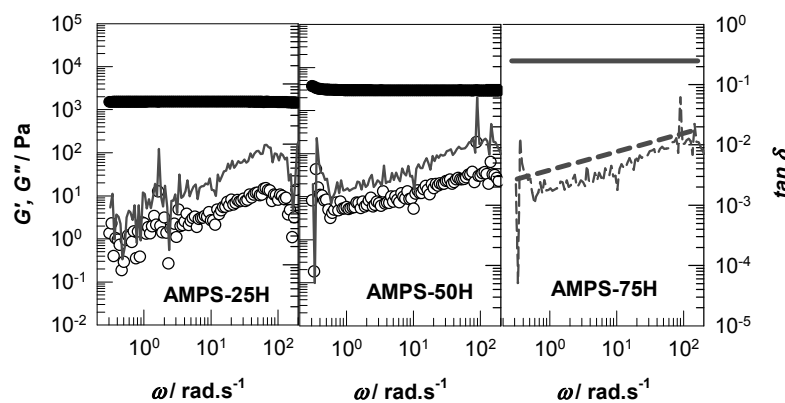
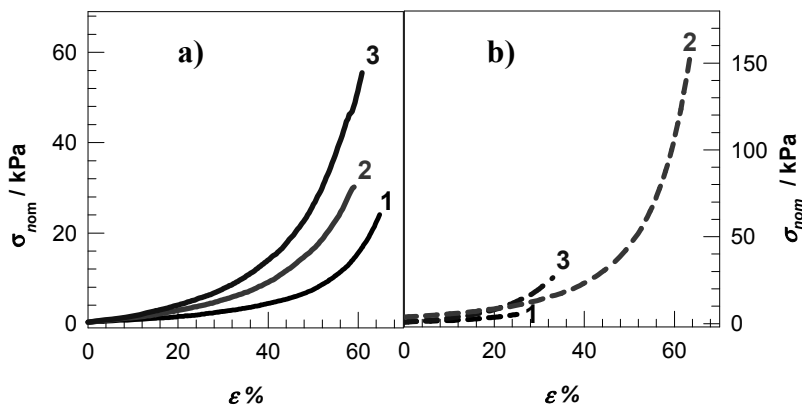


Figure 4. Storage G' (filled symbols), loss modulus G'' (open symbols) and loss factor $\tan \delta$ (red lines) of QPA hydrogels prepared between rheometer plates at $60 \text{ }^\circ\text{C}$ for 1 h at $25 \text{ }^\circ\text{C}$. $\gamma_0 = 0.01$. Hydrogel codes are indicated in the graphs. Note that the green lines are approximated data for AMPS-75H

The corrected strain-stress curves of as-prepared and swollen QPA hydrogels at various AMPS concentrations are shown in Figures 5*a, b*. The Young's modulus E , fracture stress σ_f and fracture strain $\varepsilon\%$ (or elongation) of QPA hydrogels as a function of AMPS content are represented in Figures 6*a, b*. The highest values of Young's modulus E and fracture stress σ_f exhibit as-prepared AMPS-75H sample. However, in swollen state the AMPS-50H shows significantly improved mechanical characteristics. It should be noted that dialysis of as-prepared hydrogel samples in pure water plays the crucial role in enhancing the ionic bond formation whereupon the polymer concentration governs the competition between intra-chain and inter-chain complexation to form a tough hydrogel [11]. In case of equimolar AMPS-50H hydrogel, the formation of intra-ionic contacts between oppositely charged monomers leads to toughening of hydrogel sample (Figs. 5*b* and 6*b*). Compression tests of swollen hydrogel samples are shown in Figure 7.



MBAA = 20 mol.%; $R = 3 \text{ mm} \cdot \text{min}^{-1}$. 1 — AMPS-25H; 2 — AMPS-50H; 3 — AMPS-75H

Figure 5. Compressive stress-strain curves of as-prepared (*a*) and dialyzed (*b*) QPA hydrogels

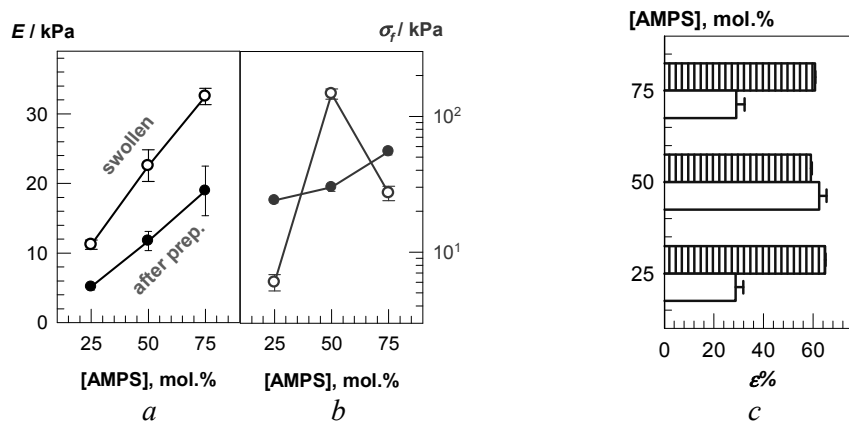


Figure 6. The compressive moduli E_c (*a*), fracture stress σ_f (*b*) and fracture strain $\varepsilon\%$ (*c*) of as-prepared (filled symbols and bars) and swollen QPA hydrogels (open symbols and bars) as a function of AMPS content in the feed

Due to the fact that swollen AMPS-25H contains the excess of cationic monomer — APTAC and absorbs much water in comparison with AMPS-50H hydrogel, the former is mechanically stable while the latter is ruptured under compression. However, the fracture stress (σ_f) of swollen AMPS-50H is 6 times higher than as-prepared state. The elongation (ε) values of as-prepared hydrogels are in the same level (62 ± 2), but for swollen AMPS-50 the value of ε (in %) is much higher than that of AMPS-25H and AMPS-75H (Fig. 6*c*). Thus both the fracture stress (σ_f) and fracture strain (ε) of swollen AMPS-50H are much higher in comparison with swollen AMPS-25H and AMPS-75H (Fig. 6*b, c*). The reasonable explanation of this phenomenon is that the opposite charges within AMPS-50H stabilized by intra- or interionic contacts act as physical crosslinks. Such globular conformation of AMPS-50H is unfolded and extended upon stretching.

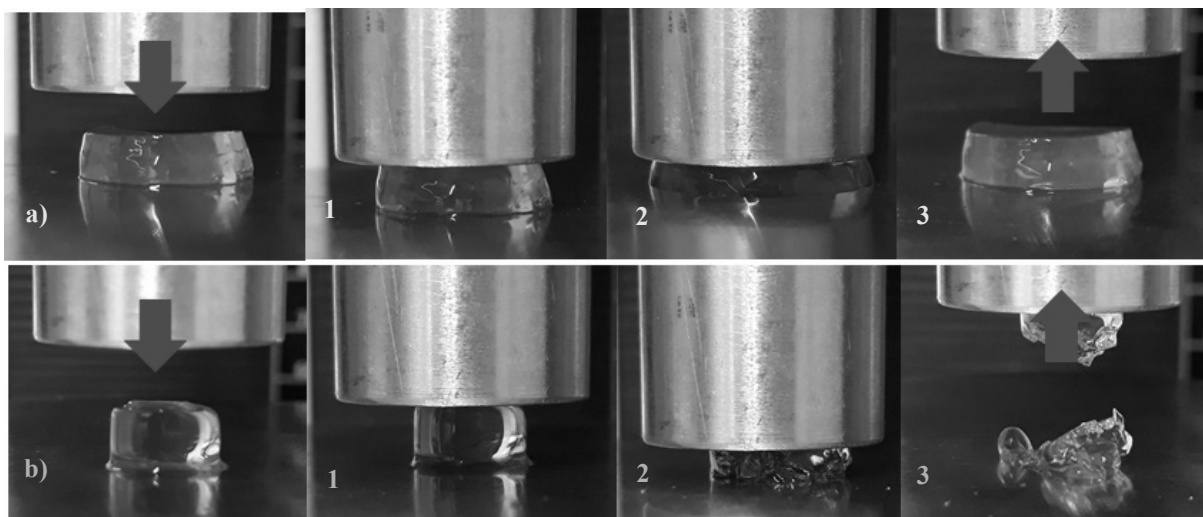


Figure 7. Photographs of swollen AMPS-25H (a) and AMPS-50H (b) hydrogel samples during the compression tests. Images a1–a3 show during uniaxial compression up to a strain ε of 40 %. The images b1–b3 show the rupture of hydrogel specimen upon compression

Our data are in good agreement with results of authors [11] who studied the effect of the charge fraction on the swelling degree, Young's modulus E , elongation ε , and the compressive fracture stress σ_f for QPA hydrogels based on [3-(methacryloylamino)propyl]trimethylammonium chloride-*co*-sodium 4-vinylbenzenesulfonate.

Conclusion

Three samples of quenched (or high-charge-density) polyampholyte hydrogels were prepared from anionic AMPS and cationic APTAC monomers in the presence of MBAA. They were characterized by swelling measurements, rheological experiments, and mechanical tests. The swelling and mechanical properties of as-prepared and equilibrated QPA hydrogels are different due to excess or equal numbers of anionic and cationic monomers. In dependence of composition they behave as polyelectrolyte and polyampholyte hydrogels. The shrinking of the AMPS-50H gels is accompanied by dramatic increase in the fracture stress σ_b and fracture strain ε , %. It is outlined that dialysis of as-prepared hydrogel samples in pure water plays the crucial role in competition between repulsive polyelectrolyte effect for AMPS-25H and AMPS-75H, and attractive polyampholyte effect AMPS-50H due to intra-ionic complexation between oppositely charged monomers. Both the fracture stress (σ_f) and fracture strain ($\varepsilon\%$) of swollen AMPS-50H are much higher than AMPS-25H and AMPS-75H. This is explained by globular structure of AMPS-50H stabilized by ionic bonds between oppositely charged monomers. Upon stretching the globular parts unfold and extend exhibiting improved mechanical properties. Supramolecular QPA prepared by random copolymerization of oppositely charged ionic monomers at relatively high monomers concentration and equimolar monomers ratio represents a new class of hydrogels containing both strong and weak ionic bonds. The former serves as permanent crosslinks to maintain the shape of the gel the latter as sacrificial network is responsible for elongation, deformation, adhesion, self-healing, shape memory, and other important functions.

Acknowledgments

This research was funded by the Ministry of Education and Science of the Republic of Kazakhstan (IRN AP05131003, 2018–2020). E.S. thanks TUBITAK-BIDEB for a Ph.D. scholarship. G.T. thanks Prof. O. Okay from Istanbul Technical University (Turkey) for giving the possibility to perform experiments.

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Г. Төлеутай, Э. Су, С.Е. Кұдайбергенов

Анион мономері акриламид-2-метил-1-пропансульфон қышқылы натрий тұзы (AMPS) және катион мономері 3-акриламидопропил-триметиламмоний хлориді (АРТАС) негізінде жоғары зарядталған полиамфолитті гидрогельдердің механикалық және ісіну қасиеттері

Біздің алдыңғы жұмыста (Қарағанды университетінің хабаршысы. Химия сериясы, 2019, № 2(94), 35–43 бет) біз толық зарядталған анион-мономер акриламид-2-метил-1-пропансульфон қышқылы натрий тұзы (AMPS) және катион мономері 3-акриламидопропил-триметиламмоний хлориді (АРТАС) негізінде полиамфолиттердің су-тұз ерітінділерінде әрекетін қарастырдық. Бұл мақалада N,N-метилден бисакриламидінің (МВАА) байланыстырушы агент ретінде қатысуымен ескерілген мономерлердің еркін радикалды сополимеризациясы арқылы синтезделген жоғары зарядталған полиамфолитті гидрогельдердің механикалық қасиеттері туралы баяндаймыз. AMPS молярлық мөлшеріне байланысты гидрогель үлгілері AMPS-75Н, AMPS-50Н және AMPS-25Н ретінде қысқартылды. Жоғары зарядталған полиамфолитті гидрогельдердің реологиялық және механикалық қасиеттері әртүрлі сополимерлі композициялар үшін тұрақты бастапқы мономер концентрациясы $C_0 = 0,5$ мас.% және тұрақты мөлшері $[МВАА] = 20$ моль% алынды. Қарама-қарсы зарядталған мономерлердің сополимеризациясы кезінде гидрогельдердің түзілуі МВАА қатысуымен $\omega = 6,3$ рад·с⁻¹ және кернеудің амплитудасы $\gamma_0 = 0,01$ болғанда тербелмелі деформация тесттерін қолданып, реометриялық өлшеулер көмегімен бақыланды. Постинтезделген және ісінген полиамфолитикалық гелдерге арналған кернеудің қисық сызықтары синтезделген AMPS-75Н үлгілері сондай-ақ AMPS-50Н ісінген күйінде ең жоғары механикалық қасиеттерін көрсетті. Бұл нәтижелер полиэлектролит пен полиамфолиттің әсері тұрғысынан түсіндіріледі.

Кілт сөздер: күшті зарядталған полиамфолиттер, ісіну, реологиялық және механикалық қасиеттері, кернеу-деформация, Юнг модулі, иондық өзара әрекеттесу.

Г. Толеутай, Э. Су, С.Е. Кудайбергенов

Механические и набухающие свойства сильнозаряженных полиамфолитных гидрогелей на основе анионного мономера 2-акриламид-2-метил-1-пропансульфоновой кислоты (AMPS) и катионного мономера — 3-акриламидопропилтриметиламмоний хлорида (APTAC)

В нашей предыдущей работе (Вестник Карагандинского университета. Сер. Химия, 2019, 2(94), с. 35–43) мы рассмотрели поведение «quenched» (или сильно заряженных) полиамфолитов на основе полностью заряженного анионного мономера — 2-акриламид-2-метил-1-пропансульфоновой кислоты (AMPS) и катионного мономера — 3-акриламидопропилтриметиламмоний хлорида (APTAC) в водно-солевых растворах. В настоящей статье сообщаем о механических свойствах сильно заряженных полиамфолитных гидрогелей, синтезированных путем свободнорадикальной сополимеризации тех же мономеров в присутствии N,N-метиленбисакриламида (МВАА) в качестве сшивающего агента. Образцы гидрогеля в зависимости от молярного количества AMPS были сокращенно обозначены как AMPS-75Н, AMPS-50Н и AMPS-25Н. Реологические и механические свойства сильно заряженных полиамфолитных гидрогелей были оценены для различных составов сополимеров при фиксированной начальной концентрации мономера $C_0 = 0,5$ мас.% и постоянном количестве [МВАА] = 20 мол.%. Образование гидрогелей в ходе сополимеризации противоположно заряженных мономеров в присутствии МВАА контролировали с помощью реометрических измерений с использованием тестов колебательной деформации при угловой частоте $\omega = 6,3$ рад·с⁻¹ и амплитуде деформации $\gamma_0 = 0,01$. Кривые напряжения-деформации для свежесинтезированных и набухших полиамфолитных гелей показывают, что самые высокие значения модуля Юнга E , степень разрушения σ_f и относительного удлинения характерны для синтезированных образцов AMPS-75Н и в набухом состоянии AMPS-50Н. Эти результаты интерпретируются с точки зрения эффектов полиэлектролита и полиамфолита.

Ключевые слова: сильнозаряженные полиамфолиты, набухание, реологические и механические свойства, напряжение-деформация, модуль Юнга, ионные взаимодействия.

Ya.I. Popp¹, T.I. Bokova², Ye.A. Issabayev³

¹*Novosibirsk State University of Architecture and Civil Engineering, Russia;*

²*Novosibirsk State Agricultural University, Russia;*

³*National Center for Expertise of Medicines and Medical Devices, Nur-Sultan, Kazakhstan
(E-mail: y.aspirant@mail.ru)*

**Levels of heavy metals in the «soil – medicinal plants» system
in relation to the geographical location and ecological
and genetic zone of the Irtysh river floodplain**

The article provides the material on the levels of zinc, copper, and cadmium in the «soil-medicinal plants» system in relation to the territorial location and ecological and genetic zonality of the Irtysh river floodplain. The heavy metals (zinc, copper, cadmium) contents of medicinal plants growing in the Irtysh river floodplain (Semey, Ozerki village) were assessed in order to determine the safety of the medicinal plant therapeutic application. Standard procedures for collection, transportation, preparation and storage of soil and plant samples and also for chemical analysis were applied in the study. The contents of all studied chemical elements in the total aggregate of medicinal plants descend as follows: zinc 45.8 mg/kg; copper 6.2 mg/kg; cadmium 0.23 mg/kg. As is evident from the findings (*Glycyrrhiza glabra* (Zn = 17.3 ± 0.79 mg/kg); *Inula helenium* (Cu = 2.3 ± 0.17 mg/kg); *Taraxacum officinale* (Cd = 0.12 ± 0.01 mg/kg)), no average values were found to exceed the maximum permissible limits. This information is certainly essential for selecting sites for harvesting safe herbal raw materials; also, medicinal plants can be considered as indicators of environmental pollution. This determines the rationale for research study in this direction and puts forward a vital task: to strengthen quality control of herbal medicinal raw materials taking into account the content of heavy metals.

Keywords: zinc, copper, cadmium, metals, floodplain soils, medicinal plants, chemical analysis.

Introduction

The prospects for the use of medicinal plants are evaluated by their pharmacological properties and chemical composition. The use of many wild plants can be hampered by their capacity to accumulate toxic elements in their natural vegetation areas. Regional scope of the study of a problem of contamination of herbal raw materials is conditioned by varying geochemical and climatic conditions of territories where the raw materials are harvested [1].

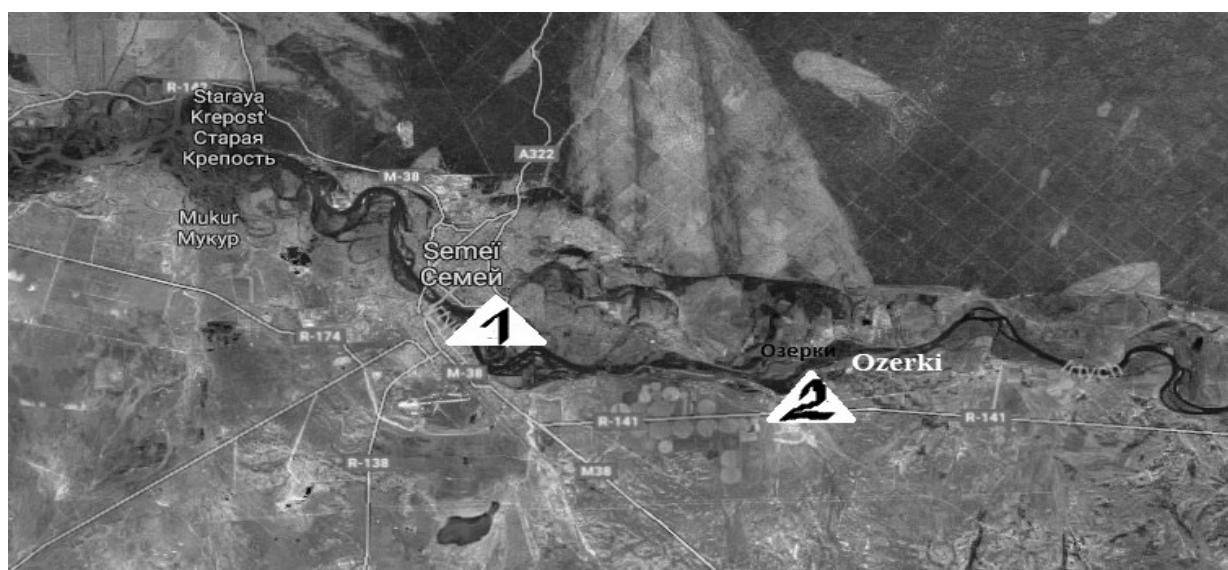
The study of the mineral composition of herbal raw materials has a two-part implication. In one respect, medicinal raw materials contain a rich complex of macro- and microelements and are a valuable source of substances essential for the human body. On the downside, the use of plants that accumulate elements, among which are toxic ones, is a potential threat to human health, as heavy metals are capable of being conveyed along the soil-plant-human continuum.

Both the increasing demand for herbal preparations and worsening environmental pollution require conducting regional research to study the impact of external conditions on the quality of herbal raw materials and to assess its environmental safety.

Scientists who dedicated their works to the study of heavy metal levels in various objects of the environment are: V.I. Vernadsky with his disciple A.P. Vinogradov [2] (20–40-ies of XX century), works of V.V. Kovalsky [3], A.L. Kovalevsky [4], V.B. Ilyin [5], V.V. Dobrovolsky [6]. Many scientists work on solving the problem of reducing the levels of heavy metals and radionuclides in the soil — plant link [7]. A number of scientists are also involved specifically with the problem of heavy metal content of herbal raw materials [8–15].

Experimental

The research was carried out in the period between 2013 and 2016 at the premises of the laboratory of Novosibirsk State Agricultural University. Field studies were conducted on the territory of the East Kazakhstan region in areas with various anthropogenic load; in particular, sampling sites were located in the Irtysh river floodplain — Semey city, the village of Ozerki (Fig. 1).



1 — Semey; 2 — Ozerki

Figure 1. Study areas

19 medicinal plant species belonging to 9 families were targets of research; plants were divided into morphological organs — flowers, leaves, roots, which made a total of over 342 samples; and soil samples were collected along with the plants (study design) (Table 1).

Table 1

Study design

Analytes	Plants/soils investigated	Plant parts investigated	Floodplain locations investigated	Ecological and genetic zones of floodplains	Sampling times	Number of plant and soil samples
Zn Cu Cd	Plants: Valeriana officinalis, Centaurea cyanus, Persicaria hydropiper, Inula helenium, Melilotus officinalis, Trifolium pratense, Urtica dioica, Sanguisorba officinalis, Potentilla erecta, Mentha piperita, Taraxacum officinale, Tanacetum vulgare, Plantago major, Artemisia absinthium, Matricaria chamomilla, Glycyrrhiza glabra, Carum carvi, Cichorium intybus, Bidens tripartita Floodplain soils	inflorescences leaves roots	The Irtysh river floodplain: Semey city vil. Ozerki	channel-adjacent middle terrace-adjacent	during the vegetation period — August–September	342 plant samples (19 plant species × 3 eco-genetic zones × 2 investigated areas of each floodplain × 3 morphological organs = 171 × 2 floodplains) and 27 soil samples (from 3 eco-genetic zones × 2 floodplains)

Plant samples were collected by the average sample technique at the end of the vegetation season (August-September). Samples were washed with running and distilled water and conditioned to air-dry basis. Baitenov's illustrated field guide was used for the identification of plant species [16]. Latin names of medicinal plants are given according to Cherepanov [17].

Soils were collected by mixing 6–8 individual samples to obtain a composite sample. To determine the total heavy metals, the samples were digested by concentrated mineral acid mixture. Mobile forms of heavy metals in soil were also investigated: ion-exchangeable (acetate-ammonium buffer $\text{CH}_3\text{COONH}_4$, pH = 4.8), water-soluble (H_2O), acid-soluble (extraction agent 1 n. HCl).

The photocolometric dithizone assay by Rinkis [18] on the SF-2000 spectrophotometer was used to determine the contents of analytes in soil and plants. Analytical works were carried out at the premises of Novosibirsk State Agricultural University.

The observational material was processed by statistical methods given in Plokhinsky's guidances [19] with the use of Microsoft Excel software.

Results and discussions

The concentration of the element in soil is one of the main factors that determine the chemical element content of plants.

Table 2 provides total contents of heavy metals (Zn, Cu, Cd) in the floodplain soil profile investigated.

Table 2

Total content of heavy metals in soil profile of Irtysh river floodplains, mg/kg

Horzon	Depth, cm	Analytes					
		Zn		Cu		Cd	
Floodplain, chestnut, sod soils, Semey (channel-adjacent)							
A	0–10	67.1	64.7±2(2.8)	22.8	22.4±0.38(0.53)	1.45	1.33±0.12(0.17)
B	10–25	62.4		21.9		1.16	
B-C	25–45	64.7		22.5		1.39	
Floodplain meadow chestnut carbonate soils, Semey (central)							
A	0–20	86.9	77.1±8.9(12.4)	24.3	25.6±2.1(2.9)	1.46	1.55±0.25(0.35)
B ₁	20–40	78.4		23.8		1.30	
B ₂	40–60	66.0		28.7		1.89	
Floodplain meadow chestnut alkaline soils, Semey (terrace-adjacent)							
A	0–30	73.3	69.9±2.6(3.7)	27.8	25.0±2.4(3.4)	1.45	1.52±0.17(0.24)
B	30–50	69.5		25.2		1.35	
B-C	50–70	67.1		22.0		1.75	
Floodplain meadow light-brown stratified soils, Ozerki vill. (channel-adjacent)							
A	0–10	61.3	58.4±2.6(3.6)	16.4	15.3±0.76(1.07)	1.40	1.28±0.12(0.17)
B	10–25	55.2		14.6		1.11	
B-C	25–45	58.7		15.0		1.33	
Floodplain meadow light-brown middle loamy soils, Ozerki vill. (channel-adjacent)							
A	0–20	83.5	71.5±10.3(14.4)	20.3	19.6±2.1(2.9)	1.39	1.49±0.26(0.36)
B ₁	20–40	71.8		16.9		1.23	
B ₂	40–60	59.1		21.7		1.84	
Floodplain meadow light-brown saline, Ozerki vill. (terrace-adjacent)							
A	0–30	65.7	62.9±2.1(2.9)	21.6	19.1±2.3(3.2)	1.40	1.46±0.17(0.24)
B	30–50	62.3		19.5		1.29	
B-C	50–70	60.8		16.2		1.69	

Note. Arithmetic mean and its error (mg/kg); in brackets — standard deviations (mg/kg).

Elevated levels of zinc (77.1 mg/kg) and cadmium (1.55 mg/kg) were observed in the central zone of floodplain within Semey city; however, concentrations of copper in the central zone (25.6 mg/kg) and terrace-adjacent zone (25.0 g/kg) within Semey city were virtually equal.

Low levels of zinc (62.9 mg/kg) in the terrace-adjacent zone of vill. Ozerki, copper (15.3 mg/kg) and cadmium (1.28 mg/kg) in the channel-adjacent zone of vill. Ozerki were observed.

No regular patterns of distribution in soil profile of the investigated analytes (Zn, Cu, Cd) were found. There is accumulation in both upper and lower horizons. This distribution in the soil profile is probably due to different types of soils and different anthropogenic load on the soil cover of the investigated areas of the Irtysh floodplain.

In the soils of the channel-adjacent zone of the floodplain, the accumulation of the investigated analytes is significantly less prominent due to the light mechanical makeup, lower humus content and deep ground-water layer. Soils of the central and terrace-adjacent areas of the floodplain, that are characterized by more complex structure of the soil profile, heavy mechanical makeup, water regime of which is determined by not only surface but also ground waters, feature higher contents of the elements [20]. Table 3 provides the variation and statistical indicators of the total content of chemical elements in the aggregate in soils of the Irtysh river floodplain.

Table 3

Variation and statistical indicators of total heavy metal content in the aggregate in the soils of the Irtysh river floodplain, mg/kg

Analyte	n	Horizon			Average value in the profile depth	Clarke in the lithosphere [6]	Clarke in soil [6]
		A	B	C			
Zn	27	72.9±3.22(13.2)	66.6±2.55(11.5)	62.8±0.99(4.71)	67.4±2.25(9.80)	83	50
		9.65; 61.3–86.9	7.66; 55.2–78.4	2.96; 58.7–67.1	6.76; 55.2–86.9		
Cu	27	22.3±1.08(14.5)	20.4±1.18(17.4)	20.9±1.39(19.9)	21.2±1.22(17.3)	47	20
		3.24; 16.4–27.8	3.54; 14.6–25.2	4.16; 15.0–28.7	3.65; 14.6–28.7		
Cd	27	1.43±0.008(1.68)	1.24±0.03(7.26)	1.65±0.09(16.4)	1.44±0.04(8.45)	0.13	0.5
		0.024; 1.39–1.46	0.09; 1.11–1.35	0.27; 1.33–1.89	0.13; 1.11–1.89		

Note. In the numerator — arithmetic mean and its error (mg/kg); in brackets — coefficient of variation (%); in the denominator — standard deviations (mg/kg); and variation limits (mg/kg); clarke (%); $n = 27$.

As is evident from the data, the highest content of the element (mg/kg) in horizon A is typical for Zn (72.9), Cu (22.3); for Cd (1.65) — it is in horizon C. The lowest content (mg/kg) of Zn (62.8) falls on horizon C, Cu (20.4) and Cd (1.24) — on horizon B.

In terms of the total content in the humus horizon of floodplain soils, the following geochemical rank (mg/kg) is typical for the investigated elements: Zn (72.9) > Cu (22.3) > Cd (1.43).

According to GOST 25593–88, the term «mobility» is defined as the element capability to shift from the solid phase of the soil to the soil solution [21]. Table 4 provides data on the content of mobile forms of heavy metal compounds in the soils of the Irtysh river floodplain.

Table 4

Content of mobile forms of chemical elements compounds in soils of Irtysh river floodplain, mg/kg

Soils	Compound forms	Zn	Cu	Cd
1	2	3	4	5
Floodplain, chestnut, sod soils, Semey (channel-adjacent)	water-soluble	0.1±0.03(0.05)	0.14±0.07(0.11)	0.04±0.01(0.02)
	exchangeable	0.26±0.03(0.05)	1.1±0.2(0.29)	0.08±0.03(0.05)
	acid-soluble	0.54±0.11(0.16)	2.9±1.3(1.83)	0.56±0.15(0.21)
Floodplain meadow chestnut carbonate soils, Semey (central)	water-soluble	0.06±0.03(0.05)	0.28±0.07(0.11)	0.08±0.01(0.02)
	exchangeable	0.35±0.03(0.05)	1.5±0.2(0.29)	0.16±0.03(0.05)
	acid-soluble	0.72±0.11(0.16)	6.0±1.3(1.83)	0.47±0.15(0.21)
Floodplain meadow chestnut alkaline soils, Semey (terrace-adjacent)	water-soluble	0.15±0.03(0.05)	0.33±0.07(0.11)	0.09±0.01(0.02)
	exchangeable	0.34±0.03(0.05)	1.6±0.2(0.29)	0.07±0.03(0.05)
	acid-soluble	0.44±0.11(0.16)	5.5±1.3(1.83)	0.84±0.15(0.21)
Floodplain meadow light-brown stratified soils, Ozerki vill. (channel-adjacent)	water-soluble	0.03±0.07(0.1)	0.28±0.07(0.11)	0.02±0.003(0.005)
	exchangeable	0.14±0.04(0.06)	1.6±0.33(0.47)	0.22±0.1(0.14)
	acid-soluble	0.3±0.05(0.08)	5.5±0.88(1.24)	0.48±0.12(0.17)
Floodplain meadow light-brown middle loamy soils, Ozerki vill. (channel-adjacent)	water-soluble	0.04±0.07(0.1)	0.1±0.07(0.11)	0.02±0.003(0.005)
	exchangeable	0.18±0.04(0.06)	1.3±0.33(0.47)	0.37±0.1(0.14)
	acid-soluble	0.21±0.05(0.08)	4.8±0.88(1.24)	0.41±0.12(0.17)

Continuation of Table 4

1	2	3	4	5
Floodplain meadow light-brown saline, Ozerki vill. (terrace-adjacent)	water-soluble	0.2±0.07(0.1)	0.09±0.07(0.11)	0.01±0.003(0.005)
	exchangeable	0.25±0.04(0.06)	0.8±0.33(0.47)	0.47±0.1(0.14)
	acid-soluble	0.35±0.05(0.08)	3.4±0.88(1.24)	0.19±0.12(0.17)

Note. Arithmetic mean and its error (mg/kg); in brackets — standard deviations (mg/kg).

A geochemical sequence by the content of water-soluble form of the elements is established: $Cu_{0.29} > Zn_{0.16} > Cd_{0.06}$.

By the exchangeable form content of elements, the investigated soils showed similar properties. The following geochemical sequence was established: $Cu_{1.4} > Zn_{0.33} > Cd_{0.16}$.

A geochemical sequence was derived by the content of heavy metals in the acid-soluble form for the investigated types of the floodplain soils: $Cu_{4.2} > Zn_{0.66} > Cd_{0.54}$.

In terms of the average concentration, heavy metals and their compound forms investigated are ranked in the following descending order: acid-soluble form > exchangeable form > water-soluble form.

The largest mobile portion of the elements is the acid-soluble fraction, followed by the exchangeable fraction, and then the water-soluble fraction.

The revealed wide range of variations for the investigated elements in all compound forms in the soil and narrow range of variations in the total content of the elements are explained by the fact that the total level of the elements is determined by the granulometric and mineralogical composition of parent rocks; the extent of mobile elements is affected, in addition to the content of organic matter in the soil, by the soil solution reaction, oxidation-reduction processes, and the physicochemical properties of the soil [20]. Table 5 provides data on the average contents of elements in the soil in comparison with their MPCs.

Table 5

Chemical element content in soils of Irtysh river floodplain versus MPC, mg/kg

Analyte	Content, mg/kg	MPC, mg/kg	MPC, mg/kg [22]
Zn	67.4±2.25	100	55.5
Cu	21.2±1.22	100	33.0
Cd	1.4±0.04	3	1.0

Also, the content of heavy metals in medicinal plants depends upon the conditions of their growth.

The peculiarities of heavy metal accumulation in different areas of the Irtysh river floodplains were investigated: Semey city; Ozerki village (Table 6).

Table 6

Heavy metal content of medicinal plants in different areas of the Irtysh river floodplain, mg/kg

Area of the Irtysh river floodplain	Analyte		
	Zn	Cu	Cd
Semey city	<u>47.8±3.8</u>	<u>5.8±0.45</u>	<u>0.20±0.01</u>
	16.0 (18.6–77.7)	1.87 (2.6–9.5)	0.05 (0.14–0.31)
vil. Ozerki	<u>43.1±3.8</u>	<u>5.3±0.45</u>	<u>0.16±0.01</u>
	15.8 (15.6–73.9)	1.87 (2–8.9)	0.05 (0.1–0.27)

Note: in the numerator — arithmetic mean and its error (mg/kg); in the denominator — standard deviations (mg/kg); and variation limits (mg/kg).

According to the findings, the highest concentrations of the investigated chemical elements are observed in Semey city, the lowest ones — in the village of Ozerki. This may be due to different levels of anthropogenic load in the investigated areas, namely, the activity of the industrial facilities and transport.

Depending on the proximity to the river channel, the territory of the river floodplain is divided into three ecological and genetic zones (parts) (by R. Williams): channel-adjacent, central and terrace-adjacent.

Peculiarities of heavy metal accumulation in medicinal plants growing within these ecological and genetic zones were studied. The regularities in the HM distribution in the same species of plants depending on their zone of growth are presented in Table 7.

Table 7

Distribution of heavy metals in plants by different ecological and genetic zones of the Irtysh floodplain, mg/kg

Ecological and genetic zones	Zn		Cu		Cd	
Semey city						
Channel-adjacent	45.3	47.7±3.8	5.6	5.8±0.45	0.18	0.20±0.01
Central	50.4		6.2		0.23	
Terrace-adjacent	47.5		5.8		0.20	
vil. Ozerki						
Channel-adjacent	41.3	43.1±3.8	5.0	5.3±0.45	0.14	0.16±0.01
Central	45.0		5.5		0.18	
Terrace-adjacent	43.1		5.3		0.16	

As can be seen from the Table 8, all floodplain areas investigated are characterized by the lowest accumulation of elements in the channel-adjacent zone. No pronounced pattern of the analyte distribution was found in the central and terrace-adjacent zones: Semey city: central > terrace-adjacent ≥ channel-adjacent; vill. Ozerki: central ≥ terrace-adjacent ≥ channel-adjacent.

Table 8

Average levels of heavy metals in vegetation, mg/kg

Analyte	Findings	Rest of the world	Summarized research data
Zn	45.3±3.8	31	33.1
Cu	5.6±0.43	5.9	8.6
Cd	0.18±0.01	0.21	–

According to A. Kloke (Kloke, 1980), MPC of Cd in plants = 1 mg/kg. Comparing the data on Cd content in floodplain plants with the data by A. Kloke, it can be concluded that the investigated plant species accumulate Cd to lower values than the MPC value.

The findings were multiple times read over at conferences and workshops of various levels and also were published in printed publications, including four publications of the State Commission for Academic Degrees and Titles of the Russian Federation [23].

Conclusions

None of the element contents in the soil exceed the MPC comparing with the data by A. Kloke [24]; comparing with the MPC (for Kazakhstan), the Cu content does not exceed the maximum permissible limit, and the Zn content in the soil exceeds the MPC by 1.2 times, Cd by 1.4 times.

Comparing the data obtained on the heavy metal content in plants of different areas of the Irtysh river floodplain with their levels in the vegetation of different regions and countries of the world, it can be concluded that a higher content of zinc (45.3 mg/kg) and a lower content of copper (5.6 mg/kg) and cadmium (0.18 mg/kg) is characteristic for medicinal plants of the Irtysh river floodplain.

There is a rather complex relationship between the content of heavy metals in plants and their concentration in soil, which exerts differently for each chemical element in different systematic groups of plants and their morphological organs. On that premise, it seems appropriate to conduct further research in this direction, thereby expanding the areal of research.

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Я.И. Попп, Т.И. Бокова, Е.А. Исабаев

Ертіс өзенінің аумақтық орналасуына және экологиялық-генетикалық аймағына байланысты «топырақ – дәрілік өсімдіктер» жүйесіндегі ауыр металдардың мөлшері

Мақалада Ертіс өзенінің алқабының аумақтық орналасуына және экологиялық-генетикалық аймағына байланысты «топырақ – дәрілік өсімдіктер» жүйесіндегі мырыш, мыс, кадмий деңгейлері туралы материал қарастырылған. Дәрілік өсімдіктерді емдік мақсаттарда пайдаланудың қауіпсіздігін анықтау үшін Ертіс су алқабында (Семей, Озерка ауылы) өсетін дәрілік өсімдіктердегі ауыр металдардың (мырыш, мыс, кадмий) деңгейі зерттелді. Топырақ пен өсімдік үлгілерін іріктеу, тасымалдау, дайындау және сақтау үшін, сондай-ақ химиялық талдау үшін стандартты әдістер қолданылды. Дәрілік өсімдіктердің жалпы санындағы барлық зерттелген химиялық элементтердің мазмұны мынадай тәртіппен төмендейді: мырыш үшін 45,8 мг/кг; мыс 6,2 мг/кг; кадмий 0,23 мг/кг. Алынған мәліметтерге сәйкес (*Glycyrrhiza glabra* (Zn = 17,3 ± 0,79 мг/кг); *Inula helenium* (Cu = 2,3 ± 0,17 мг/кг); *Taraxacum officinale* (Cd = 0,12 ± 0,01 мг/кг)) рұқсат етілген концентрацияның орташа мәндер бойынша асып кетуі анықталмады. Бұл ақпараттың қауіпсіз өсімдік шикізатын дайындауға арналған орындарды таңдау үшін маңызы зор, сондай-ақ дәрілік өсімдіктерді қоршаған табиғи ортаның ластану көрсеткіштері ретінде қарастыруға болады. Бұл осы бағыттағы зерттеулердің орындылығын

айқындайды және ауыр металдардың мазмұнын есепке ала отырып, дәрілік өсімдік шикізатының сапасын бақылауды арттыру қажетігі туралы өзекті мәселені тудырады.

Кілт сөздер: мырыш, мыс, кадмий, металдар, тасты топырақ, дәрілік өсімдіктер, химиялық талдау.

Я.И. Попп, Т.И. Бокова, Е.А. Исабаев

Содержание тяжелых металлов в системе «почва – лекарственные растения» в зависимости от территориальной расположенности и эколого-генетической зоны поймы реки Иртыш

В статье изложен материал по уровням содержания цинка, меди, кадмия в системе «почва – лекарственные растения» в зависимости от территориальной расположенности и эколого-генетической зональности поймы реки Иртыш. Для выявления безопасности использования лекарственных растений в лечебных целях исследованы уровни содержания тяжелых металлов (цинка, меди, кадмия) в лекарственных растениях, произрастающих в пойме реки Иртыш (г. Семей, с. Озёрки). При отборе, транспортировке, подготовке и хранении почвенных и растительных образцов для исследования, а также для проведения химического анализа использовались стандартные методики. Содержание всех изученных химических элементов в общей совокупности лекарственных растений убывает в следующем порядке: для цинка 45,8 мг/кг; меди 6,2 мг/кг; кадмия 0,23 мг/кг. По полученным данным (*Glycyrrhiza glabra* (Zn = 17,3 ± 0,79 мг/кг); *Inula helenium* (Cu = 2,3 ± 0,17 мг/кг); *Taraxacum officinale* (Cd = 0,12 ± 0,01 мг/кг)) превышения предельно допустимых концентраций по средним значениям не выявлено. Эти сведения, несомненно, имеют важное значение для выбора мест заготовки безопасного растительного сырья, также лекарственные растения можно рассматривать как индикаторы загрязнения окружающей природной среды. Это определяет целесообразность исследований в данном направлении и выдвигает актуальную задачу: увеличить контроль качества растительного лекарственного сырья с учётом содержания тяжёлых металлов.

Ключевые слова: цинк, медь, кадмий, металлы, пойменные почвы, лекарственные растения, химический анализ.

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G.K. Shambilova¹, I.V. Gumennyi², V.A. Govorov²,
A.Ya. Malkin², V.E. Makhatova¹, M.Zh. Naukenov³

¹*Kh. Dosmukhamedov Atyrau State University, Kazakhstan;*

²*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia;*

³*«Atyrau oil refinery» LLP, Kazakhstan*

(E-mail: shambilova_gulba@mail.ru)

Polysulfone as a material for advanced electrical batteries

The materials based on polysulphone are used for polymer electrolyte production. The rheological properties were measured for three component system polysulphone – solvent – propylene carbonate. The varying factor was propylene carbonate used as a plasticizer for polysulphone. Experiments were carried out in a wide shear rate and frequency ranges at 25 °C. Polymer was characterized by the IR-spectral method. Rheological experiments were carried out using the technique of rotational rheometry. It was shown that the rheological behavior of all samples is linear and these three-component systems are viscoelastic liquids. It can be assumed that all systems under study are homogeneous in the absence of traces of water. The final goal of the study was the choice of the optimal composition (concentrations of a solvent and plasticizer) and the regime of preparing thin films from these systems which could provide obtaining solid state electrolyte for creating advanced electrical accumulator with a none-fragile polysulfone membrane. This part of the research is devoted to investigation of the rheological properties (viscosity and viscoelastic properties of composition of polysulfone – solvent – propylene carbonate systems).

Keywords: polysulfone, polymer solutions, plasticizer, viscosity, viscoelastic properties, solid-state electrolyte, thin-film membrane.

Introduction

Secondary sources of electrical energy are widely spread and used in the modern world. Nowadays, the basic element of such a kind is a lithium-ionic accumulator which is almost exclusively used in portable electronics as well as it is a perspective power supply for electric transport. Advantages of lithium-ionic accumulator are high store energy density, absence of a memory effect, and long term exploitation [1, 2]. Meanwhile, their essential defect is using liquid electrolytes. Thus does not allow for decreasing size of a power source to a film of several microns, impossibility to create flexible battery and provide necessary safety. Therefore, today we meet an increasing number of publications and research aimed to using a solid electrolyte/separator [3, 4].

The general way for building thin-film battery is creating a polymeric matrix which is acting of electrolyte and separator and this construction determines the mechanical properties of a battery in whole providing the formation of a stable 3D structure [5].

One of the most perspective polymers which can be used for these purposes is polysulfone. This term is common for the entire class of sulfo-group contacting compounds. A polymeric chain of these polymers contains para-aromatic groups bonded by esters and sulfonic group [6]. As a rule polysulfone is a rigid-chain amorphous polymer with relatively low molecular weight [7]. This is an engineering plastic with high mechanical performance in different modes of deformations (bending, extension, torsion) and high temperature stability (till 150–170 ± °C). For this polymer, high chemical stability (in the pH range from 1 to 13), good resistance to oxidation [8]. In the same time this polymer can be dissolved in many aprotic solvents such as dimethylacetamide and methylpyrrolidone. However there are serious difficulties in preparing polysulfone films because they appear brittle and do not resist to deformations perpendicular to the film plate.

All these reasoning were the cause for this study. It was proposed to plasticizer polysulfone by using propylene carbonate as a plasticizer. It was presumed that this liquid will occupy free volume in the polymer bulk when the solvent from the polysulfone solution will be completely deleted.

This part of the research work is devoted to investigation of the rheological properties (viscosity and viscoelastic properties of polysulfone – solvent – propylene carbonate systems).

Experimental

Objects. A sample of granulated polysulfone sample (produced under working conditions using the facility of the Institute of Plastics (Moscow), PSF-150 grade according to the manufacturer's standard) was used. N-Methylpyrrolidone purchased from LLC Ruskhim was used as the solvent. Solvent contained 0.1 % of water (determined by the Fischer method). Propylene carbonate was bought from Chemical Ltd. The mass part of water was less than 0.05 % (determined by the Fischer method).

Methods. Chemical structure of the polymer was confirmed by the Fourier IR spectroscopy using the IFS-66 v/s instrument (Bruker, Germany) — scan-30, resolution of 2 cm^{-1} , range of $0\text{--}4000\text{ cm}^{-1}$.

Three component solutions were obtained in two stages. At first stage, a plasticizer was added to a given quantity of a solvent. The mixture was placed into an ultrasonic bath for 10 min. At the second stage, the polymer was introduced into the beforehand mixture and a sample stirred in a mechanical stirrer during 7 hours at a speed of 800 RPM under permanent heating at $100\text{ }^{\circ}\text{C}$. Samples with constant polymer – solvent ratio was used and the quantity of plasticizer varied from 10 to 60 % in relation to the polymer mass.

Rheological properties of all highly concentrated systems were measured on a rotation rheometer Kinexus Pro (MalvernPananalytical). Temperature was regulated using the Peltier element with thermal stabilization of the measuring system with an active cover. The latter allowed us to prevent heat loss and minimize temperature gradients inside a sample.

The procedure of measuring has been carried out using the cone-and-plate and plate-and-plate working units. The angle between the cone and the plate was 1° ; the cone diameter was 40 mm. When the plate-and-plate system was used, the diameter of the user plate was 20 mm. All experimental data were obtained at $25\text{ }^{\circ}\text{C}$. The range of the given shear rate in measuring the apparent viscosity was from 0.01 to 100 s^{-1} . The number of points in scanning was 10.

In the amplitude test at measuring viscoelastic parameters of the samples, the amplitude of strain was varied from 0.01 % to 30 % at the frequency of 1 Hz.

In measuring frequency dependencies of the components of the dynamic modulus, the frequency varied from 0.01 to 50 Hz.

Results and Discussion

Figure 1 shows the IR spectrum of the used polysulfone sample. The aim of this test was to determine the exact molecular structure of the used polymer from great variety of possible polysulfones. As is seen, the obtained spectrum demonstrates the presence of *n*-substituted phenyl rings ($690\text{--}850\text{ cm}^{-1}$ band) corresponding to non-plane stretching vibrations C=C–H group, vibrations of C=C groups (1489 and 1585 cm^{-1} bands), and C–H stretching vibrations (3060 cm^{-1} band). $1000\text{--}1050\text{ cm}^{-1}$ band corresponds to isopropylidene group, $1360\text{--}1420\text{ cm}^{-1}$ band to C–C group, $2770\text{--}2840\text{ cm}^{-1}$ to methyl groups, bands in the range 1150 и 1330 cm^{-1} are responsible to sulfone groups < bands of 1242 и 1103 cm^{-1} are related to Ph–O–Ph bonds and angles.

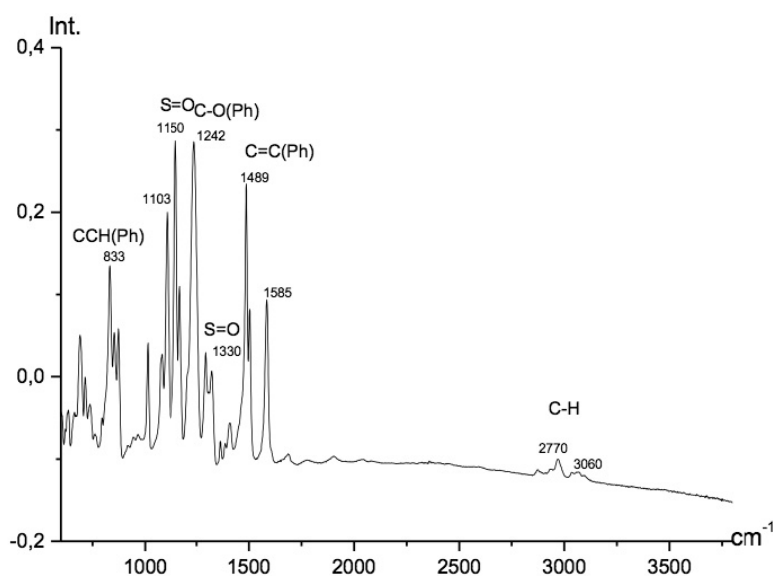


Figure 1. IR-spectrum of polysulfone sample used in the work

So, the analysis of the IR-spectrum and comparison with the database shows that our sample is identical to *p*-phenylsulfone.

The main problem in preparing polysulfone thin films is inherently connected with the pre-history of their solvation. Therefore just the rheology of polymer solutions can give answers and prompt the optimal protocol for obtaining films with necessary characteristics because the structure of solid polymer in a film is created in a previous solution.

Figure 2 shows the dependencies of the apparent viscosity on shear rate for a series of plasticized solutions. The viscosity of the initial sample (without of a plasticizer) is 40 Pa·s. This solution demonstrates the Newtonian type of the rheological behavior. The same remains true for all plasticizer solutions.

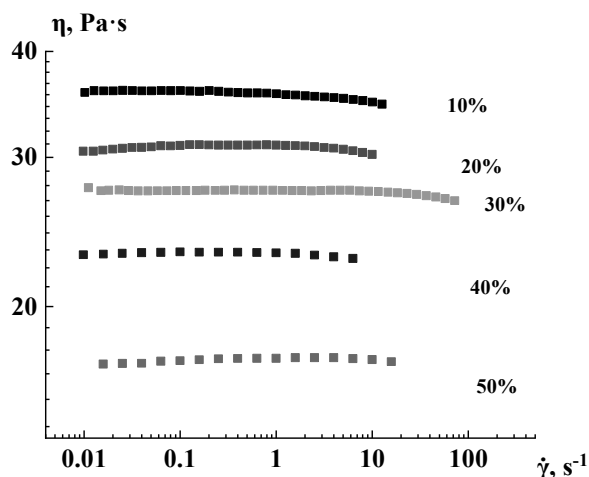


Figure 2. Dependencies of the apparent viscosity on shear rate for samples with different concentration of the plasticizer

So, there is a three — component system. This (Newtonian) character of the flow can be presumably, explained by a rather low concentration of the polymer in the composition. Indeed, the share of a plasticizer in the composition in whole varies from 3 % to 15 %. It corresponds to an increase of the total content of low-molecular weights liquids from 67 % to 71 %, i.e. it leads to dilution of a solvent. In this case, presumably, a system remains homogeneous and the decrease of the polymer concentration results to a decrease in the viscosity. Actually the viscosity of a system decreases as seen from Figure 2. This is also clearly seen in Figure 3 where the dependence of the viscosity of three-components solutions on the plasticizer concentration is presented.

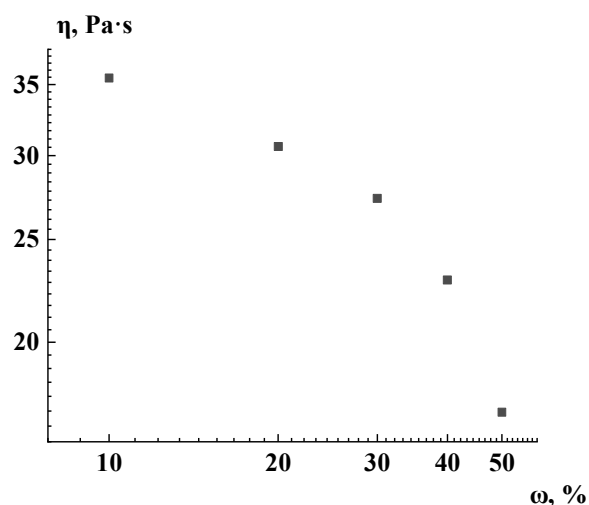


Figure 3. Dependence of the viscosity of three-components systems on the concentration of the plasticizer

The results of measuring viscoelastic properties of the systems under study are presented in Figures 4 and 5.

Amplitude dependencies of the components of the complex elastic modulus are shown in Figure 4 for a single frequency of 1 Hz. One can see that the viscoelastic response remains linear in a rather wide amplitude range. It confirmed that the structure of all these systems is rather stable. In particularly it means that the results of measuring frequency dependencies of the elastic modulus are really relate to the linear domain of the viscoelastic behavior of solutions. These results are shown in Figure 5.

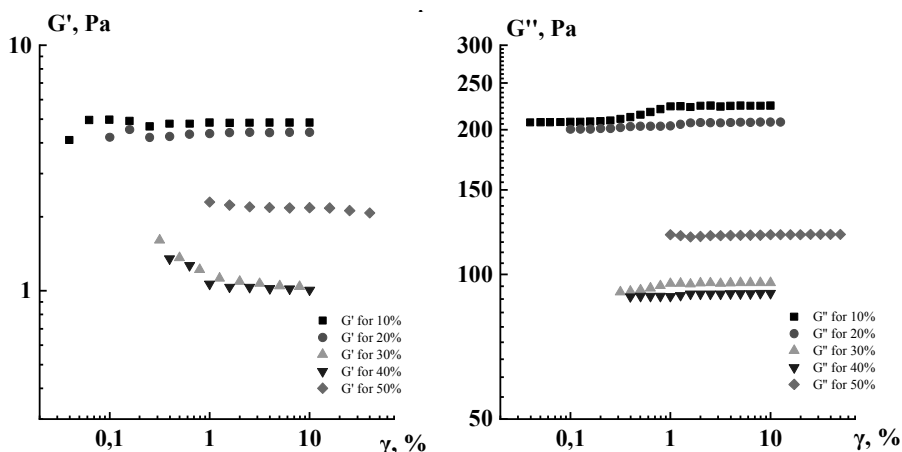


Figure 4. Amplitude test for the storage modulus (a) and the loss modulus (b) made mod different concentration of the plastisizer ($f = 1$ Hz)

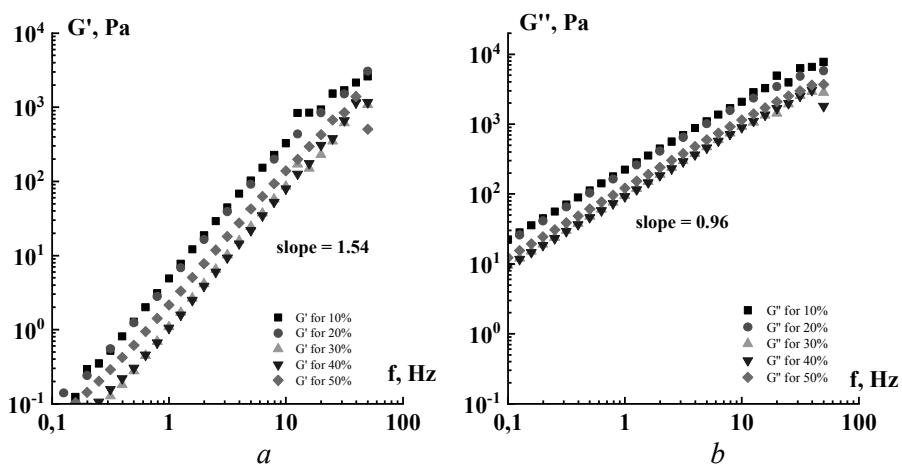


Figure 5. Frequency dependencies of the component of the dynamic modulus: the storage modulus (a) and the loss modulus (b) for systems with different concentration of the plasticizer

For all compositions, experimental data show that $G'' \gg G'$, i.e. liquid component dominates and all compositions are elastic fluids. The slope of the storage modulus is 1.54 that is much lower than the value corresponding to the Maxwell singly-relaxation-time model. So, it is necessary to assume that relaxation spectra of solutions are rather wide. This is related to the presence of polymeric chains with their inherent segmental movement because polysulfone macromolecules are rather semi-rigid than rigid.

Experimental curves are placed rather systematically with exclusion of the most concentrated (50 %) solution. It is reasonable to suspect that this is a limit of solubility of polysulfone. Similar results have been obtained for a two-component polysulfone solutions in our previous publication [9].

Conclusion

The results of the rheological study of complex tree-component solution (polysulfone, solvent, plasticizer) have been presented. These results include data on the apparent viscosity and viscoelastic properties in

a wide concentration range. These data are important for the choice of the optimal composition and regime of preparing thin-film solid membrane and solid electrolyte for advanced electrical accumulators.

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Г.К. Шамбилова, И.В. Гуменный, В.А. Говоров,
А.Я. Малкин, В.Е. Махатова, М.Ж. Наукенов

Заманауи электр аккумуляторлары үшін полисульфонды қолдану туралы

Полимерлі электролиттер мен сепараторды жасау үшін полисульфон негізіндегі материалдар қолданылды. Полисульфон негізіндегі үшкомпонентті жүйелер үшін реологиялық сипаттамалары (көрінуші тұтқырлықтың ығысу жылдамдығынан тәуелділігі, тұтқырсерпімді кешен модулінің амплитудалық және жиеліктік тәуелділігі) зерттелді. Бастапқы жүйе N-метилпирролидондағы полимердің ерітіндісі. Пластификатор ретінде пропиленкарбонат қолданылды, жұмыста ерітінділердің реологиялық қасиеттерінің пластификатор концентрациясына тәуелділігі зерттелді. Эксперименттер 25 °C температурада, жылдамдықтар мен жылжу жиіліктерінің кең ауқымында жүргізілді. Бастапқы полимер ИҚ-спектроскопия әдісімен сипатталды. Реологиялық эксперименттер ротациялық реометрия техникасын пайдалану арқылы жүргізілді. Барлық зерттелген үлгілер үшін жылжу жылдамдығына тұтқырлықтың тәуелділігі ньютондық болып және мұндай үш компонентті жүйелер тұтқыр-шенбер сұйықтықтар болып табылатыны көрсетілді. Зерттелген үлгілердің реологиялық сипаттамалары сызықтық және мұндай үш компонентті жүйелер тұтқырсерпімді сұйықтықтар болып табылатыны көрсетілді. Барлық зерттелетін жүйелерді су іздері болмаған кезде біртектес деп болжауға болады. Зерттеудің соңғы мақсаты оңтайлы құрамды материал (еріткіштің және пластификатордың концентрациясы) және осы жүйелерден жұқа пленкаларды дайындау режимін таңдау болды, олар электролит пен сепаратор рөлінде қолдануға жарамды, икемді полисульфон мембранамен жетілдірілген электр аккумуляторын жасау үшін қатты электролит алуды қамтамасыз ете алады. Бұл жұмыс полисульфон – еріткіш – пропиленкарбонат жүйелерінің тұтқырлығы мен тұтқырсерпімділігі сияқты реологиялық қасиеттерін және олардың ерітінділердің құрамы мен құрылымына тәуелділігін зерттеуге арналған.

Кілт сөздер: полисульфон, полимерлі ерітінділер, пластификатор, тұтқырлық, тұтқырсерпімділік қасиеттері, қатты электролит, жұқа пленкалы мембрана.

Г.К. Шамбилова, И.В. Гуменный, В.А. Говоров,
А.Я. Малкин, В.Е. Махатова, М.Ж. Наукенов

Полисульфон как материал для современных электрических аккумуляторов

Материалы на основе полисульфона используются как основа для создания полимерных электролитов и сепараторов. Реологические свойства (зависимость кажущейся вязкости от скорости сдвига, а также амплитудные и частотные зависимости компонента модуля вязкоупругого комплекса) были измерены для трехкомпонентных систем на основе полисульфона. Исходная система — это раствор полимера в N-метилпирролидоне. В качестве пластификатора применен пропиленкарбонат, в работе изучена зависимость реологических свойств растворов от концентрации пластификатора. Эксперименты прово-

дилься в широком диапазоне скоростей и частот сдвига при 25 °С. Исходный полимер характеризовали методом ИК-спектроскопии. Реологические эксперименты проводились с использованием техники ротационной реометрии. Было показано, что зависимость вязкости от скорости сдвига для всех исследованных образцов является ньютоновской, и такие трехкомпонентные системы являются вязкоупругими жидкостями. Можно предположить, что все исследуемые системы однородны при отсутствии следов воды. Конечной целью исследования был выбор оптимального состава (концентрации растворителя и пластификатора) и режима приготовления тонких пленок из этих систем, которые могли бы обеспечить получение твердого электролита для создания усовершенствованного электрического аккумулятора с гибкой полисульфоновой мембраной, выступающей в роли электролита и сепаратора. Данная работа посвящена исследованию реологических свойств, таких как вязкость и вязкоупругие свойства системы «полисульфон – растворитель – пропиленкарбонат» и зависимости их от состава и структуры растворов.

Ключевые слова: полисульфон, полимерные растворы, пластификатор, вязкость, вязкоупругие свойства, твердотельный электролит, тонкопленочная мембрана.

E.Zh. Tuleshova¹, A.B. Bayeshov², G.K. Aibolova¹

¹*Kh.A. Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan;*
²*D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan*
(E-mail: elmira.tuleshova@ayu.edu.kz)

Kinetics of silver dissolution in aqueous solutions of hydrochloric acid

In this article results of the kinetic regularities of the processes of electrochemical oxidation-reduction of silver in a solution of hydrochloric acid by the recorded potentiodynamic polarization curves method were presented. The electrochemical behavior of silver electrodes was studied by voltammetry on an SVA-1BM potentiostat to elucidate the mechanism of oxidations. The main polarization current-voltage curves were taken at a sweep rate of 10 mV/s and were recorded on a flat two-coordinate potentiometer of H 301/1. A silver rod was used as the working electrode; its working surface was the front part, the area of which was 4 mm². The measurements were carried out in a three-electrode cell relative to the silver chloride electrode ($E_0 = +0.203$ V). Platinum was used as an auxiliary electrode. Voltammograms are mainly obtained in the temperature range of 20–70 °C (293–343 K), with potential sweep rates of 5–100 mV/sec. To clarify the mechanism of the processes occurring during the polarization by alternating current, the electrodes were subjected to cyclic polarization, i.e. the curves were recorded first in the direction of the cathode-anode, then the anode-cathode. The effect of electrolyte concentration and temperature, sweep rate on the electrochemical behavior of silver has been studied. The peculiarities of silver oxidation kinetics in an acidic medium were revealed. These data and the results of our previous studies serve as the theoretical foundations of electrode processes during the polarization of silver and other noble metals by alternating current and are prerequisites for the creation of new methods of metal extraction from waste solutions and wastewater and procedures for the synthesis of compounds for use in various industries. The following kinetic parameters were calculated to characterize the mechanism of the silver electro-oxidation: the ion transfer number (α_n), the diffusion coefficient (D), the heterogeneous constant of the electrode process rate (K_s) and the effective energy of the activation process (E_a).

Keywords: potentiodynamic polarization curves, electrochemical behavior, silver, hydrochloric acid, electrode, concentration, temperature, electro-oxidation.

Introduction

The use of unsteady currents in the electrolysis processes led to the creation of a new scientific direction in applied electrochemistry — the development of unsteady electrolysis methods. The study of the behavior of electrochemical systems in alternating current is one of the most powerful experimental methods of modern electrochemistry. This method allows to solve a large number of various problems, starting with a precise study of the electrode-electrolyte boundaries structure, and ending with the clarification of fine details of the mechanism of electrochemical processes and the dissolution of sparingly soluble and sometimes insoluble metals and synthesis of their compounds [1]. In a number of works it was established [2, 3] that the non-stationary mode of electrolysis contributes to the intensification of electrochemical processes. However, the advantages of non-stationary electrolysis are not fully utilized due to insufficient knowledge. Until now electrode processes on silver electrodes have not been practically studied during polarization with industrial alternating current with a frequency of 50 Hz. In this regard the study of the electrochemical behavior of silver during the polarization of alternating current is an urgent task and has both theoretical and practical significance.

However, the question of studying the electrochemical behavior of silver during polarization by industrial alternating current remains open, since there are only fragmentary data in the scientific literature. In addition, it should be noted that the tendency of the silver surface to passivation during anodic electro-oxidation as a result of the oxide films formation by which the characteristics of its electrochemical behavior is determined.

Experimental

The electrochemical behavior of silver electrodes was studied by voltammetry on an SVA-1BM potentiostat to elucidate the mechanism of oxidations.

The main polarization current-voltage curves were taken at a sweep rate of 10 mV/s and were recorded on a flat two-coordinate potentiometer of H 301/1. A silver rod was used as the working electrode; its working surface was the front part, the area of which was 4 mm².

The measurements were carried out in a three-electrode cell relative to the silver chloride electrode ($E_0 = +0.203$ V). Platinum was used as an auxiliary electrode.

Voltammograms are mainly obtained in the temperature range of 20–70 °C (293–343 K), with potential sweep rates of 5–100 mV/s. To clarify the mechanism of the processes occurring during the polarization by alternating current, the electrodes were subjected to cyclic polarization, i.e. the curves were recorded first in the direction of the cathode-anode, then the anode-cathode. Thus, to a certain extent, a change in the direction of the current that occurs during the passage of an alternating current was imitated.

The cyclic polarization curves to a certain extent reflect the situation when the metal alternately is either the anode or the cathode.

The measurements were carried out in the following way: after the electrode surface was renewed, a potential sweep was switched on with a certain speed in the range of 5–100 mV/s and the corresponding potentiodynamic polarization curve was recorded.

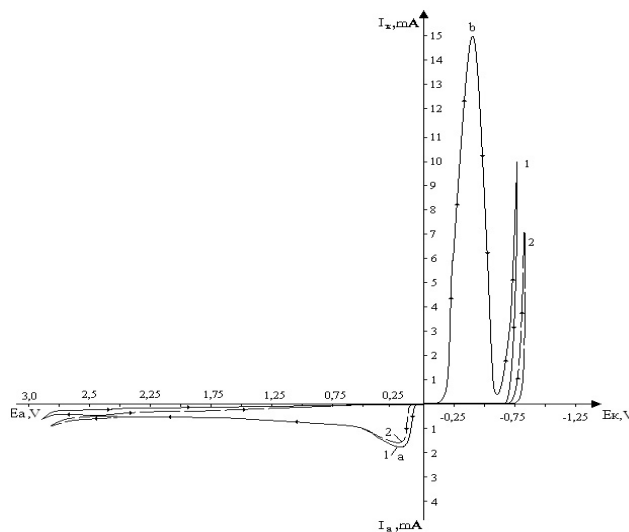
For research at a constant temperature, a special electrolytic cell of the YSE-2 brand, mounted in the thermostat of the ITZh-0–03 brand, was used.

Results and Discussion

The purpose of this work is to investigate the anodic silver dissolution in hydrochloric acid solution. In this paper, we studied the effect of acid concentration and temperature, potential sweep rate on anodic silver oxidation by removing potentiodynamic polarization curves.

We have previously conducted a series of studies on the electrochemical behavior of various elements, including silver, during polarization with alternating current of industrial frequency [4–7].

Figure 1 shows the anodic-cathodes and cathode-anodic cyclic polarization curves of silver obtained by us.

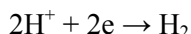


$C = 0.5$ M; sweep rate is 10 mV/s

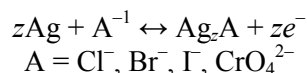
Figure 1. Anodic-cathodes (1) and cathode-anodic (2) potentiodynamic cyclic polarization curves of silver in hydrochloric acid solution

When the current-voltage curves are shifted to the region of cathode potentials, a current maximum is observed, due to the reverse recovery of the formed silver chloride.

When removing the cathode-anodic cyclic polarization curves in the region of the cathode potentials, only a current of hydrogen evolution is observed. As is well known in chloride environments, silver chloride is always present on the surface of a silver electrode. In the polarogram, a wave of silver chloride reduction is not observed; this is probably due to the fact that chloride films on the silver surface passivate the electrode. The release of hydrogen is observed at more negative potentials («minus» 0.75–1.0 V):



The data we obtained are consistent with the literature. Under the conditions of a linear potential sweep in solutions of halides [8, 9] and chromates [10], the oxidation of silver occurs by the formation of salt films by the reaction:



Next, we investigated the effect of various factors on the anodic silver dissolution in a solution of hydrochloric acid with the formation of AgCl by the method of removing polarization curves.

The electrochemical silver dissolution depending on the hydrochloric acid concentration was studied at a solution concentration of 0.5–5.0 M (Fig. 2a). In a solution of hydrochloric acid with an increase in the concentration of acid to 3.0 M, the height of the current maximum increases, and then it falls due to a decrease in the rate of silver oxidation.

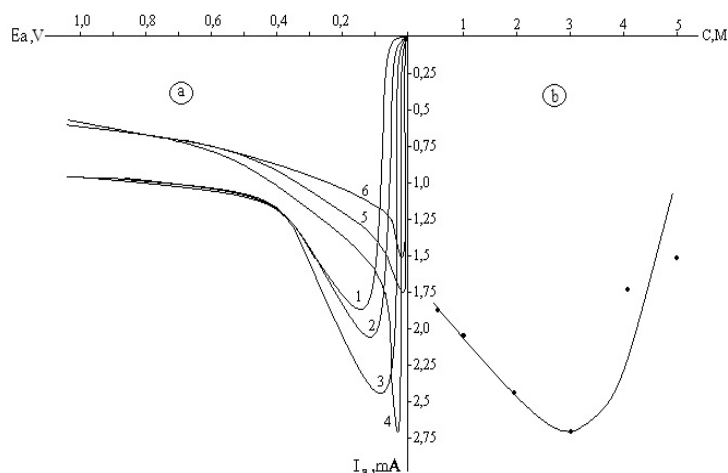
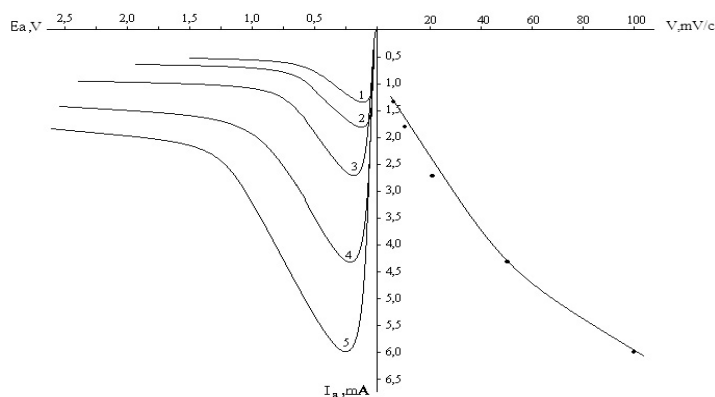


Figure 2. Anodic polarization curves of silver at different concentrations of hydrochloric acid (a), $V = 10 \text{ mV/s}$ and its effect on the height of the maximum oxidation current (b)

First, with an increase in the chloride ion concentration, the reaction rate increases, since formation of silver chloride is facilitated, and then denser silver chloride films are formed, and partial passivation occurs and the reaction rate decreases.

Based on the processing of the polarization curves results, the order of the silver oxidation reaction was determined from the $\lg i - \lg[\text{HCl}]$ dependence, which corresponds to a value of 0.23.

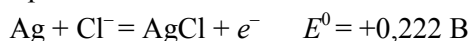
Figure 3 shows the anodic polarization curves of a silver electrode in a 0.5 M hydrochloric acid solution at various potential sweep rates in the range of 5–100 mV/s.



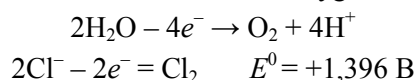
$V, \text{ mV/c}: 1 - 5; 2 - 10; 3 - 20; 4 - 50; 5 - 100$

Figure 3. Anodic polarization curves of silver at different potential scan rates and its effect on the height of its oxidation current maximum

In the anodic-cathodic cyclic polarogram the maximum current in the acid solution in the potential regions +0.075... +0.4 V reflects the process of silver anodic oxidation to form silver chloride:



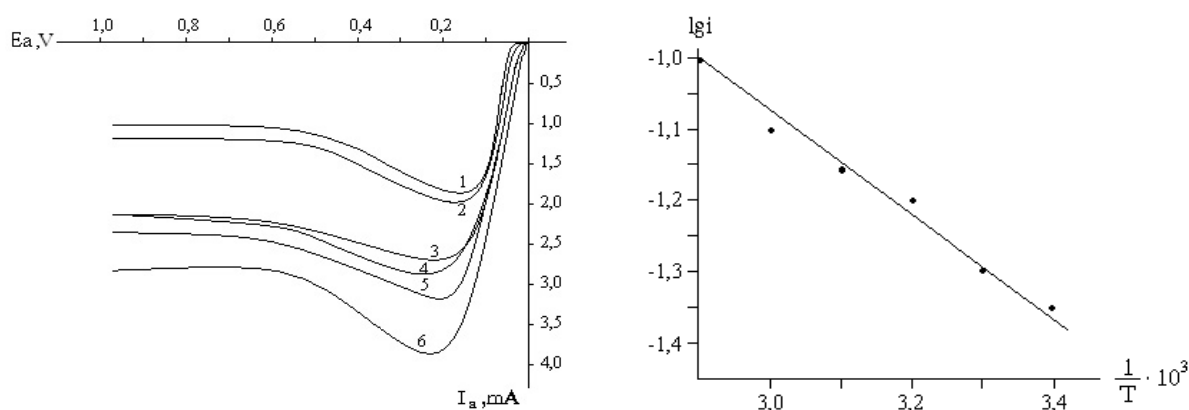
With more positive anodic potentials, a weak release of oxygen and chlorine is observed:



With an increase in the potential scan rate, the height of the silver oxidation current maximum, which indicates that the process proceeds in the diffusion mode increases.

Based on the processing of the polarization curves using the Galyus method [11], the transfer number of silver ions (α_n), the diffusion coefficient (D) and the heterogeneous constant of electrochemical processes rate (K_s) were calculated, they are respectively equal to: $\alpha_n = 1,28 \cdot 10^{-1}$, $D = 8,07 \cdot 10^{-3} \text{ cm}^2/\text{s}$, $K_s = 6,6 \cdot 10^{-2} \text{ cm/s}$.

In this paper, the effect of temperature on the silver oxidation process was also investigated. As can be seen from Figure 4, the height of the current maximum increases with rising temperature. The activation energy calculated by the temperature-kinetic method is equal to 11.43 kJ/mol. This indicates the flow of anodic dissolution is on the diffusion mode.



Acid temperature (K): 1 — 293; 2 — 303; 3 — 313; 4 — 323; 5 — 333; 6 — 343

Figure 4. Anodic polarization curves of silver at different solution temperatures and the logarithmic dependence of height current maximum temperature

Conclusions

Thus in the solution of hydrochloric acid, as a result of current-voltage research, we considered the effect of the potential sweep rate, electrolyte concentration and temperature. The activation energy, the reaction order, the diffusion coefficient, and the heterogeneous constant of the electrochemical process rate were calculated. The mechanism and peculiarities of oxidation in acidic medium are shown.

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Э.Ж. Тулешова, А.Б. Баешов, Г.К. Айболова

Тұз қышқылының сулы ерітінділерінде күмістің еру кинетикасы

Мақалада тұз қышқылы ерітіндісінде күмістің электрохимиялық қасиеті потенциодинамикалық поляризациялық қисықтар түсіру арқылы зерттелді. Негізгі поляризациялық вольтамперлік қисықтар потенциал беру жылдамдығы 10 мВ/с түсіріліп, екі координатты Н 301/1 планшетті потенциометрде жазылды. Жұмысшы электрод ретінде күміс сымы қолданылды, оның жұмысшы ауданы 4 мм². Өлшеулер үш электродты ұяшықта хлоркүміс электродқа қатысты ($E_0 = +0,203$ В) жүргізілді. Көмекші электрод ретінде платина қолданылды. Вольтамперограммалар негізінен 20–70 °С (293–343 К) температура аралығында, потенциал беру жылдамдығы 5–100 мВ/с болғанда алынды. Айнымалы токпен поляризацияланғанда жүретін механизм процестерін түсіну үшін электродтар циклдік поляризацияға ұшырайды, яғни қисықтар алдымен катод-анод, содан кейін анод-катод бағытына жазылады. Күмістің электрохимиялық қасиетіне электролиттің концентрациясы мен температурасының әсері зерттелді. Қышқыл ортадағы тотығу ерекшеліктері, механизмдері көрсетілді. Алдыңғы және осы зерттеулерде алған мәліметтер күміс және басқа да асыл металдарды айнымалы токпен поляризациялауда өтетін электродты процестердің теориялық негіздері болып табылады, сондай-ақ өңделген ерітінділер мен ағынды сулардан металдарды алудың жаңа тәсілдерін, өнеркәсіптің түрлі салаларында кеңінен қолданылатын бірқатар қосылыстарды синтездеу тәсілдерін жасаудың алғышарты болып табылады. Күмістің электродты тотығу механизмін сипаттайтын келесі кинетикалық параметрлер есептелді: иондарды тасымалдау саны (α_n), диффузия коэффициенті (D), электрод процесінің (K_s) гетерогенді жылдамдық константасы және процесінің эффективті активтендіру энергиясы (E_a).

Кілт сөздер: потенциодинамикалық поляризациялық қисықтар, электрохимиялық қасиет, күміс, тұз қышқылы, электрод, концентрация, температура, электрототығу.

Э.Ж. Тулешова, А.Б. Баешов, Г.К. Айболова

Кинетика растворения серебра в водных растворах соляной кислоты

В статье представлены результаты исследования кинетических закономерностей процессов электрохимического окисления-восстановления серебра в растворе соляной кислоты методом снятия потенциодинамических поляризационных кривых. Основные поляризационные вольтамперные кривые снимались при скорости развертки 10 мВ/с и записывались на планшетном двухкоординатном потенциометре Н 301/1. В качестве рабочего электрода использовали серебряный стержень, его рабочей поверхностью являлась торцовая часть, площадь которой составляла 4 мм². Измерения проводились в трехэлектродной ячейке относительно хлорсеребряного электрода ($E^0 = +0,203$ В). Вспомогательным электродом служила платина. Вольтамперограммы, в основном, получены в интервале температур 20–70 °С (293–343 К), при скоростях развертки потенциала 5–100 мВ/с. Для выяснения механизма процессов, протекающих при поляризации переменным током, электроды подвергались циклической поляризации, т.е. кривые записывались сначала в направлении катод-анод, затем анод-катод. Изучено влияние концентрации и температуры электролита, скорости развертки на электрохимическое поведение серебра. Были показаны особенности кинетики окисления серебра в кислой среде. Эти и другие данные, полученные нами в предыдущих исследованиях, служат теоретическими основами электродных процессов, протекающих при поляризации серебра и других благородных металлов переменным током, а также являются предпосылкой создания новых способов извлечения металлов из отработанных растворов и сточных вод, способов синтеза ряда соединений, находящихся широкое применение в различных отраслях промышленности. Для характеристики механизма процесса электроокисления серебра рассчитаны следующие кинетические параметры: число переноса ионов (α_n), коэффициент диффузии (D), гетерогенная константа скорости электродного процесса (K_s) и эффективная энергия активации процесса (E_a).

Ключевые слова: потенциодинамические поляризационные кривые, электрохимическое поведение, серебро, соляная кислота, электрод, концентрация, температура, электроокисление.

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B.Sh. Sarsembayev¹, K.S. Ibishev², M.M. Dospayev²

¹Karaganda Economic University of Kazpotrebsoyuz, Kazakhstan;

²Zh.N. Abishev Chemical-Metallurgical Institute, Karaganda, Kazakhstan
(E-mail: bolat_s@mail.ru)

Synthesizing copper phosphide in interacting of elemental phosphorus with copper (II) oxide in aqueous solutions

The article deals with a possibility of the copper phosphide synthesis by interaction of copper (II) oxide and elemental phosphorus in the water solutions. The method of multifactorial experiment planning was used for more complete assessment of the influence of various factors on the copper phosphide yield, in particular, the concentration of phosphoric acid, the solution temperature, the process duration, the stirring rate and the weight ratio of copper oxide and phosphorus. The target product was identified by the chemical, X-ray phase and electron-optical analyses. Based on the experimental data, taking into account the significant particular functions, a multifactorial generalized equation for the output of copper phosphide was obtained. The equation is used to find the optimal conditions for the copper phosphide synthesis. The partial point dependences of the product yield on the studied factors show that they have a real impact on the process, and the mathematical models are adequate. The yield of copper phosphide is 95.1 %, which is in good agreement with the calculated data (96.5 %). The proposed method of obtaining copper phosphide in interacting of elemental phosphorus with copper (II) oxide in aqueous solutions can be used for industrial large-tonnage synthesis of copper phosphide and phosphoric acid. In this case, the proposed method does not involve appreciable costs for the production re-equipment.

Keywords: elemental phosphorus, copper phosphide, mathematical planning, generalized multifactor equation.

Introduction

Copper-phosphorus alloys are widely used in a number of technological processes in non-ferrous metallurgy. They are used to deoxidize copper, to make phosphorous bronzes, to obtain solders, as well as modifiers of silumin. Today according to some data the demand for copper phosphide in the world market is estimated at 20–30 thousand tons per year [1].

Traditionally copper phosphide is mainly obtained by direct action of copper powder on elemental red phosphorus at very high temperatures [2; 205; 3, 4; 158–161]. However direct fusion of metals with phosphorus is hampered by the high elasticity of phosphorus vapor that causes contamination of the resulting phosphides with the components of the crucible material and the furnace lining.

It is known that at present copper phosphide is obtained in interacting of the copper sulfate solution with phosphate sludge according to the method described in [5].

The basis for obtaining copper phosphide is the reaction of phosphorus interaction with the copper sulfate solution that is represented in equation (1)



However despite the simplicity of the technological design this method has several disadvantages: firstly, copper phosphide obtained by this method contains sulfate sulfur, the presence of which affects dramatically the quality of the product obtained; secondly, the secondary waste is generated in the form of a mixture of sulfuric and phosphoric acids in the filtrate requiring respectively further processing that is associated with additional operations and costs.

In this regard the development of fundamentally new, cheap, and environmentally friendly technologies for synthesizing metal phosphides is a very topical issue.

In order to obtain pure copper phosphide and to simplify the process we carried out preliminary experiments and showed the possibility of obtaining copper phosphide in interaction of elemental phosphorus with copper (II) oxide in the solution of phosphoric acid.

Method

For a more complete assessment of the various factors influence on the yield of copper phosphide studies were carried out according to the method of rational experiment planning [6; 37; 7; 116].

We studied the effect of various factors on the yield of copper phosphide, in particular, the concentration of phosphoric acid, the solution temperature, the process time, the stirring rate and the weight ratio of copper oxide and phosphorus (Table 1).

Table 1

Factors studied and their levels

Factor	Level				
	1	2	3	4	5
X_1 is the concentration of phosphoric acid, g/l	50	100	150	200	250
X_2 is the temperature t , °C	45	55	65	75	85
X_3 is duration, h	0.5	1.0	1.5	2.0	2.5
X_4 is the stirring rate, W, rev/min	800	900	1000	1100	1200
X_5 is the weight ratio, CuO/P	2.5	3.0	3.5	4.0	4.5

The experiments were carried out in a thermostated cell with the capacity of 300 ml equipped with an agitator with the adjustable rotation speed. Elemental white phosphorus and copper (II) oxide were introduced into the heated phosphoric acid solution and mixed using a mechanical stirrer.

In accordance with the planning matrix for 5 factors there were carried out 25 experiments for each factor with variations at 5 levels. The experiment plan and results are shown in Table 2.

Table 2

Experiment plan and results of elemental phosphorus interaction with copper (II) oxide in the phosphoric acid solution

No.	X_1	X_2	X_3	X_4	X_5	Y_E	Y_P
1	50	45	0.5	800	2.5	0.73	0.74
2	50	65	1.5	1000	3.5	0.80	0.79
3	50	55	1.0	900	3.0	0.81	0.82
4	50	85	2.5	1200	4.5	0.89	0.84
5	50	75	2.0	1100	4.0	0.82	0.86
6	150	45	1.5	900	4.5	0.66	0.65
7	150	65	1.0	1200	4.0	0.82	0.78
8	150	55	2.5	1100	2.5	0.83	0.85
9	150	85	2.0	800	3.5	0.89	0.88
10	150	75	0.5	1000	3.0	0.87	0.88
11	100	45	1.0	1100	3.5	0.79	0.79
12	100	65	2.5	800	3.0	0.84	0.83
13	100	55	2.0	1000	4.5	0.84	0.83
14	100	85	0.5	900	4.0	0.79	0.82
15	100	75	1.5	1200	2.5	0.78	0.77
16	250	45	2.5	1000	4.0	0.76	0.76
17	250	65	2.0	900	2.5	0.74	0.77

Continuation of Table 2

No.	X ₁	X ₂	X ₃	X ₄	X ₅	Y _E	Y _P
18	250	55	0.5	1200	3.5	0.74	0.79
19	250	85	1.5	1100	3.0	0.89	0.83
20	250	75	1.0	800		0.90	0.82
21	200	45	2.0	1200	3.0	0.79	0.76
22	200	65	0.5	1100	4.5	0.75	0.83
23	200	55	1.5	800	4.0	0.87	0.86
24	200	85	1.0	1000	2.5	0.88	0.83
25	200	75	2.5	900	3.5	0.76	0.76

Note. X₁...X₅ are the factors studied; Y_E is an experimental value of the recovery degree; Y_P is calculated according to Protodyakonov's equation.

The phosphorus sample mass in all the experiments was constant and equal to 0.8 g. After a specified period of time the solid and liquid phases were separated by filtration and residual copper was determined in the filtrate, copper and phosphorus in the sediment [8; 715, 865].

Results and Discussion

According to X-ray phase, electron-optical and chemical analyses the product of the reaction is copper phosphide.

Electron microscopy of copper phosphide shows that the maxima in the electron diffraction pattern of phosphide at 2.68; 2.40; 2.17; 1.75; 1.57 coincide with the X-ray phase analysis data 2.17 (26); 2.40 (23); 1.75 (34) (Fig. 1, 2).

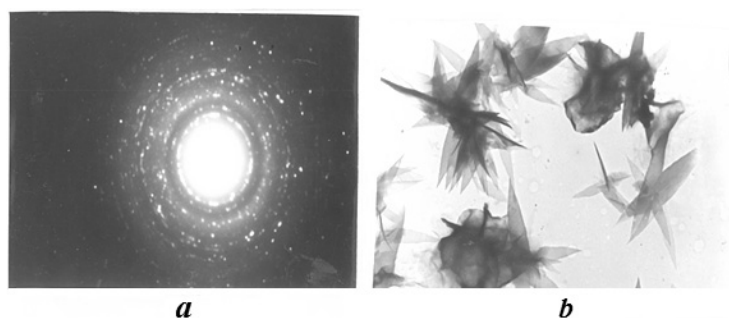


Figure 1. Electron-diffraction pattern (a) and microphotography (b) of copper phosphide ($\times 7000$)

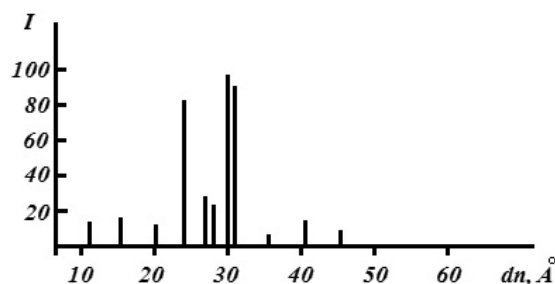


Figure 2. Bar X-ray pattern of copper phosphide

The partial point dependences of the target product yield on the studied factors are presented in Figures 3–5. The equations describing their coefficients are listed in Table 3. The $t_R > 2$ signification shows that all the factors studied have a real impact on the process, and the resulting mathematical models are adequate [6; 37; 7; 116].

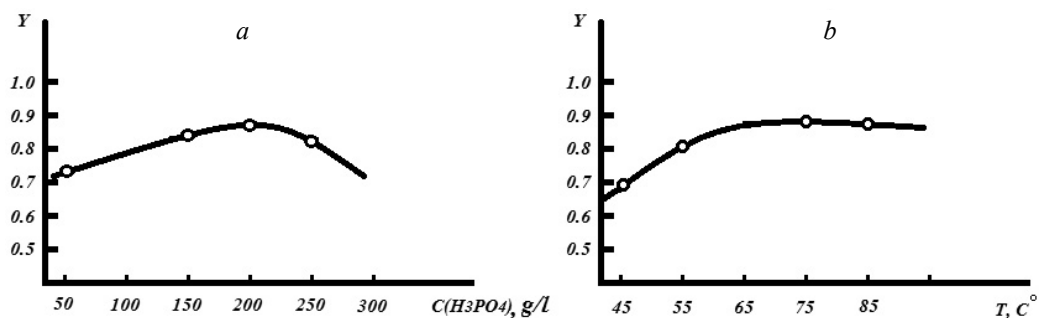


Figure 3. Copper phosphide yield dependence on the concentration (a) and the temperature (b) of the solution

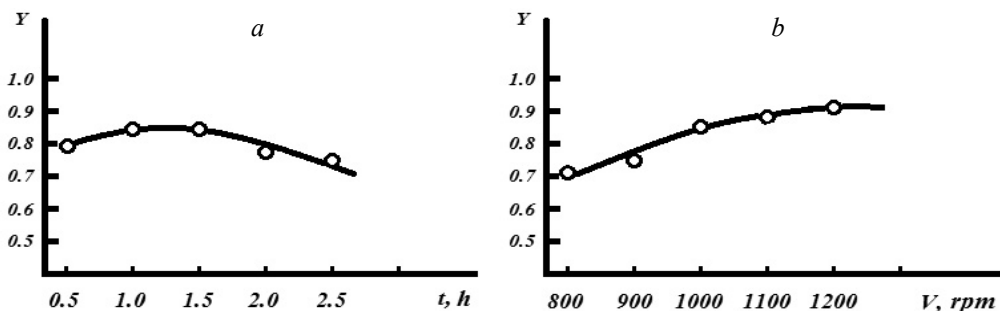


Figure 4. Copper phosphide yield dependence on the duration (a) and the stirring rate (b) of the process

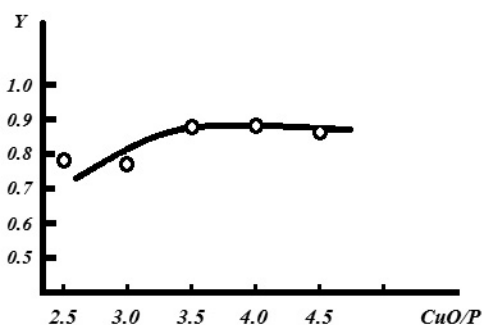
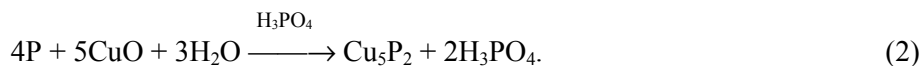


Figure 5. Copper phosphide yield dependence on the copper oxide/phosphorus ratio

The nature of the obtained partial dependences can be explained as follows. With increasing the concentration of phosphoric acid to 200 g/l (Fig. 3a) the copper phosphide yield increases by the reaction



Further increasing the concentration of electrolyte leads to decreasing the product yield. This is probably due to the fact that solubility of copper oxide in concentrated solutions of phosphoric acid decreases with increasing the concentration [9; 283–285].

Table 3

Correlation coefficients R and their significations t_R for private functions

Function equations	R	t_R	Function signification
$Y_1 = 3.64 \times X_1^{0,0189} - 3.17$	0,77	3,36 > 2	significant
$Y_2 = -1,85 \times 10^{-4} \times X_2^2 + 0,0296 \times X_2 - 0,292$	0,98	3,61 > 2	significant
$Y_3 = -5,31 \times X_3^2 + 0,14 + 0,736$	0,78	3,78 > 2	significant
$Y_4 = 9,62 \times 10^{-29} \times X_4^{8,84} + 0,766$	0,80	3,83 > 2	significant
$Y_5 = -9,61 \times X_5^2 + 1,19 \times X_5 - 2,79$	0,73	3,33 > 2	significant

As the results of chemical analysis show one half of the initial phosphorus is bound to copper to form copper phosphide, and the remainder goes to the solution in the form of phosphate ions.

As it can be seen from Figures 3b, 4b the maximum dependence of the copper phosphide yield on the temperature and stirring rate is at the temperature of 65 °C and the stirring rate of 1100 rev/min. Further increasing the temperature and stirring rate does not increase the yield of the target product.

The degree of copper phosphide formation dependence on the duration of the process is also maximum when the duration of the process is 1.5 hours (Fig. 4a).

With increasing the duration of the process the degree of copper phosphide formation falls. Decreasing the product yield is apparently caused by partial dissolution of freshly formed copper phosphide.

As it can be seen from Figure 5 increasing the weight ratio of copper oxide when phosphorus is more than 3.5–4.0:1 is not advisable, since there is no significant increase in the product yield. Based on the experimental data taking into account the significant particular functions a multifactor generalized equation for the output of copper phosphide is obtained:

$$Y = Y_1 + Y_2 + Y_3 + Y_4 + Y_5 - 3,25. \quad (3)$$

After substituting partial dependences, the generalized equation has the form:

$$Y_c = 3.64 \times X_1^{0.0189} - 3.17 - 1.85 \times 10^{-4} \times X_2^2 + 0.0296 \times X_2 - \\ - 0.292 - 5.31 \times 10^{-2} \times X_3^2 + 0.14 + 0.736 + 9.62 \times 10^{29} \times X_4^{8.84} + \\ + 0.766 - 9.61 \times 10^{-2} \times X_5^2 + 1.19 \times X_5 - 2.79 - 3.25. \quad (4)$$

The obtained generalized multifactor equation was used to find the optimal conditions for obtaining copper phosphide. The calculated optimal process conditions had the following values: the phosphoric acid concentration 200 g/l, the temperature 65 °C, the process time 1.5 hours, the stirring rate 1100 rev/min, CuO:P weight ratio was 3.5:1. Under these conditions the calculated yield of copper phosphide is 96.5 %.

To test the multifactor equation a control experiment was performed in the optimal mode.

The yield of copper phosphide is 95.1 %, which is in good agreement with the calculated data.

According to the results of the tests it was established that the use of copper oxide as a copper donor eliminates all the main disadvantages inherent in the above mentioned vitriol technology [5]. Below there are given the component compositions of copper phosphide samples obtained by the vitriol and the proposed oxide technologies (Table 4).

Table 4

Data of the component compositions of copper phosphide samples obtained by the vitriol and the proposed oxide technologies

Requirements of standard specifications 113-25-04-06-88. Mass. share, %			The average component composition in (%) of copper phosphide obtained by the vitriol technology					The average component composition in (%) of copper phosphide obtained by the oxide technology				
Grade	A	B	1	2	3	4	5	1	2	3	4	5
Cu	50–80	50–80	53.87	54.04	54.56	52.02	53.25	53.02	53.42	59.21	58.20	53.40
P ₄	7–14	6–14	5.1	9.49	10.1	11.18	6.2	13.82	14.05	14.10	13.90	14.01
S no more	1,0	8,0	2.63	2.45	2.47	2.99	2.21	0.084	0.079	0.095	0.089	0.065
F	1–3	8,0	0.12	0.17	0.23	0.37	0.30	0.048	0.039	0.055	0.042	0.051
Fe	1,0	1,6	0.42	0.26	0.24	0.29	0.32	0.04	0.03	0.05	0.03	0.04

Conclusions

Thus according to the method of rational experiment planning there was studied the impact of various factors on obtaining copper phosphide in interacting of elemental phosphorus with copper (II) oxide in the solution of phosphoric acid. It is shown that the yield of copper phosphide really depends on the concentration and the temperature of the solution, the duration of the process, the stirring rate and the copper oxide/phosphorus weight ratio.

The proposed method of obtaining copper phosphide can be successfully used for industrial large-tonnage synthesis of copper phosphide and phosphoric acid wherein the proposed method does not involve appreciable costs for the production re-equipment.

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Б.Ш. Сарсембаев, К.С. Ибишев, М.М. Доспаев

Сулы ерітінділерде элементарлы фосфорды мыс (II) тотығымен әрекеттестіру арқылы мыс фосфидін алу

Мақалада элементарлы фосфордың сулы ерітінділерінде мыс (II) тотығымен өзара әрекеттесуі арқылы мыс фосфидін алу мүмкіндігі зерттелген. Мыс фосфидінің шығымына әртүрлі факторлардың, атап айтқанда фосфор қышқылының концентрациясы, ерітінді температурасы, процестің ұзақтығы, араластыру жылдамдығы және мыс оксиді мен фосфордың салмақтық арақатынасының әсерін толығырақ бағалау үшін тәжірибені математикалық жоспарлаудың көпфакторлы әдістемесі қолданылды. Мақсатты өнім химиялық, рентгенфазалық және электронды-оптикалық анализдер арқылы анықталды. Маңызды жеке функцияларды ескере отырып, тәжірибелік деректер негізінде мыс фосфиді шығымының көпфакторлы жалпылама теңдеуін алдық. Ол өнімді алудың оптималды жағдайларын анықтау үшін қолданылды. Қарастырылған факторларға мыс фосфиді шығымының тәуелділіктері олардың процеске нақты әсерін және математикалық үлгінің дұрыстығын көрсетті. Мыс фосфидінің шығымы 95,1% құрады, бұл есептеулік деректерге сәйкес келеді (96,5%). Ұсынылатын мыс фосфидін алу әдісі мыс фосфидін және фосфор қышқылын өнеркәсіптік ірі тоннажды синтездеу үшін қолданылуы мүмкін. Сонымен қатар, бұл өндірісті қайта жабдықтауға елеулі шығындарды талап етпейді.

Кілт сөздер: элементарлы фосфор, мыс фосфиді, математикалық жоспарлау, жалпылама көпфакторлы теңдеу.

Б.Ш. Сарсембаев, К.С. Ибишев, М.М. Доспаев

Синтез фосфида меди при взаимодействии элементарного фосфора с оксидом меди (II) в водных растворах

В статье исследована возможность получения фосфида меди при взаимодействии элементарного фосфора с оксидом меди (II) в водных растворах. Для более полной оценки влияния различных факторов на выход фосфида меди, а именно: концентрации фосфорной кислоты, температуры раствора, продолжительности процесса, скорости перемешивания и весового соотношения оксида меди и фосфора использовали методику многофакторного математического планирования эксперимента. Целевой продукт идентифицировали с помощью химического, рентгенофазового и электронно-оптического анализов. На основании экспериментальных данных с учетом значимых частных функций было получено многофакторное обобщенное уравнение выхода фосфида меди, которое использовали для нахождения оптимальных условий получения продукта. Частные точечные зависимости выхода фосфида меди от рассмотренных факторов показали их действительное влияние на процесс и адекватность математической модели. Выход продукта составил 95,1%, что хорошо согласуется с расчетными данными (96,5%). Предлагаемый нами метод получения фосфида меди может быть использован для

промышленного крупнотоннажного синтеза фосфида меди и фосфорной кислоты. При этом он не требует существенных затрат на переоборудование производства.

Ключевые слова: элементарный фосфор, фосфид меди, математическое планирование, обобщенное многофакторное уравнение.

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N.V. Khan¹, M.M. Burkitbayev¹, F. Kh. Urakaev²¹*Al-Farabi Kazakh National University, Almaty, Kazakhstan;*²*V.S. Sobolev Institute of Geology and Mineralogy of the Russian Academy of Sciences, Novosibirsk, Russia
(E-mail: natasha.khan.v@gmail.com)*

Development of the synthesis technology of S@AgCl–Ag₂S nanocomposite in aqua medium

This research work is devoted to the development of the synthesis technology of nanocomposite based on sulfur, silver chloride and silver sulfide. The components which included in this nanocomposite make it possible to use it in various fields of science and technology: from biomedicine to agriculture. S@AgCl–Ag₂S nanocomposite was synthesized in aqua medium by two stages: 1) separate obtaining of each component; 2) mixing of all systems (products of reactions). The first stage is based on the interaction of aqueous solutions of silver nitrate with sodium chloride and sodium thiosulfate (in excess) with hydrochloric acid. Each of these reactions was carried out separately. At the second stage there was formation of silver sulfide and directly the S@AgCl–Ag₂S nanocomposite, under interaction of all products of the first stage. The physicochemical characteristics of the samples were determined by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDAX). The results of XRD and Raman spectroscopy of the samples showed that nanocomposite represented by silver chloride, silver sulfide and sulfur. EDAX analysis identified the presence of silver, chlorine and sulfur. Meanwhile SEM analysis revealed that investigated material has range of particles size from micro to nano ones. Morphology of particles mostly represented by oval and spherical forms, and smooth surface.

Keywords: nanocomposite, nanoparticles, sulfur, silver halides, silver chloride, silver sulfide, aqua medium, aqueous solution.

Introduction

Nowadays nanomaterials are made a big breakthrough in science and technology. By turns nanomaterials can be obtained by various methods from mechanochemical synthesis to liquid phase synthesis [1, 2]. It is known that nanocomposites are multicomponent materials and each individual component must have useful properties. Combining of different elements and their compounds can give a new material with enhanced properties.

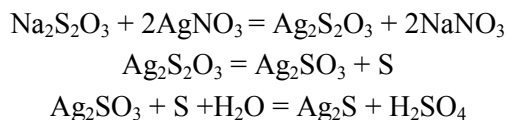
There are a lot of researches devoted to the study of silver and silver chloride, its antimicrobial and photocatalytic properties [2–5]. Silver sulfide is a functional material which has semiconductor, thermoelectric and photoluminescence properties [6, 7] also in the study [8] it is assumed that this compound may show some biological activity. As for sulfur it is widely applied as fungicide, fertilizer in agriculture and in production of Li-S batteries [9, 10].

It is obvious that the production of nanocomposite based on the above elements and compounds can lead to the creation of a universal material with a set of features applicable in various fields. At the initial stage of investigation it was important to get the final product corresponding to the claimed composition. Therefore, the aim of this study was development of the synthesis technology of the nanocomposite with S@AgCl–Ag₂S composition.

Experimental

The synthesis proceeded in two stages: 1) separate obtaining of each component; 2) mixing of all systems. The first stage included interaction between aqueous solutions of silver nitrate and sodium chloride. The solutions were poured drop by drop with constant stirring. During this reaction there was obtained silver chloride. Then, through the interaction of aqueous solutions of hydrochloric acid with excess of sodium thiosulfate under conditions similar to previous reaction, there was formation of sulfur.

The second stage included the mixing of solutions with the products which were obtained on the first stage. Silver sulfide is formed in the process of mixing of all solutions. The formation of silver sulfide was observed not only visually (black precipitate), but also subsequently confirmed by a number of physicochemical methods of analysis. The formation can be explained by the next scheme [11]:



After mixing the solutions, the excess of sodium thiosulfate reacts with silver nitrate, which is not all amount reacted with sodium chloride at the first stage. As a result, silver sulfide is formed according to the scheme described above and after some time the system comes to balance and forms a composite S@AgCl-Ag₂S.

Further, the solid precipitate is precipitated using a centrifuge ROTINA 380 R, for 15 minutes and at a speed of 4000 rpm. Eventually the samples had been dried at 45 °C, for 12–16 hours.

Results and Discussion

The phase composition of the sample was identified by XRD using X-ray diffractometer Rigaku MiniFlex 600. Identification of the sample was carried out using the databases PDF Card № 00–014–0072 for silver sulfide and PDF Card № 01–085–1355 for silver chloride. The results of analyses (Fig. 1) showed that investigated material represented by clear peaks of silver sulfide and silver chloride and correspond to standard data. On the Fig. 1 spectrum with red color is investigated sample, blue columns are standard peaks of silver sulfide and green columns are standard peaks of silver chloride. Sulfur could not be found. The explanation may consist of that sulfur present in amorphous state; therefore, the XRD analyzer was unable to fix it. Consequently, Raman spectroscopy was performed to detect sulfur and confirm the presence of silver chloride and silver sulfide in the sample.

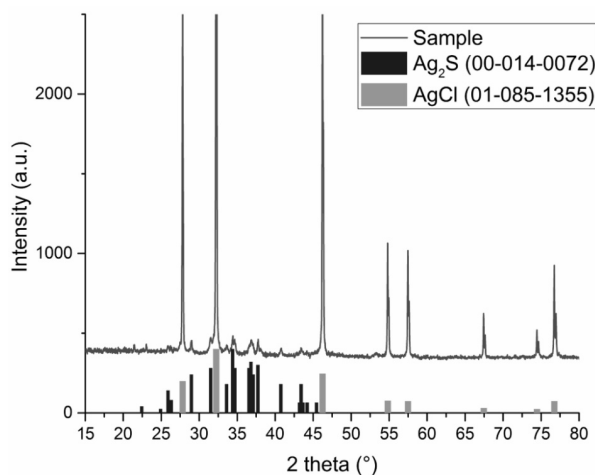


Figure 1. XRD patterns of the sample. Characteristic peaks of the silver sulfide and silver chloride

Raman spectra were excited by a He-Ne laser with a wavelength of 633 nm and recorded by a Raman spectrometer Solver Spectrum (NT-MTD) using a diffraction grating 1800/500, which provides a spectral resolution of 1 cm⁻¹. So, there are quite clear Raman peaks on the Figure 2, fully corresponding to the sulfur. Other components do not show clear peaks, which may indicate their metallic nature. The peaks at 95 and 190 cm⁻¹ maybe, relates to Ag-Ag lattice vibrations, while the bands at 240 and 400 cm⁻¹ are caused by the Ag-Cl bond stretching and compression mode [12]. According to [13] Ag₂S correspond to two intense peaks between 90 and 109 cm⁻¹ and there should be a weak band at 245 cm⁻¹. Silver chloride appears at 233 cm⁻¹, and there should be two small peaks in the area from 324 to 470 cm⁻¹. Thus, it can be seen from the spectrum (Fig. 3), our results echoes in some means with literature data.

The structural morphology of prepared samples and elemental composition were examined by SEM and EDAX, using scanning electron microscope Quanta 200i 3D. Figure 4a showed the SEM images of the S@AgCl-Ag₂S nanocomposite which revealed homogeneous structure of the sample. Closer examination of the sample shows that the majority of particles is represented by oval and sphere form with smooth surface (Fig. 4b). Figure 4c revealed that investigated material has both micro- and nano-sized particles. It can be seen that the powder is mainly represented by light particles. But at the same time, on closer examination, there can be seen the gray areas (particles) in the sample. The EDAX analysis (see Table) shows there is the highest percentage (At%) of such elements like Ag (24.05), Cl (16.46) and S (8.63 %). It should be noted

that Ag and Cl are presented by pronounced peaks and wave shoulders (Fig. 5). Thus, based on the obtained data, it can be assumed that the light areas are silver chloride and sulfur (smaller particles), and the gray areas is silver sulfide. Also in the composition of nanocomposite present a small amount of Na, O, C, Si, P.

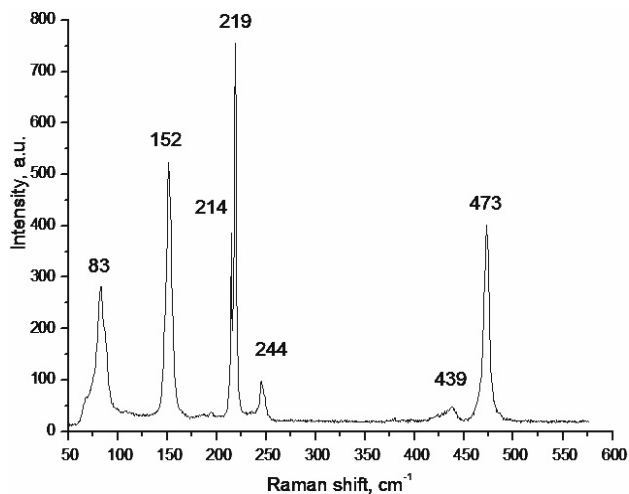


Figure 2. Raman spectra of elemental sulfur

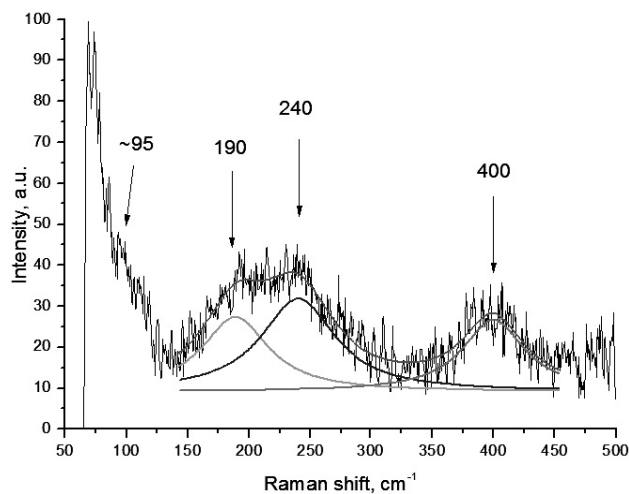


Figure 3. Raman spectra corresponding to AgCl and Ag₂S

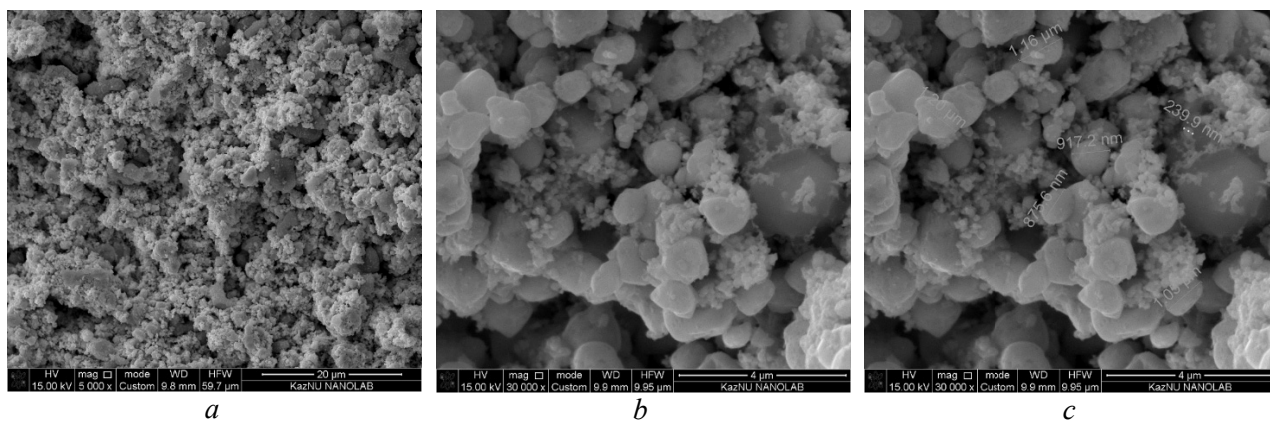


Figure 4. SEM images of S@AgCl-Ag₂S nanocomposite

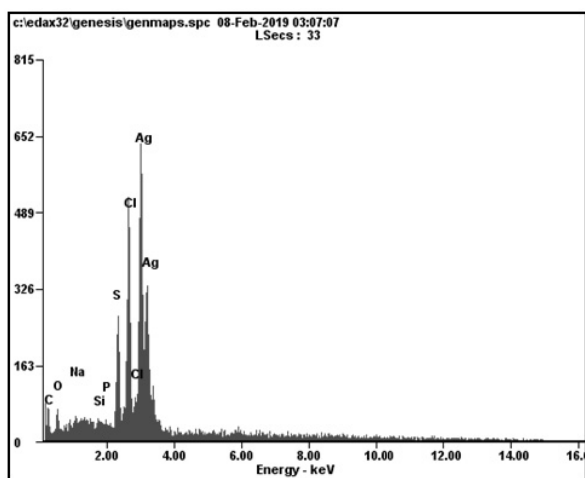


Figure 5. EDAX analysis of the S@AgCl-Ag₂S

Table
Elemental composition of S@AgCl-Ag₂S nanocomposite

Element	Wt. %	At. %
C	10.22	35.40
O	4.62	13.02
Na	1.11	2.01
Si	0.58	0.86
P	0.42	0.57
S	6.66	8.63
Cl	14.03	16.46
Ag	62.35	24.05

Conclusions

In summary S@AgCl-Ag₂S nanocomposite has been synthesized in aqua medium by two stages. The results of XRD analysis revealed that samples represented by silver chloride and silver sulfide. The Raman spectroscopy showed the presence of sulfur in composition of nanocomposite, also illustrated some areas, which can indicate the silver chloride and silver sulfide. EDAX analysis demonstrated the presence of elements like Ag (24.05 At%), Cl (16.46 At%) and S (8.63 At%). SEM analysis proved that S@AgCl-Ag₂S nanocomposite has micro- and nano-sized particles with oval and sphere form, and smooth surface.

As a result the goal of this study was successfully achieved.

This research work was supported by scientific projects of the Ministry of Education and Science of the Republic of Kazakhstan AP05133115 and BR05234566 (program-target financing).

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Н.В. Хан, М.М. Бүркітбаев, Ф.Х. Уракаев

Сулы ортадағы S@AgCl-Ag₂S нанокөмпозитін синтездеудің технологиясын дайындау

Мақала құрамында күкірт, күміс хлориді және сульфиді бар нанокөмпозиттерді синтездеудің технологиясын дайындауға арналған. Аталған нанокөмпозиттің құрамына кіретін компоненттер оның ғылым мен техниканың әртүрлі салаларында қолдануға мүмкіндік береді: яғни, биомедицинадан бастап ауылшаруашылығына дейін. S@AgCl-Ag₂S нанокөмпозиті сулы ортада екі сатымен синтезделді: 1) компоненттерді жеке-жеке синтездеу; 2) барлық жүйелерді (реакция өнімдері) араластыру арқылы. Бірінші саты күміс нитраты мен натрий хлориді ерітінділерінің және натрий тиосульфаты (артық мөлшерде) мен тұз қышқылының әрекеттесуіне негізделген. Одан бөлек, аталған реакциялар жеке дара да жүргізілді. Екінші сатыда бірінші сатының реакция өнімдерінің әрекеттесуінің нәтижесінде күміс сульфидінің және S@AgCl-Ag₂S нанокөмпозитінің түзілуі жүзеге асады. Сынамалардың физика-химиялық қасиеттері рентгенофазалық талдау (РФТ), Раман спектроскопиясы, сканирлеуші электронды микроскопия (SEM) және энергодисперсионды рентгенді

спектроскопия (SEM-EDAX) әдістерінің көмегімен анықталды. РФТ және Раман спектроскопиясы талдауларының нәтижелері нанокөмірдің құрамында күкірт, күміс хлориді және сульфиді бар екенін анықтады. EDAX талдауы нанокөмірдің құрамында күміс, хлор, күкірт және де т.б. элементтердің бар екенін дәлелдеді. Зерттелінген материалдың пішіні микроөлшеммен бастап наноөлшемге дейін таралғанын SEM талдауының нәтижелері көрсетті. Бөлшектердің морфологиясы негізінен сопақ және шар тәрізді, беттік қабаты тегіс екені анықталды.

Кілт сөздер: нанокөмір, нанобөлшектер, күкірт, күміс галогенидтері, күміс хлориді, күміс сульфиді, сулы орта, сулы ерітінділер.

Н.В. Хан, М.М. Буркитбаев, Ф.Х. Уракаев

Разработка технологии синтеза нанокompозита S@AgCl–Ag₂S в водной среде

Статья посвящена разработке технологии синтеза нанокompозита на основе серы, хлорида серебра и сульфида серебра. Компоненты, входящие в состав данного нанокompозита, позволяют использовать его в различных отраслях науки и техники: от биомедицины до сельского хозяйства. Нанокompозит S@AgCl–Ag₂S был синтезирован в водной среде, в две стадии: 1) раздельное получение каждого из компонентов; 2) смешение всех систем (продуктов реакций). Первая стадия основана на взаимодействии водных растворов нитрата серебра с хлоридом натрия, а также тиосульфата натрия (в избытке) с соляной кислотой. Причем каждая из этих реакций проводилась отдельно друг от друга. На второй стадии происходит образование сульфида серебра и непосредственно самого нанокompозита S@AgCl–Ag₂S, при взаимодействии всех продуктов реакций первой стадии. Физико-химические характеристики образцов были определены с помощью рентгенофазового анализа (РФА), рамановской спектроскопии, сканирующей электронной микроскопии и энергодисперсионной рентгеновской спектроскопии (SEM-EDAX). Результаты РФА-анализа и рамановской спектроскопии показали, что образцы представлены хлоридом серебра, сульфидом серебра и серой. EDAX-анализ установил присутствие в составе нанокompозита серебра, хлора, серы и других элементов. В то время как SEM анализ показал, что исследуемый материал представлен частицами от микро- до наноразмеров. Морфология частиц представлена в основном овальными и сферическими формами, с гладкой и ровной поверхностью.

Ключевые слова: нанокompозит, наночастицы, сера, галогениды серебра, хлорид серебра, сульфид серебра, водная среда, водные растворы.

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D.E. Aitbekova¹, Xintai Su², Fengyung Ma², A. Tusipkhan¹, M.I. Baikenov¹

¹*Ye.A. Buketov Karaganda State University, Kazakhstan;*

²*Xinjiang University, Urumqi, China*

(E-mail: darzhan91@mail.ru)

Effect of catalytic systems on the hydrogenation of phenanthrene

This paper shows the effectiveness of the synthesized catalytic additives in the process of hydrogenation of phenanthrene in the presence of ethanol as a hydrogen donor. Ferrosphere, NiO/SiO₂ covered the surface of ferrosphere and Fe₂O₃/SiO₂ covered the surface of ferrosphere were used as catalytic additives. Ferrosphere was extracted from energy ashes of Karaganda thermal power plant. NiO/SiO₂ and Fe₂O₃/SiO₂ covered the ferrosphere were prepared by the method of «wet mixing». The phase composition, surface morphology, average size and distribution of particles of ferrospheres and nanocatalytic additives NiO/SiO₂ and Fe₂O₃/SiO₂ covered the ferrospheres were determined. The composition of the reaction products was determined by the method of chromatography-mass spectrometry on the gas chromatograph of Agilent Technologies 7890A with mass spectrometric detector 5975C. Identification of the substances was carried out using the NIST 98 mass-spectral database. A synergistic effect of nanocatalytic additives NiO/SiO₂ and Fe₂O₃/SiO₂ covered the ferrospheres was established. The high degree of phenanthrene conversion is observed on the hydrogenation in the presence nickel and iron catalytic additives on the ferrosphere. According to the results of hydrogenation of phenanthrene efficiency range of the catalytic additives was built: NiO/SiO₂ on the ferrosphere > Fe₂O₃/SiO₂ on the ferrosphere > NiO/SiO₂ > Fe₂O₃/SiO₂ > ferrosphere.

Keywords: polyaromatic hydrocarbons, phenanthrene, hydrogenation, catalytic systems, ferrosphere, sol-gel method, «wet mixing» method, coal.

Introduction

Currently due to the shortage of the «light oil» resource most of the researches related to the processing of heavy oil and solid hydrocarbon raw materials is being considered. As it is known synthetic liquid fuel get 7–8 times more from coal than from oil. Despite the high losses scientific works on improvement of hydrogenation of coal, coal tar and liquefaction of products are continued in most countries.

According to modern concepts the main part of the organic mass of coal is a three-dimensional polymer of irregular structure, the rigidity of the framework of which is enhanced by internal donor-acceptor interactions. Studies show that the products of destruction of the organic mass of coal are complex combination of hydrocarbons in which compounds with the number of aromatic rings up to three predominate, but hydrocarbon derivatives with four or more rings form a certain part [1].

The decomposition of the organic mass of coal is carried out to obtain liquid products. Liquefaction of the initial product and saturation with hydrogen are carried out during hydrogenation. Depending on the process conditions and the depth of conversion of the organic mass of coal, hydrogenation allows to turn solid fuel into high-quality motor fuel (gasoline, diesel fuel) or raw materials for organic synthesis (hydrocarbons, phenols, nitrogenous compounds). The composition of the hydrogenation products depends on the amount of hydrogen entering into the reaction, the quality of the catalysts and the parameters of the process itself (pressure, temperature, contact time) [2].

The study of destructive hydrogenation of polyaromatic compounds was carried out to improve the process of coal liquefaction mentioned above. One of the polycyclic aromatic compounds in solid fuels is phenanthrene, which was first obtained from coal tar.

The purpose of this work is to investigate the process of catalytic hydrogenation of phenanthrene as a model object, which constitutes the organic mass of coal.

Experimental

For experiments phenanthrene was used as model object; ferrosphere, synthesized nanocatalytic additives NiO/SiO₂ and Fe₂O₃/SiO₂ separately covered the ferrosphere were used as catalytic additives. Ferrosphere was extracted from the energy ashes which were obtained by burning coal at Karaganda thermal power plant.

Ferrosphere was used as a carrier of catalytic additives NiO/SiO₂ and Fe₂O₃/SiO₂. Catalytic additives added to the ferrosphere were prepared by the «wet mixing» method.

The catalytic additive Fe₂O₃/SiO₂ was covered the ferrosphere by mixing the ferrosphere with 20 % solutions of ferric chloride and sodium silicate, followed by heating the mixture to a temperature of 70–80 °C for 2 hours. Then the resulting suspension of the initial compounds was dried at a temperature of 100–105 °C. The dry mass was calcined at a temperature of 500–550 °C for 60 minutes and then molded into a tablet. The second catalytic additive NiO/SiO₂ covered the ferrosphere was prepared similarly. Ferrosphere was mixed with 20 % solutions of nickel sulfate and sodium silicate.

The activity of the prepared catalytic additives in the hydrogenation of phenanthrene was determined under autoclave conditions: T — 380 °C, P — 3 MPa, t — 120 min, the amount of catalytic additive 1.0 mass %, 5 ml of ethanol as a hydrogen donor. The use of alcohols allows to obtain significant yields of liquid products in the absence of catalysts and molecular hydrogen. The ability to interact with active radical centers, preventing their recombination, determines the stabilizing role of aliphatic alcohols [3].

The mixture of phenanthrene and catalytic additives was pre-mixed, and then the prepared mass and ethanol were loaded into the autoclave. The reactor was purged with molecular hydrogen and pressurized with it. Then the reactor was heated to the required temperature (380 °C) and kept for a given time. The heating rate of the autoclave was 10 °C/min. After the experiment, it was cooled to room temperature; the reaction mixture was dissolved by chloroform. The composition of the reaction products was determined by the method of chromatato-mass spectrometry on the gas chromatograph of *Agilent Technologies 7890A* with mass spectrometric detector *5975C*. Identification of the substances was carried out using the *NIST 98* mass-spectral database.

Results and Discussion

The phase composition of catalytic additives was studied on a X-ray diffractometer *MiniFlex 400/300*. The diffractograms of the synthesized samples of NiO/SiO₂ on the ferrosphere (sample 1) and Fe₂O₃/SiO₂ on the ferrosphere (sample 2) are presented (Fig. 1).

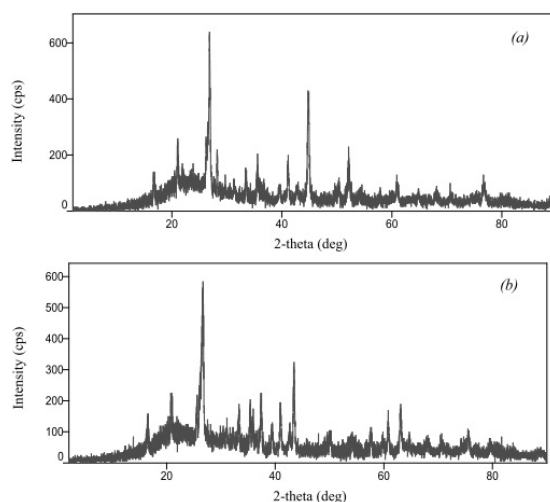


Figure 1. X-ray diffractograms of NiO/SiO₂ catalytic additives covered the ferrosphere (a); Fe₂O₃/SiO₂ catalytic additives covered the ferrosphere (b)

The diffractograms of samples 1 and 2 show the presence of phases respectively NiO/SiO₂ and Fe₂O₃/SiO₂.

Electronic micrographs of initial ferrosphere and the samples 1 and 2 are shown in Figure 2.

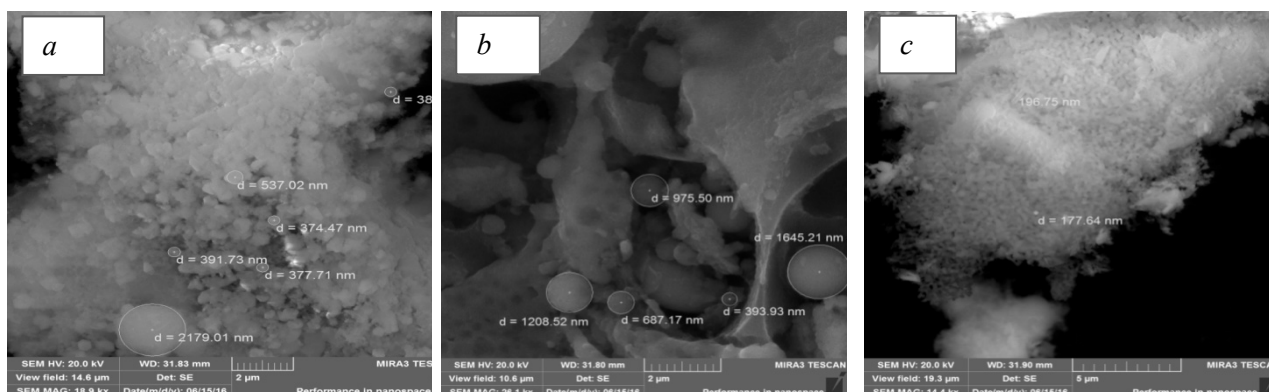


Figure 2. Electronic micrographs of NiO/SiO₂ on the ferrosphere (*a*), Fe₂O₃/SiO₂ on the ferrosphere (*b*), initial ferrosphere (*c*)

The study showed that spherical formations of ferrospheres have a particle size of 975.5 nm. The nickel-silicon composition (sample 1, *b*) is spherical formations with the diameter of 374 nm. These formations tend to coalesce, forming conglomerates with fouling of small spheres of nickel oxides and iron oxides.

The average particle size of the prepared nickel and iron samples was determined by using nanosizer NanoS90 (Fig. 3).

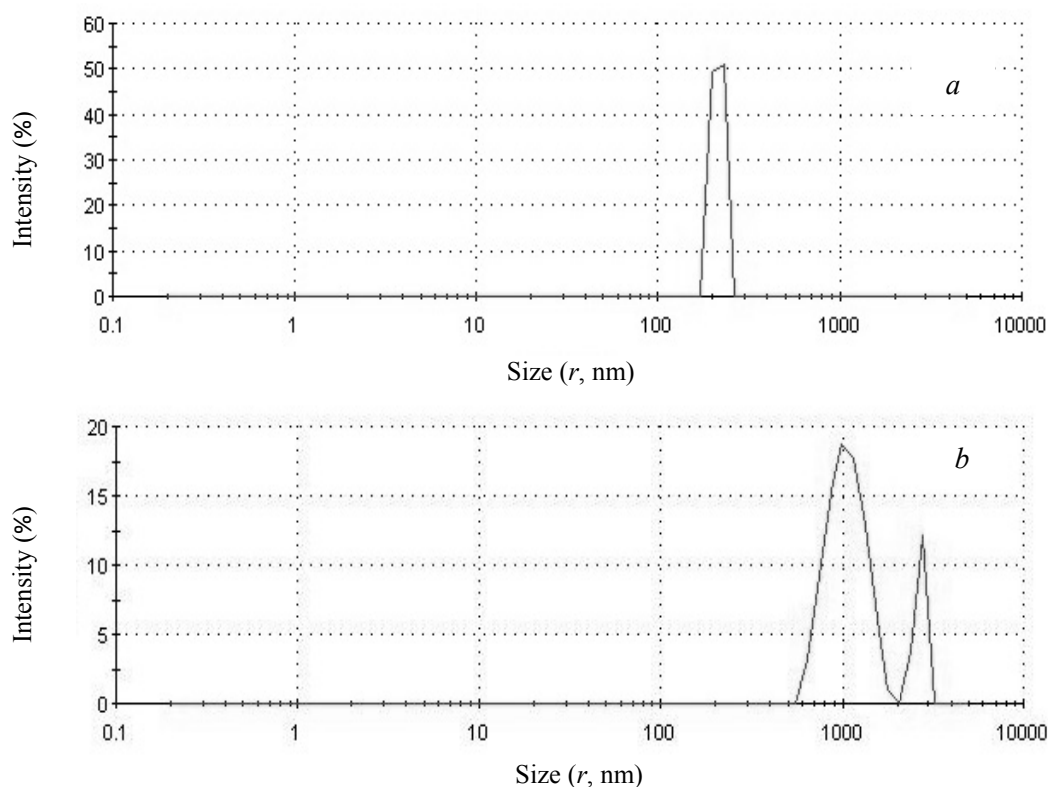


Figure 3. Average particle size of NiO/SiO₂ on the ferrosphere (*a*), Fe₂O₃/SiO₂ on the ferrosphere (*b*)

The average particle size was 213.9 nm for sample 1 and 1064 nm for sample 2.

The results of phenanthrene hydrogenation are presented in Table. The main products of hydrogenation of phenanthrene in the presence of the catalytic additives are the products of the hydrogenolysis and hydriding.

The yield of the products of phenanthrene hydrogenation without catalyst and in the presence of the catalytic additives

Individual chemical composition	Yield of the products, %					
	Without catalyst	Ferrosphere	NiO/SiO ₂ [4]	Fe ₂ O ₃ /SiO ₂ [4]	NiO/SiO ₂ on the ferrosphere	Fe ₂ O ₃ /SiO ₂ on the ferrosphere
	1	2	3	4	5	6
Naphthalene	–	–	0.14	0.08	–	–
1-Methylnaphthalene	–	–	0.11	–	3.6	–
2-Ethylnaphthalene	–	–	–	0.05	–	–
2-Butylnaphthalene	–	0.9	–	–	–	4.2
Fluorene	–	–	0.98	0.97	–	–
9-Methylfluorene	–	–	0.42	0.18	–	–
9,10-Dihydroanthracene	–	0.7	0.41	0.44	–	7.5
9,10-Dihydrophenanthrene	–	–	4.5	4.3	34.3	16.4
1,2,3,4-Tetrahydrophenanthrene	–	3.2	–	–	13.2	3.5
1,2-Dihydrophenanthrene	4.2	–	–	–	–	–
1,1-Biphenyl	–	–	1.54	0.03	11.2	–
Benzene	–	–	–	–	2.2	–
2-Methyl-1,1-biphenyl	–	–	–	–	–	5.7
Anthracene	–	–	8.8	9.3	–	–
Phenanthrene	95.8	95.2	83.1	84.65	35.5	62.7
Conversion	4.2	4.8	16.9	15.35	64.5	40.0

There are isomerization reactions along with the hydrogenation reactions as a result of the polyaromatic hydrocarbon processing in the presence of ferrosphere and Fe₂O₃/SiO₂ on the ferrosphere as catalytic additives: 9,10-dihydrophenanthrene isomerized into linear 9,10-dihydroanthracene. Angular-linear isomerization of 9,10-dihydrophenanthrene into 9,10-dihydroanthracene and further dehydrogenation of 9,10-dihydroanthracene with the formation of anthracene were shown in the work [5].

Experimental results of hydriding and hydrogenolysis reactions of polyaromatic hydrocarbon hydrogenation process are presented in Figure 4.

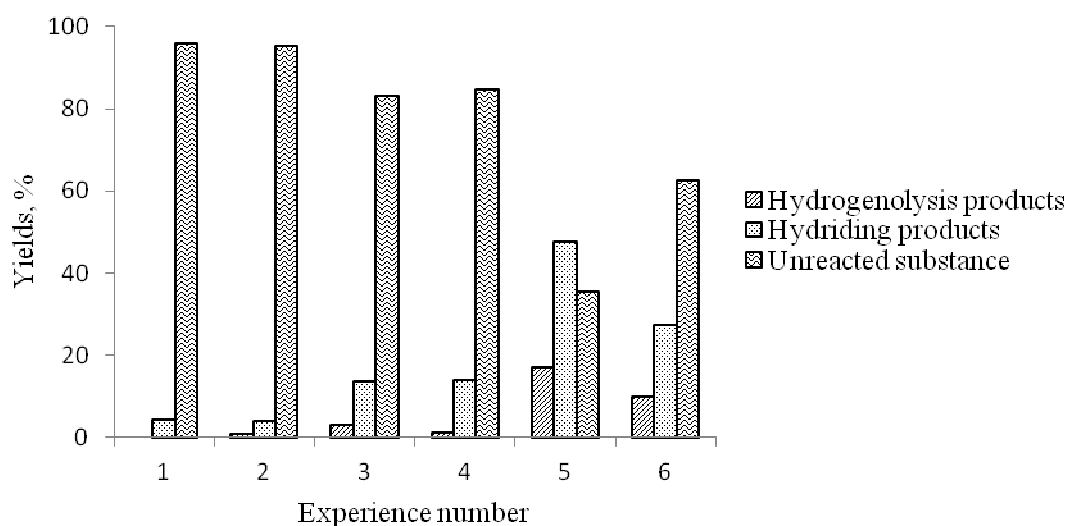


Figure 4. The yield of the hydrogenolysis and hydriding products of phenanthrene hydrogenation (experience numbers taken from Table)

It has been established that the yield of hydrogenation products of phenanthrene is 64.5 % in the presence of NiO/SiO₂ covered the ferrosphere, in contrast to the using the ferrosphere as catalytic additive, where the yield of hydrogenation products is 4.8 %. This fact may indicate a synergistic effect.

Conclusions

So the synergistic effect of binary nanocatalysts in the process of phenanthrene hydrogenation was revealed. The results indicated high activity of the catalytic additive NiO/SiO₂ covered the ferrosphere. The high degree of phenanthrene conversion is observed on the hydrogenation in the presence nickel and iron catalytic additives on the ferrosphere. An efficiency range of the studied catalytic additives was obtained on the basis of products yield data: NiO/SiO₂ on the ferrosphere > Fe₂O₃/SiO₂ on the ferrosphere > NiO/SiO₂ > Fe₂O₃/SiO₂ > ferrosphere.

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Д.Е. Айтбекова, Синтай Су, Фэньюнь Ма, А. Түсіпхан, М.И. Байкенов

Каталитикалық жүйелердің фенантрен гидрогенизациясына әсері

Мақалада сутегі доноры ретінде этанолдың қатысуымен фенантренді гидрогенизациялау үрдісінде синтезделген каталитикалық қоспалардың тиімділігі көрсетілген. Каталитикалық қоспалар ретінде ферросфера, ферросфера бетіне қондырылған NiO/SiO₂ және ферросфера бетіне қондырылған Fe₂O₃/SiO₂ қолданылды. Ферросфера Қарағанды ЖЭО-ның энергетикалық күлдерінен алынған. Ферросфера бетіне қондырылған NiO/SiO₂ және Fe₂O₃/SiO₂ каталитикалық қоспалары «дымқыл араластыру» әдісімен алынды. Ферросфераның және ферросфера бетіндегі NiO/SiO₂ және Fe₂O₃/SiO₂ нанокаталитикалық қоспаларының фазалық құрамы, бетінің морфологиясы, орташа өлшемі және таралуы анықталған. Реакция өнімдерінің құрамы 5975C масс-спектрометриялық детекторы бар *Agilent Technologies 7890A* газды хроматографында хромато-масс-спектрометрия әдісімен зерттелді. *NIST 98* масс-спектрлік деректер базасын қолдану арқылы заттарға сәйкестендірілу жүргізілді. Ферросфераға қондырылған NiO/SiO₂ және Fe₂O₃/SiO₂ нанокаталитикалық қоспалардың синергетикалық әсері анықталды. Фенантрен конверсиясының жоғары дәрежесі ферросферадағы никель мен темірдің каталитикалық қоспаларының қатысуымен гидрогенизациясы кезінде байқалады. Фенантрен гидрогенизациясы нәтижесі бойынша каталитикалық қоспалардың тиімділік қатары анықталды: ферросферадағы NiO/SiO₂ > ферросферадағы Fe₂O₃/SiO₂ > NiO/SiO₂ > Fe₂O₃/SiO₂ > ферросфера.

Кілт сөздер: полиароматты көмірсутектер, фенантрен, гидрогенизация, каталитикалық жүйелер, ферросфера, золь-гель әдісі, «дымқыл араластыру» әдісі, көмір.

Д.Е. Айтбекова, Синтай Су, Фэньюнь Ма, А. Тусипхан, М.И. Байкенов

Влияние каталитических систем на гидрогенизацию фенантрена

В статье показана эффективность синтезированных каталитических добавок в процессе гидрогенизации фенантрена в присутствии этанола в качестве донора водорода. В роли каталитических добавок выступали ферросфера, NiO/SiO₂ на поверхности ферросферы и Fe₂O₃/SiO₂ на поверхности ферросферы. Ферросферу извлекли из энергетической золы Карагандинской ТЭЦ. NiO/SiO₂ и Fe₂O₃/SiO₂ на ферросферах получили методом «мокрого смешения». Определены фазовый состав, морфология поверхности, средний размер и распределение частиц ферросфер и нанокаталитических добавок NiO/SiO₂ и Fe₂O₃/SiO₂ на ферросфере. Состав продуктов реакции выявили методом хромато-масс-спектрометрии на газовом хроматографе *Agilent Technologies 7890A* с масс-спектрометрическим детектором 5975C. Идентификацию веществ проводили с использованием масс-спектральной базы

данных *NIST 98*. Было установлено синергетическое действие нанокаталитических добавок NiO/SiO₂ и Fe₂O₃/SiO₂ на ферросфере. Высокая степень конверсии фенантрена наблюдалась при гидрогенизации в присутствии каталитических добавок никеля и железа на ферросфере. По результатам гидрогенизации фенантрена построен ряд эффективности каталитических добавок: NiO/SiO₂ на ферросфере > Fe₂O₃/SiO₂ на ферросфере > NiO/SiO₂ > Fe₂O₃/SiO₂ > ферросфера.

Ключевые слова: полиароматические углеводороды, фенантрен, гидрогенизация, каталитические системы, ферросфера, золь-гель метод, метод «мокрого смешения», уголь.

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A.K. Bayeshova¹, A.M. Kongyratbay¹, F.M. Zhumabay¹,
A. Bayeshov², B. Leska³

¹*Al-Farabi Kazakh National University, Almaty, Kazakhstan;*

²*D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan;*

³*Adam Mickiewicz University in Poznan, Poland*

(E-mail: azhar_b@bk.ru)

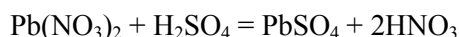
Obtaining of lead (II) sulfate by polarization of bipolar lead electrodes with alternating current

The process of electrolysis using bipolar lead electrodes at polarization by alternating current of industrial frequency (50 Hz) in sulfuric acid solutions was studied for the first time. It is shown that the oxidation of lead to the bivalent state on all monopolar and bipolar electrodes takes place in the anode half-period of alternating current. Next, the anode half-period is replaced by a cathode half-period, then the lead electrode becomes a cathode and hydrogen is released on its surface. Lead (II) ions react with sulfate anions in the near-electrode space to form lead (II) sulfate. It was found that the total loss of electrode mass increases with increasing current density up to 1200–1400 A/m², and in the region of 2000 A/m² — significantly decreases, which is associated with increased adverse reactions. In the interval of experiment duration 0.5–2 hours the total loss of electrode mass increases. However, after 2 hours this value remains almost constant. Apparently, lead (II) sulfate begins to be accumulating on the electrodes and interfere with the dissolution process. It was found that when using bipolar electrodes, the mass of lead (II) sulfate is about 2.4 times greater at the same current strength than when conducting electrolysis with only two monopolar electrodes.

Keywords: lead, bipolar electrode, electrolysis, alternating current, oxidation, anodic half-period, sulfuric acid.

Introduction

Lead (II) sulfate is used in the paint industry as additives in the manufacture of minium [1; 771] for filling the cells of a lead-acid battery plates [2; 519], in the synthesis of certain acids as a necessary component of technological processes, and also performs the role of a stabilizer in the production of plasticized PVC [3, 4]. Obtaining of lead (II) sulfate is usually carried out [1; 771, 5; 322] by precipitation from soluble salts of divalent lead (nitrate, acetate) with sulphuric acid.



The authors of article [6] proposed a method for obtaining lead (II) sulfate by electrochemical dissolution of lead electrode in sulfuric acid during polarization by alternating current of industrial frequency of 50 Hz. In this case, one electrode is a metallic lead and titanium is used as the second electrode. Electrolysis is carried out at a current density of 1500 A/m² on lead electrode and 8000–12000 A/m² on a titanium electrode. The highest current outputs are observed at current densities at the lead electrode equal to 3000 A/m² and reach 53.5 %.

The proposed method has certain disadvantages, which include the fact that the formation of lead (II) sulfate occurs on only one lead electrode in the anode half-cycle of alternating current, as a result of which the productivity of the process is low.

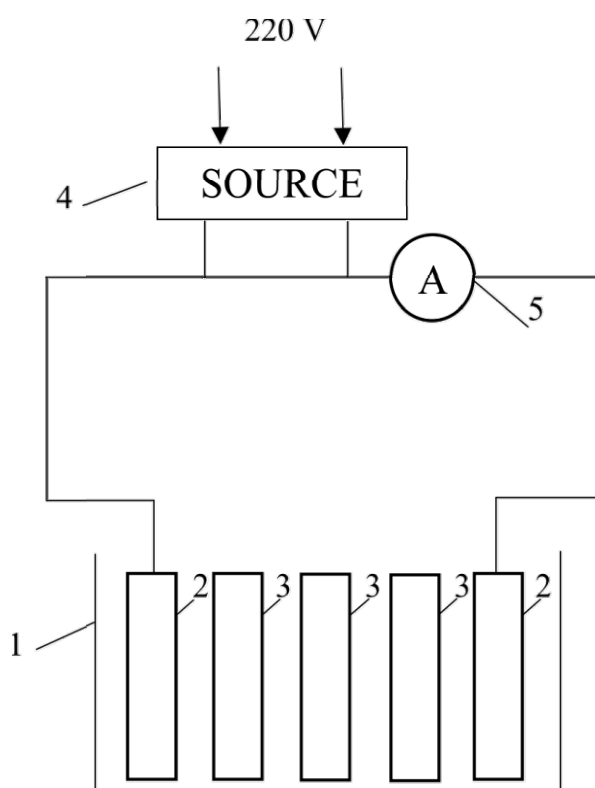
In addition, at high current densities, lead oxidation reactions may occur with the formation of lead oxides, which can contaminate the resulting product. Besides, the use of titanium causes possible contamination of the reaction product with titanium ions, since it is known that during alternating current polarization, titanium also passes into solution [7]. The process of formation of lead (II) sulfate as a result of oxidation of lead sulfide with hydrogen peroxide solution was studied by the authors [8]. It is established that the yield of the product (lead (II) sulfate) and its purity depend on the amount of oxidant.

In connection with the demand in a number of technological processes, the development of new methods for producing lead sulfate seems to be an urgent problem. The aim of our work is to develop a method for producing lead (II) sulfate by electrolysis with polarization by alternating current using bipolar electrodes and, in this regard, to analyze literature sources covering the issues of bipolar electrode connection.

Experimental technique

The unit shown in Figure 1 was used for the research. The unit consists of an electrolyzer (1) in which two extreme monopolar (2) and three (3) bipolar lead electrodes are installed. The electric current of the required power is supplied through SOURCE (MATRIX of single-phase TDGC-1 1 KVA, 4A), the magnitude of current measured by the ammeter (laboratoryA-meterE538). Lead plates of C-1 grade were used as electrodes, electrolyte solutions were prepared from sulfuric acid of chemically pure grade. The electrolysis was carried out with polarization by alternating current of industrial frequency (50 Hz). Two electrodes were attached to the current source, located closer to the wall of the electrolyzer, which are conventionally called «terminal». Between them three more electrodes were installed vertically and parallel to each other. The distance between them was equal to 1.4 cm. Surface area of all electrodes were the same and equal to 12.5 cm². The electrolyzer was made of plexiglass and had a rectangular shape.

The electrodes were placed in such a way that there were no large gaps between the side walls of the electrolyzer and the electrodes. Before the experiment, the lead electrodes were thoroughly cleaned with sandpaper, washed with water and treated with alcohol. After electrolysis, the electrode mass loss was determined by weighing.



1 — electrolyzer; 2 — monopolar electrodes; 3 — bipolar electrodes;
4 — adjustable electric source; 5 — ammeter

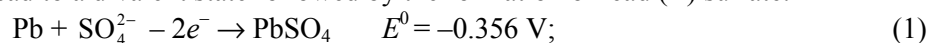
Figure 1. Schematic diagram of the installation for the obtaining of lead (II) sulfate by electrochemical method

The effect of the current density and duration of the experiment on the mass loss of lead electrodes was studied. As a result of electrolysis in the electrode spaces in the solution, the interaction of lead ions with sulfate ions occurred with the formation of lead (II) sulfate, which in the form of a white precipitate fell to the bottom of the cell. After the experiment, the electrolyte was filtered, the precipitate was separated from the solution, washed with water and dried. The sediment was identified by x-ray fluorescence, x-ray phase and elemental analysis methods.

Results and discussion

As it is known from the literature [9; 178, 10], anodic polarization of lead in an aqueous solution of sulfuric acid may result in the following electrode reactions:

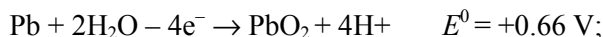
1) oxidation of metallic lead to a divalent state followed by the formation of lead (II) sulfate:



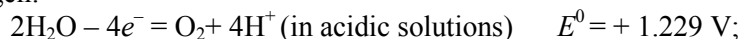
2) oxidation of divalent ions of lead to a tetravalent state with the formation of lead dioxide:



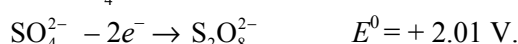
3) direct oxidation of metallic lead to tetravalent state:



4) release of oxygen:



5) the possible discharge of ions SO_4^{2-} with the formation of acid:



Of the several possible reactions at the anode, first of all, the one that requires the lowest energy costs, i.e. a reaction with more negative potential, i.e. a reaction (1), should occur. It was found [11; 339] that a fairly dense porous layer of lead sulfate is formed on the surface of the lead electrode. After a certain time, the reaction (2) takes place, i.e. the formation of lead dioxide, the reaction of the formation of lead sulfate completely stops, although the supply of metallic lead has not been used up yet. Passivation occurs when the thickness of the lead sulfate layer is about 1 μm .

In contrast to the known methods of electrolysis, our experiments were carried out under the influence of alternating current of industrial frequency using bipolar electrodes.

It is known [12; 35] that electrolyzers with mono- and bipolar inclusion of electrodes in the DC circuit are used in electrochemistry. In a monopolar circuit, all electrodes of the same sign are connected to the corresponding pole of the current source. In this case, the current passing through one electrode, in accordance with the law of parallel connection of conductors is equal to the total current divided by the number of electrodes. The voltage that occurs between a pair of electrodes of the opposite sign is equal to the total voltage on the electrolyzer.

In the bipolar scheme of inclusion of electrodes, the current is supplied only to the terminal electrodes, which are monopolar electrodes. All other electrodes located between the terminal monopolar electrodes have no current leads and work as bipolar — one side of the electrode is the cathode, and the other is the anode. Through each cell of the bipolar electrolyzer all the current coming from an external current source passes and the total voltage is equal to the product of the voltage on one cell by the number of cells. It is noted [13] that when sufficient voltage is applied to the solution in which the bipolar electrode (BPE) is immersed, oxidation and reduction reactions occur on the opposite sides of the BPE. Since no direct electrical contact with a current source is required to activate redox reactions, large electrode arrays can be controlled by only one DC source or even a battery in an electrochemical circuit. The wireless aspect of the BPE also allows for electrosynthesis and screening of new materials for a wide range of applications. Additionally, the bipolar connection of the electrodes allows the movable electrodes, called microswitch to move freely in the solution. Practical application of bipolar electrodes is widespread in water electrolysis [14; 39, 15; 97, 126]. The advantages of electrolyzers with bipolar electrodes are compact design, there is no need to supply current to each electrode, the ability to impose high voltages. Advantages of electrolyzers with bipolar electrodes are compact design, no need to supply current to each electrode, the ability to impose large voltages.

Known literature sources [16] present the results on study using bipolar electrodes and show that the effective removal of fluoride ions from water occurs when the electrodes are bipolar.

In addition, in the review [17], the authors note the prospects for the use of bipolar electrodes, using the expression «bipolar electrochemistry». They stress that this method of electrolysis has attracted new interest in the last two decades, due to the use in several fields — from materials science to sensing and so on.

The same review presents new examples of the use of the bipolar connection, focused on the sensing of electrotransplantations, the electrodeposition and the use of graphene as a bipolar electrode.

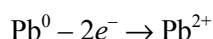
The authors of [18] demonstrated that bipolar electrode coupling can be used for high-performance corrosion tests covering a wide range of potentials in one experiment, and that this, combined with rapid image analysis, is a simple and convenient way to verify the corrosion properties of conductive materials.

Interesting studies have been carried out in the work of the authors [19]. They show that the rotation of the bipolar electrode in a constant electric field between the supply electrodes causes an alternating bipolar current with alternating current frequency, which depends on the rotation speed.

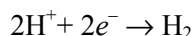
It should be noted that the use of bipolar connection of electrodes in direct current polarization is described in the known literature sources.

In this report, we present the results of the use of bipolar connection of lead electrodes at polarization by alternating current of industrial frequency. In this regard, we note: it was previously shown [20; 43, 21] that when metals are polarized by alternating current, the anode half-period of the alternating current is quickly replaced by the cathode half-period. In this regard, oxidation processes can occur in the anode half-cycle.

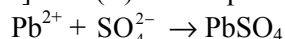
But at the same time, changing the direction of the alternating current does not favor the flow of all possible anode processes. Consequently, in the case of alternating current polarization of lead in the anode half-period, the reaction first proceeds, which has a more negative potential, i.e. oxidation of lead to the divalent state:



Then, in a matter of seconds, the anode half-cycle is replaced by the cathode half-cycle, i.e. the lead electrode becomes the cathode and hydrogen is released on its surface:



Bivalent lead ions formed in the near-electrode space interact with sulfate anions. Due to the low value of the solubility product ($1,6 \cdot 10^{-8}$) [22; 739] lead (II) sulfate precipitates to the bottom of the electrolyzer:



Bubbles of hydrogen release carry crystals of lead sulfate formed from the electrode surface. The described processes are periodically repeated with a change in the direction of the current depending on its frequency, i.e. in our case 50 times per second. It becomes possible to purposefully proceed with the formation of lead sulfate (II). Moreover, when using bipolar electrodes, the oxidation reaction of lead occurs on those electrodes that are not directly connected to the current source. In the cathode half-cycle, the reduction of lead ions to the elemental state does not occur, since this reaction proceeds with a high overvoltage.

We have studied the effect of current density on the mass loss of lead electrodes during alternating current polarization in the presence of bipolar electrodes. As shown in Table 1, the mass loss of monopolar and bipolar electrodes increases with increasing current density to 1200–1400 A/m², and significantly decreases in the region of 2000 A/m², which is associated with increased adverse reactions. Terminal monopolar electrodes are conventionally designated 2¹ and 2², bipolar electrodes located between them — 3¹, 3² and 3³.

Table 1

Effect of current density on the mass loss of monopolar and bipolar lead electrodes during alternating current polarization ($C(\text{H}_2\text{SO}_4) = 150 \text{ g/l}$; $\tau = 0.5 \text{ hour}$)

Magnitude of mass loss	Current density, A/m ²					
	800	1000	1200	1400	1600	2000
$\Delta m (2^1)$	0.1272	0.1892	0.2348	0.2512	0.2214	0.2095
$\Delta m (3^1)$	0.0813	0.1406	0.1413	0.1411	0.1402	0.1344
$\Delta m (3^2)$	0.0675	0.0928	0.0959	0.0952	0.0822	0.0811
$\Delta m (3^3)$	0.0914	0.1371	0.1368	0.1485	0.1236	0.1208
$\Delta m (2^2)$	0.1244	0.1912	0.2125	0.2487	0.2257	0.2136
Σm		0.7509	0.8213	0.8847	0.7931	0.7594

Figure 2 graphically shows the dependence of the mass loss of one monopolar electrode — 2¹ and the total decrease in the mass of the electrodes from the current density. We note that the values of the mass loss of monopolar and bipolar electrodes are quite close to each other, in this regard, these values are not graphically reflected, but are given in detail in Table 2.

As shown in Table 1, the dissolution process of the electrodes is intense at a current density of 1200–1400 A/m², the rate of electrochemical dissolution is reduced at 2000 A/m², as the reverse process.

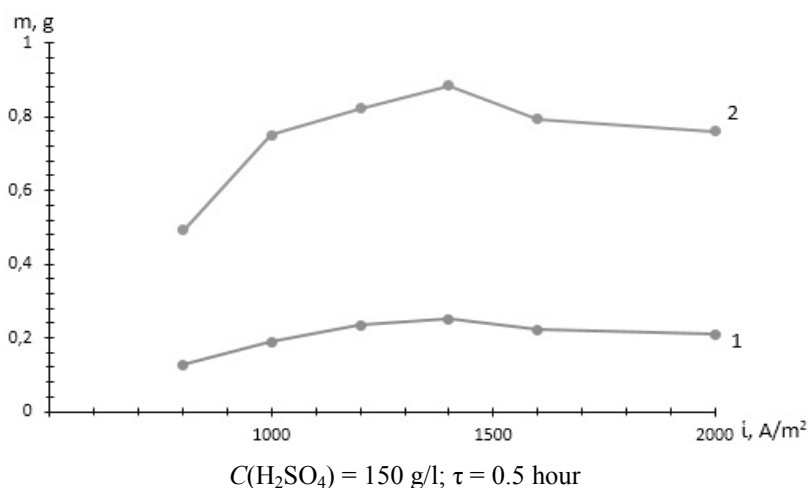
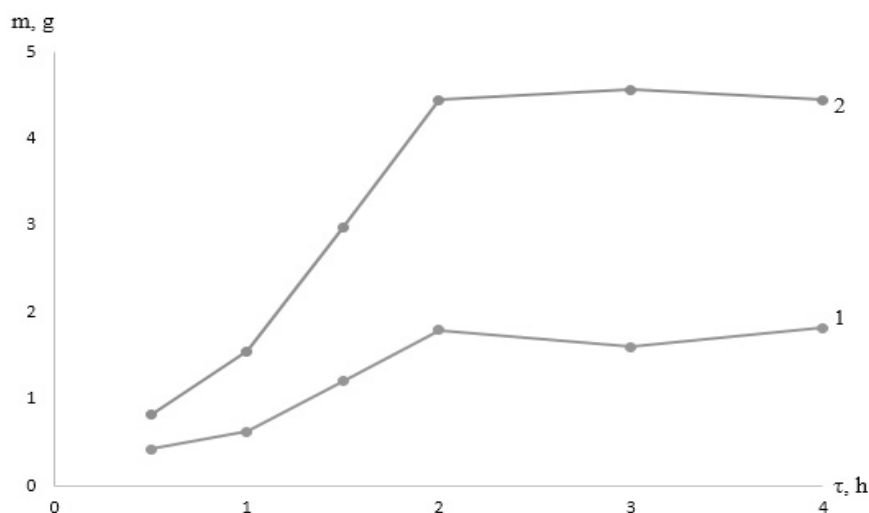


Figure 2. Dependence of the mass loss of one monopolar (2^1) electrode (curve 1) and the total mass loss of all electrodes (curve 2) on the current density on the electrodes

The study of the effect of the duration of the experiment showed that in the range of 0.5–2 hours the total mass of lead ions transferred to the solution increases (Fig. 3, curve 2). However, after 2 hours the mass remains almost constant. Apparently, the resulting lead sulfate begins to accumulate on the surface of the electrode and prevent the process of dissolution of the metal electrode. Table 2 shows the values of the mass loss of monopolar and bipolar lead electrodes depending on the duration of electrolysis.



1 — in electrolysis with monopolar electrodes; 2 — in electrolysis with bipolar electrodes;
 $i = 1200 \text{ A/m}^2$; $C(\text{H}_2\text{SO}_4) = 150 \text{ g/l}$

Figure 3. Dependence of the total mass of lead ions (m , g), passed into the solution of the duration of the experiment

The results of the experiments show that the mass loss of two monopolar (terminal) electrodes have similar values. Also, the values of the mass loss of two bipolar electrodes located next to the terminal monopolar ones are quite close, although their values are slightly lower than the mass loss of the two extreme monopolar electrodes. Nevertheless, in the case of dissolution of each monopolar and each bipolar electrode, it is noticeable that after 2 hours the mass loss remains practically unchanged. Note that the Table shows the values of the mass loss of all electrodes, and the Figure shows only the curve of the total mass loss of all electrodes (monopolar and bipolar) and for comparison shows the curve of the mass loss of only one monopolar electrode.

Table 2

Effect of the duration of the experiment on the dissolution of monopolar and bipolar electrodes in sulfuric acid during industrial alternating current polarization, $i = 1200 \text{ A/m}^2$, $C(\text{H}_2\text{SO}_4) = 150 \text{ g/l}$

Magnitude of mass loss	Electrolysis duration, hour					
	0.5	1	1.5	2	3	4
$\Delta m (2^1)$	0.2348	0.4112	0.8255	0.9748	0.9684	0.9538
$\Delta m (3^1)$	0.1413	0.2939	0.5584	0.8283	0.9148	0.8481
$\Delta m (3^2)$	0.0959	0.1771	0.2011	0.8108	0.8871	0.7811
$\Delta m (3^3)$	0.1368	0.2921	0.5546	0.8384	0.8916	0.8943
$\Delta m (2^2)$	0.2125	0.3811	0.8369	0.9961	0.9088	0.9783
Σm	0.8213	1.5554	2.9765	4.4484	4.5707	4.4556

In order to show the advantages of using bipolar electrodes, experiments with two monopolar electrodes were conducted separately. A comparison of the results of electrolysis carried out using two electrodes and electrolysis using five electrodes showed that during electrolysis using two monopolar and three bipolar electrodes, the oxidation of lead in sulfuric acid with the formation of lead sulfate is intensified more than 2.4 times. Table 3 shows the results of the process of dissolution of lead electrodes in bipolar compounds (5 electrodes in total) and in monopolar (2 electrodes in total) compounds under industrial alternating current polarization.

Table 3

Comparison of the total mass that passed into the solution in experiments with 5 electrodes and 2 electrodes

Electrolysis duration, hour	0.5	1	1.5	2	3	4
Σm (in the experience with 5 electrodes)	0.8213	1.5554	2.9765	4.4484	4.5707	4.4556
Σm (in the experience with 2 electrodes)	0.43	0.6315	1.2101	1.7997	1.6037	1.825
n	1.91	2.46	2.46	2.47	2.85	2.41

Note. Table «n» shows how many times more dissolved lead electrode using five electrodes compared to the experience with two lead electrodes.

In our experiments the prospects of bipolar connection of electrodes at polarization by industrial alternating current with frequency of 50 Hz are shown. The rapid change of the current direction on the electrodes noted above contributes to the fact that lead oxidation reactions stop at the first stage and the phenomenon of electrode passivation is practically not observed due to the formation of electrically conductive oxide compounds directly on the electrode surface.

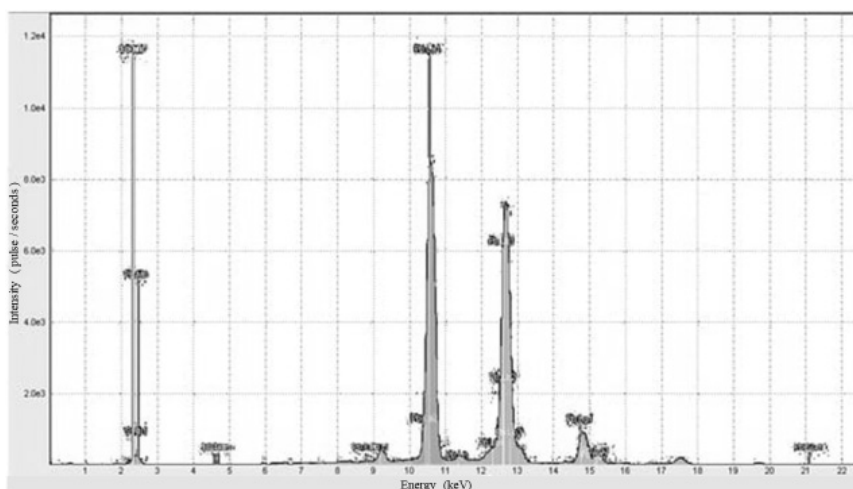


Figure 4. X-ray Fluorescence analysis of lead (II) sulfate obtained by using bipolar electrodes during alternating current polarization

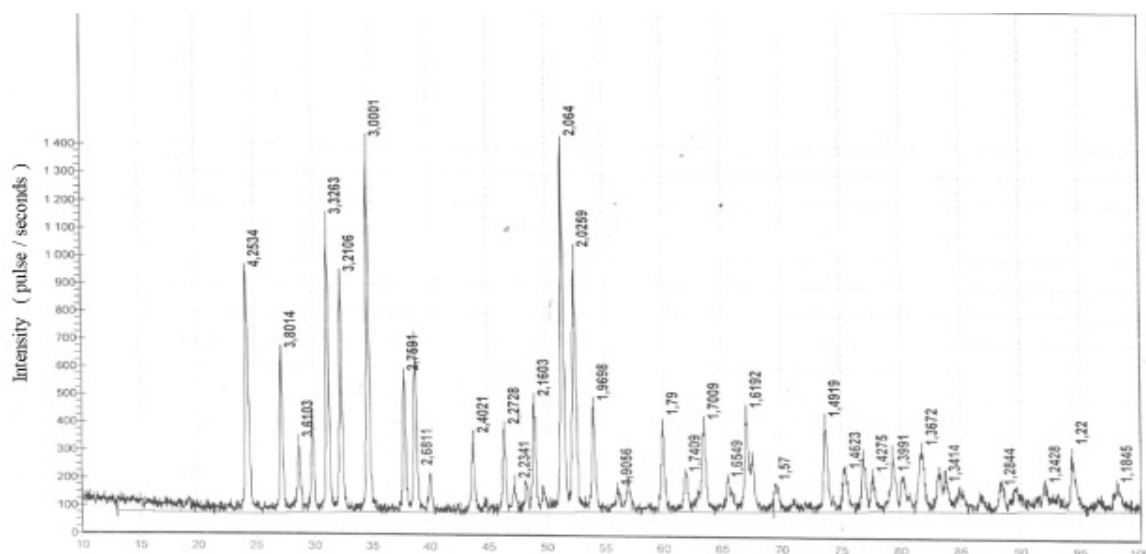


Figure 5. Diffractogram of lead (II) sulfate obtained by using bipolar electrodes during alternating current polarization

The composition and purity of the resulting lead (II) sulfate were determined by x-ray fluorescence, elemental and x-ray phase analysis methods (Fig. 4 and 5). It is shown that all the reflexes of the x-ray belong to lead (II) sulfate, i.e. to PbSO_4 , the ratio of the elements allow us to judge the production of lead sulfate PbSO_4 of high purity.

Conclusions

Thus, this article presents a number of literature data on the electrochemistry of lead and bipolar connection of electrodes. For the first time, the process of dissolution of bipolar lead electrodes under alternating current polarization with an industrial frequency of 50 Hz was studied. It was found that when using BPE, the mass of the resulting lead (II) sulfate is approximately 2.4 times greater at the same current strength in the electrochemical circuit than during electrolysis with only two monopolar electrodes.

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А.К. Баешова, А.М. Қоңыратбай, Ф.М. Жұмабай, А. Баешов, Б. Леска

Биполярлы қорғасын электродтарын айнымалы токпен поляризациялау арқылы қорғасын (II) сульфатын алу

Алғаш рет өндірістік жиіліктегі (50 Гц) айнымалы токпен поляризациялау арқылы күкірт қышқылы ерітінділерінде биполярлы (БПЭ) қорғасын электродтарын пайдаланумен электролиз процесі зерттелді. Айнымалы токтың анодты жартылай периодында қорғасынның екі валентті күйге дейін барлық монополярлы және биполярлы электродтарда тотығатыны көрсетілді. Содан кейін анодты жартылай период катодты жартылай периодқа ауысады, демек, қорғасын электроды катод қызметін атқарады және оның бетінде сутек бөлінеді. Екі валентті қорғасын иондары электрод аумағындағы кеңістікте сульфат-аниондарымен әрекеттеседі де, қорғасын (II) сульфаты түзіледі. Қорғасын электродтарының массасының азаю мөлшеріне ток тығыздығының әсері зерттелді. Электродтардың массаларының жиынтықты түрде азаю мөлшері ток тығыздығын 1200–1400 А/м²-ге дейін арттырғанда көбейетіні, ал 2000 А/м² аумағында — айтарлықтай төмендейтіні көрсетілген, бұл қосымша реакциялардың жылдамдығының артуына байланысты. Тәжірибе ұзақтығының 0,5–2 сағат аралығында электродтар массасының азаю мөлшері артады. Бірақ 2 сағаттан кейін — бұл шама тұрақты қалыпқа түседі. Мұның себебі, электродтар бетінде қорғасын (II) сульфаты жинақталады да, еру процесіне кедергі келтіре бастайды деп болжауға болады. БПЭ қолданған кезде түзілген қорғасын (II) сульфатының массасы екі монополярлы электрод қолданып жүргізген электролизбен салыстырғанда, бірдей ток күшінде, жуық шамамен 2,4 есе артық екені анықталды.

Кілт сөздер: қорғасын, биполярлы электрод, электролиз, айнымалы ток, тотығу, анодтық жартылай период, күкірт қышқылы.

А.К. Баешова, А.М. Коныратбай, Ф.М. Жумабай, А. Баешов, Б. Леска

Получение сульфата свинца (II) при поляризации биполярных свинцовых электродов переменным током

Впервые изучен процесс электролиза с использованием биполярных (БПЭ) свинцовых электродов при поляризации переменным током промышленной частоты (50 Гц) в растворах серной кислоты. Показано, что в анодном полупериоде переменного тока протекает окисление свинца до двухвалентного состояния на всех монополярных и биполярных электродах. Далее анодный полупериод сменяется катодным полупериодом, тогда свинцовый электрод становится катодом и на его поверхности выделяется водород. Ионы свинца (II) взаимодействуют с сульфат-анионами в приэлектродном пространстве с образованием сульфата свинца (II). Установлено, что суммарная убыль массы электродов возрастает с увеличением плотности тока до 1200–1400 А/м², а в области 2000 А/м² — заметно уменьшается, что связано с усилением побочных реакций. В интервале продолжительности опыта 0,5–2 ч суммарная убыль массы электродов увеличивается. Однако после 2-х ч эта величина практически остается постоянной. По-видимому, сульфат свинца (II) начинает накапливаться на электродах и препятствовать

процессу растворения. Установлено, что при использовании БПЭ масса сульфата свинца (II) больше примерно в 2,4 раза при одинаковой силе тока, чем при проведении электролиза только с двумя монополярными электродами.

Ключевые слова: свинец, биполярный электрод, электролиз, переменный ток, окисление, анодный полупериод, серная кислота.

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U. Besterekov¹, A.D. Kydyralieva¹, I.A. Petropavlovskiy², M.M. Yeskendirova¹,
K.N. Urakov¹, I.A. Pochitalkina², A.A. Bolysbek¹

¹M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

²D. Mendeleev Russian Chemical Technological University, Moscow, Russia
(E-mail: aziza_kydyralieva@mail.ru)

Mass balance calculations of processes of ammonia saltpeter thermal decomposition and nitric acid absorption of ammonia

The ability of ammonia saltpeter to decompose at elevated temperatures causes a rather serious concern both its manufacturers and its consumers as for this reason the ammonia saltpeter quality and value meet the modern market requirements in incomplete measure. The purpose of present research is the material assessment of effect of the ammonia saltpeter solution concentration on its thermal decomposition degree, and also determination of conditions of as much as possible complete recycling of the product of its decomposition — ammonia — using a water solution of nitric acid. Scientific-applied importance of the research lies in the fact that its results will allow us to solve the questions concerning the quantitative dependence of ammonia saltpeter thermal decomposition degree and ammonia recycling on initial concentration of ammonia saltpeter and nitric acid solutions. During the experiments the quantitative and qualitative changes, observed in the ammonia saltpeter and nitric acid solutions, were judged by readout of the pH instrument placed in the absorption medium. It was established, that the higher the ammonium nitrate concentration and the lower the nitric acid concentration in their initial solutions are, the lower the ammonia saltpeter thermal decomposition degree is. And vice versa, the lower the ammonium nitrate concentration and the higher the nitric acid concentration in their initial solutions are, the higher the ammonia saltpeter decomposition degree is. The experimental study was implemented using a modelling laboratory installation, which can be recommended to use at the development of an industrial technological line of ammonia recycling.

Keywords: ammonia saltpeter, ammonia, nitric acid, absorption, solution, thermal decomposition, technology, production

Introduction

It is generally known that ammonia saltpeter is inclined to thermal decomposition [1]. As a result a certain part of marketable ammonia saltpeter, both at plant conditions and at its storage, transportation and practical use as a basic nitrogen-containing fertilizer, is irrevocably lost decomposing into nitric acid and ammonia. Simultaneously its qualitative measures and consumer properties become worse. For this reason obtaining the reliable information about the scale of nitrogen loss and material damage of the ammonia saltpeter thermal decomposition is of great importance.

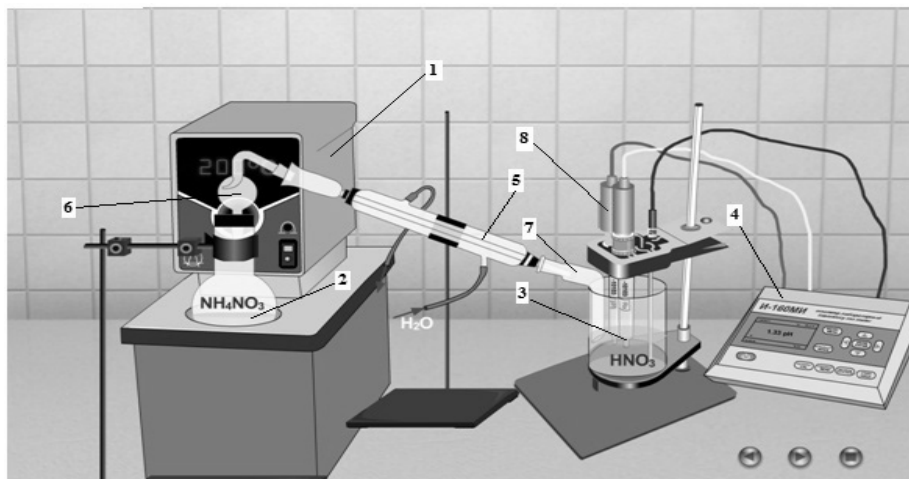
At present judging by the published data including the latest information [2], balance data about the weights of thermally decomposed part of ammonia saltpeter and products of its decomposition — ammonia and nitric acid — are absent. In addition there is no sufficiently scientifically and experimentally substantiated information about recycling the gaseous product of the ammonium nitrate thermal decomposition — ammonia [3]. In this connection planning and organization of researches connected with working out of mass balances for the processes of ammonia saltpeter thermal decomposition and nitric acid absorption of ammonia are actual problems. For solving the assigned research tasks the experimental setup has been developed, which allowed us practically completely to recover the ammonia formed at the thermal decomposition of ammonium nitrate solutions with various concentrations.

Experimental techniques

The research was implemented under laboratory conditions of chair «Chemical technology of inorganic substances» of M. Auezov South Kazakhstan State University using model solutions of the ammonia saltpeter produced at joint-stock company «Kazazot» [4] with concentration of 7.45 mol/l and 11.76 mol/l. All the solutions contained the same mass of the granulated ammonia saltpeter. Nitric acid water solutions with concentration of 0.05 mol/l, 0.1 mol/l, 0.2 mol/l, 2.0 mol/l were used as absorbents. In all cases the residual nitric acid content in a waste absorption solution was determined based on the consumption of a 0.1N sodium hydroxide solution used for its neutralisation. At implementation of the experiments a temperature re-

gime of the ammonium nitrate thermal decomposition from its solutions was maintained by means of a thermostat (LOIP LT-200); the working solution used in the thermostat was a water-glycerine mixture. It made possible to heat an ammonia salt peter solution in the thermostat to 150 °C.

A main indicator of course of the experiments was pH of an ammonia salt peter initial solution and a final water nitric acid solution. For measurement of pH of the above mentioned solutions we applied an ion meter I-160 MI. The experimental laboratory setup is represented in Figure.



1 — a thermostat LOIP LT-200; 2 — an ammonia salt peter solution; 3 — a nitric acid solution; 4 — an ion meter I-160 MI; 5 — a backflow condenser; 6 — a drop catcher; 7 — an adapter; 8 — electrodes

Figure. The model experimental installation for studying the ammonia salt peter thermal decomposition and nitric-acid ammonia absorption processes

An ammonia salt peter solution of the necessary concentration was poured in flask (2) which was tightly closed with the cover with drop catcher (6) built-in in it. The drop catcher was connected to backflow water condenser (5), which output end was joined to adapter (7). The lower end of the adapter was dipped into an absorption nitric acid solution in absorber (3). A vessel with the ammonia salt peter solution was immersed in the thermostatic liquid in thermostat (1). Electrodes (8) of ion meter (4) were placed in the absorber filled with a nitric acid solution (3). The thermostat maintained the specified temperature regime of boiling the ammonia salt peter solution (110 °C for concentration of 7.45 mol/l, 120 °C for concentration of 11.76 mol/l). At the specified temperatures the ammonium nitrate, contained in the solutions, was partially decomposed according to the reaction:



At the steady boiling conditions the water vapour and gaseous ammonia liberated from the ammonia salt peter solution in the flask were fed in the backflow water condenser, where they condensed and became cool, and then they mixed with the nitric acid solution in the absorber. As a result, the volume of the nitric acid solution was increasing at its simultaneous neutralisation with the gaseous ammonia giving an ammonia salt peter solution under the reaction:



In the sequel when a certain part of the water, contained in the solution, has been evaporated, the solution concentration has increased, and the solution in the thermostat has stopped to boil at the given temperature we specified the following temperature regime corresponding to the boiling temperature of the solution with raised concentration. In the process the new concentration and boiling temperature of the investigated solution were determined each time by means of the calculation taking into account the weight of the evaporated water which has got to the absorber together with the absorbed ammonia. Transition from the water solution of ammonia salt peter to its melt with the final boiling temperature not above 150 °C was the indication of the termination of the ammonia salt peter thermal decomposition process.

Results and Discussion

The data about the initial and final composition and properties of water solutions of ammonia salt-peter and nitric acid, and also results of the implemented experiments are represented in Table 1 [5].

Table 1

The initial data and the research results

No.	Ammonia salt-peter solution (AS)					Nitric acid solution (NA)							AS thermal decomposition degree, %
	Initial solution			Melt		Initial solution			Waste absorbent				
	pH	C, mol/l	t, °C	C, mol/l	t, °C	pH	C, mol/l	t, °C	pH	C _{res} ^{NA} , mol/l	t, °C	C _{form} ^{AS} , mol/l	
1	4.75	11.76	25	17.6	200	1.30	0.05	25	1.69	0.020	27	0.008	0.06
2	4.75	11.76	25	17.6	200	1.00	0.10	25	1.59	0.026	27	0.031	0.26
3	4.80	11.75	25	17.6	200	0.70	0.20	25	1.24	0.058	27	0.056	0.40
4	5.10	7.45	25	17.6	200	0.21	2.00	25	0.68	0.210	30	0.415	5.50

Material calculations of the studied process were performed on the basis of the data presented in Table 1, which are the arithmetical mean of not less than three experiments. The calculations were made for 1000 kg of ammonia salt-peter. Taking into consideration the standard requirements to its quality according to State Standard 2–2013 [6] this quantity contains 988 kg of pure ammonia salt-peter.

Results of the mass balance calculations are represented in Tables 2, 3.

Table 2

Initial material balance data on a composition of experimental ammonia salt-peter and nitric acid solutions per 1000 kg of dissolved ammonia salt-peter

No.	Initial ammonia salt-peter solution	kg	No.	Initial nitric acid solution	kg
1	NH ₄ NO ₃	1000	1	HNO ₃ (100 %)	6.3
	including:		2	H ₂ O solvent	494.5
	NH ₄ NO ₃	988			
	H ₂ O (1 %)	9.98			
	Insoluble residue (0.2 %)	2.00			
	HNO ₃ initial residual	0.0123			
2	H ₂ O solvent	400			
	Total mass	1400		Total mass	500.8

Table 3

Final balance data on a composition of waste experimental ammonia salt-peter and nitric acid solutions per 1000 kg of initial dissolved ammonia salt-peter

No.	Final ammonia salt-peter solution	kg	No.	Final nitric acid solution	kg
1	NH ₄ NO ₃ melt	1006.31	1	NH ₄ NO ₃ formed	3.936
	including:			including:	
	NH ₄ NO ₃	984.06		NH ₃ absorbed	0.836
	H ₂ O	17.14	HNO ₃ (100 %) neutralized	3.100	
	Insoluble residue	2.00	2	HNO ₃ (100 %) residual	3.200
	HNO ₃ initial residual	0.0123		3	H ₂ O solvent
	HNO ₃ (100 %) formed	3.1	H ₂ O condensed		392.84
	Total mass	1006.31		Total mass	894.48

As follows from the data of Tables 2 and 3, at the conditions of the experiment 3 (Table 1) only 3.936 kg of ammonia salt-peter was decomposed from its general mass of 988 kg. The residual mass of ammonia salt-peter in the melt formed was 984.06 kg. Thus the ammonia salt-peter thermal decomposition degree is 0,4 %. As the result of thermal decomposition of the above mass of ammonia salt-peter under reaction (1) 0.836 kg of gaseous ammonia was formed, which reacts with the nitric acid contained in the absorption solution in the absorber according to reaction (2) again forming 3.936 kg of ammoniac salt-peter.

During the boiling the initial ammonia saltpeper solution the condensed water vapour formed in the backflow condenser in quantity of 392.84 kg also incomes in the absorber simultaneously with the gaseous ammonia. Thus, after termination of experiment 3 the flask 2 contained 1006.31 kg of the ammonia saltpeper melt formed of 1400 kg of the initial ammonia saltpeper solution, and the weight of the absorption solution in the absorber increased from 500.8 kg to 894.48 kg, respectively.

On the basis of the above mentioned data obtained during the studying the ammonia saltpeper decomposition and nitric acid absorption of the decomposition product — ammonia — we calculated the mass balances of the studied processes on nitrogen (Table 4).

Table 4

Nitrogen content in initial and waste experimental solutions of ammonia saltpeper and nitric acid

No.	Nitrogen content	kg	No.	Nitrogen content	kg
1	2	3	4	5	6
1	In the initial ammonia saltpeper solution: in NH_4NO_3 dissolved	345.80	1	In the final ammonia saltpeper solution: in NH_4NO_3 melt	344.40
	in HNO_3 initial residual	0.00274		in HNO_3 initial residual	0.0027
				in HNO_3 (100 %) formed	0.6888
2	In initial nitric acid solution: in HNO_3 (100 %)	1.40	2	In final nitric acid solution: in NH_4NO_3 formed	1.3776
				in HNO_3 (100 %) residual	0.711
	Total mass	347.20		Total mass	347.20

Conclusions

The obtained results allow us to draw the following conclusions:

1. For the first time in research practice the reliable balance data about thermal decomposition of ammonium nitrate in its boiling solutions and nitric acid absorption of the decomposition product — ammonia — have been obtained.

2. It was established, that at the specified concentration of the initial ammonia saltpeper solution (11.76 mol/l) with increase in nitric acid concentration in the sorption solution the ammonia saltpeper decomposition degree increases approximately in 8 times and makes 0.06 % and 0.40 % at concentration of the sorption solution of 0.05 mol/l and 0.20 mol/l, respectively. It was also noticed, that the simultaneous decrease in ammonia saltpeper concentration in the initial solution (to 7.45 mol/l) and increase in nitric acid concentration in the absorption solution (to 2.0 mol/l) leads to the sharp increase in the ammonia saltpeper decomposition degree (to 5.57 %). These facts can be logically explained as a consequence of the well-known Le Chatelier principle.

3. The assembled and successfully tested experimental setup can be really used as a prototype for development of industrial technological lines for recycling and utilization of ammonia; that is especially important with reference to manufacture of ammonia saltpeper of nitric acid and gaseous ammonia. At the same time, as follows from the analysis of the data obtained, it permits us almost completely to exclude the losses of the raw materials and products unavoidable on operating enterprises.

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У. Бестереков, А.Д. Кыдыралиева, И.А. Петропавловский,
М.М. Ескендинова, К.Н. Ураков, И.А. Почиталкина, А.А. Болысбек

Аммиак селитрасының термиялық ыдырауы және аммиактың азот қышқылды абсорбциясы үрдістерінің баланстық материалдық есептеулері

Аммиак селитрасы өндірушілері мен тұтынушыларын оның термиялық ыдырауға қабілеттілігі, осыған байланысты оның сапалық және құндылық көрсеткіштерінің заманауи нарық талаптарына сәйкес келмеуінен елеулі алаңдатууда. Аммиак селитрасы ерітіндісі шоғырларының оның термиялық ыдырау дәрежесіне әсерін және ыдырау өнімі — аммиактың азот қышқылының судағы ерітіндісінде мүмкіндікті толықтай пайдаға асыру шарттарын сандық бағалау жұмыстың мақсаты болып табылады. Жұмыстың ғылыми-қолданбалық маңыздылығы оның нәтижелерінің аммиак селитрасының термиялық ыдырауы мен аммиакты пайдаға асыру дәрежелерінің, аммиак селитрасы және азот қышқылы ерітінділерінің бастапқы шоғырларына қатысты сандық тәуелділіктерге байланысты сұрақтарға айқындылық беруінде. Аммиак селитрасы мен абсорбенттік бастапқы ерітінділік орталарда байқалынатын сандық және сапалық өзгерістер туралы мәліметтер рН-метрдің көрсеткіштері арқылы тағайындалды. Бастапқы ерітінділерде аммиак селитрасы ерітіндісі шоғыры неғұрлым жоғары, ал азот қышқылы ерітіндісі шоғыры неғұрлым төмен болса, аммиак селитрасының термиялық ыдырау дәрежесі соғұрлым төмен болатыны және керісінше, аммиак селитрасы ерітіндісі шоғыры неғұрлым төмен, ал азот қышқылы ерітіндісі шоғыры неғұрлым жоғары болса, солғұрлым аммиак селитрасының термиялық ыдырау дәрежесі жоғары болатыны анықталды. Тәжірибелік зерттеулер аммиакты пайдаға асырудың өндірістік технологиялық желісін дайындауда қолданылуға ұсыныла алынатын модельдік зертханалық қондырғыда орындалды.

Кілт сөздер: аммиак селитрасы, аммиак, азот қышқылы, абсорбция, ерітінді, термиялық ыдырау, технология, өндіріс.

У. Бестереков, А.Д. Кыдыралиева, И.А. Петропавловский,
М.М. Ескендинова, К.Н. Ураков, И.А. Почиталкина, А.А. Болысбек

Балансовые материальные расчеты процессов термического разложения аммиачной селитры и азотнокислотной абсорбции аммиака

Способность аммиачной селитры к термическому разложению все еще вызывает достаточно серьезную озабоченность как у ее производителей, так и у потребителей, так как вследствие этого качества и ценность аммиачной селитры недостаточно полно отвечают современным рыночным требованиям. Цель работы — материальная оценка влияния концентрации раствора аммиачной селитры на степень ее термического разложения, а также выяснение условий максимально полной утилизации продукта ее распада — аммиака — водным раствором азотной кислоты. Научно-прикладная значимость работы состоит в том, что ее результаты внесут ясность в вопросы, касающиеся количественной зависимости степени термического разложения аммиачной селитры и утилизации аммиака от исходных концентраций аммиачной селитры и азотной кислоты. О количественно-качественных изменениях, наблюдаемых в средах исходных растворов аммиачной селитры и абсорбента, судили по показаниям рН-метра, установленного в абсорбционной среде. Установлено, чем выше концентрация аммиачной селитры и чем ниже концентрация азотной кислоты в их исходных растворах, тем ниже степень термического разложения аммиачной селитры, и, наоборот, чем ниже концентрация аммиачной селитры и чем выше концентрация азотной кислоты в их исходных растворах, тем выше степень термического разложения аммиачной селитры. Экспериментальные исследования выполнены на модельной лабораторной установке, которая может быть рекомендована к использованию при разработке промышленной технологической линии утилизации аммиака.

Ключевые слова: аммиачная селитра, аммиак, азотная кислота, абсорбция, раствор, термическое разложение, технология, производство.

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R.T. Dinzhumanova¹, B.B. Bayakhmetova¹, N.B. Kassenova², A.N. Klivenko³

¹*Semey Medical University, Kazakhstan;*

²*Nazarbayev University, Nur-Sultan, Kazakhstan;*

³*Shakarim State University of Semey, Kazakhstan*

(E-mail: raushan.dinzhuma@mail.ru)

Physico-chemical investigation of stone coals of «Karazhyra» field

Results of physico-chemical research of stone coals from the Karazhyra field presents in this work. The following technical indicators of coals were studied: moisture, ash, yield of volatile component, sulfur content, elemental composition, heat capacity, morphology and particle size. The results of the technical analysis indicate low ash and moisture. X-ray fluorescence spectral analysis indicates the presence of rare earth metals in the composition of coal. The surface morphology and particle size of coal samples were characterized by scanning electron microscopy. Results show that the surface is heterogeneous with areas characterized by a dense structure and porous texture. On the surface also observed micron-sized clusters. The average fraction size is 0–300 millimeters. Areas with a porous texture has a corrugated surface with open slit-like and tunnel-like exits forming a system of pores with a size 2–10 microns. Thermal stability was determined by differential scanning calorimetry. On the sample surface was spectroscopically identified oxygen-containing and nitrogen-containing groups. Coal has a relatively high heat of combustion, a high yield of volatile compounds, characterized by a relatively low ash value, moisture, low sulfur and nitrogen content. Demonstrated the possibility of using the Karazhyra field coals in almost all branches of the national economy.

Keywords: stone coals, spectroscopy, X-ray fluorescence analysis, electron microscopy.

Introduction

Stone coals are the largest source of organic raw materials. Its relevance in the near future is significantly increasing due to the depletion of oil, this predetermines the possibility of use it in almost all branches of the national economy from an elementary household furnace to space vehicles [1–4]. Coal is the most complex organomineral formation, and therefore has variety properties. Deep knowledge is need about the features of the chemical structure and reactivity of the organic component of coal and the role of mineral components in the processing and mining of coal. The increased interest in the coals of the Karazhyra field because of their high quality stimulates the search for new innovative methods of its application. Section «Karazhyra» is a coal-mining enterprise of Kazakhstan located in the East Kazakhstan region, on the territory of the former Semipalatinsk nuclear test site. The area of the deposit is 21.4 km², which located 9 kilometers from the site «Balapan» [5]. Coal reserves are 1.3 billion tons [6]. D grade coal produces in this deposit, and the size of the fraction is 0–300 millimeters [7]. The volume of production for 2017 is about 7–9 million tons. According to the journal «Kazakhstan», the coal of the Karazhyra field is suitable for the production of rare earth metals [8]. Previously, the coal extraction process of the Karazhyra deposit was carried out and optimized on the Soxhlet apparatus with organic solvents [9]. According to the results of the extraction products study by IR spectroscopy and chromatography-mass spectrometry (CMS) was shown a preferential presence of alkanes (38.17 %), aromatic hydrocarbons (7.72 %), naphthenes (6.38 %) and oxygen-containing hydrocarbons (5.53 %).

Experimental

Materials and methods

Moisture. Moisture is an important component of coal, from both scientifically and practically point of view. Moisture is ballast and reduces the useful mass of coal when coal is used as energy fuel. Wet coal ignites faster during storage, it freezes at minus temperature throughout transportation, creates certain difficulties on the heat supply route of the combined heat and power (CHP), etc. According to the results of the analysis, the coals of the Karazhyra deposit are generally characterized by a low analytical moisture content, on average, it is 14.0 %. Content of moisture in the fuel depends on several factors: coal mining technology, transportation and storage conditions, natural factors, petrographic composition of coal, coalification degree, formation depth and ash content.

Ash content is one of the most important and the most variable indicators of coal quality. In the course of field operation, additional dilution of coal by rocks of soil, roof or rock interlayers occurs. The average ash content for the deposit was 19.8 %.

The yield of the volatile components of coal from Karazhyra field is average 47.0 % value and depends on the number of microcomponents of the ininitite group in the composition of coals. Increasing these components reduces the yield of volatile components.

Coals of the Karazhyra field are low-sulfur, the average content of sulfur is 0.4 %.

Elemental composition of coals is closely related to their physical and technological properties [10]. Determination of sulfur, carbon, hydrogen, nitrogen, oxygen and phosphorus content was carried out on the Labsys Evo analyzer (Setaram, France).

Results and Discussion

The results of the technical analysis of coal presented in Table 1. According to this table the studied coal has low ash and humidity.

Table 1

Qualitative characteristics of coal

No.	Indicators	Index	Average value, %
1	Moisture	W	14.0
2	Ash	A	19.8
3	Yield of the volatile components	V	47.0
4	Sulfur	S	0.4
5	Carbon	C	75.5
6	Hydrogen	H	5.3
7	Nitrogen	N	1.7
8	Oxygen	O	16.8
9	Phosphorus	P	0.04

The *qualitative composition* of the carbon samples was determined from group bands in IR spectra, which obtained by IR Fourier spectrometer Cary 660 FTIR (Agilent technologies, USA). Figure 1 shows the IR spectra of the investigated coal. The spectra show peaks characteristic of stretching vibrations of amides, aromatic hydrocarbons, aromatic and aryl alkyl ethers, alcohol hydroxyls (Table 2).

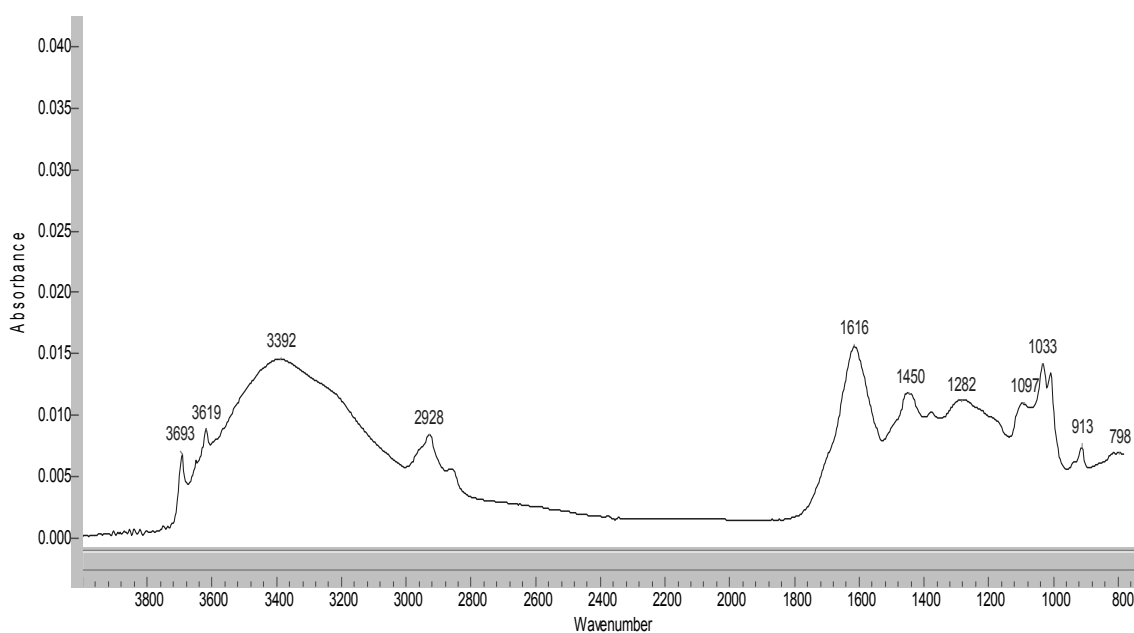


Figure 1. IR spectra of the coal from the «Karazhyra» field

Characteristics of IR spectra of the investigated coal from the «Karazhyra» field

Nature of oscillation	Type of groups	Frequency, cm^{-1}
ν_{OH}	Hydroxyl groups	3693 (m), 3619 (m), 3392 (m)
ν_{CH}	Methylene groups in the benzene ring	2928 (m)
$\nu_{\text{C=C}}$	Double carbon bonds of primary amides	1616 (s)
$\nu_{\text{HC-CH}}$	Unsaturated compounds (aromatic hydrocarbons)	913 (m) – 798 (m)
ν_{COC}	Aromatic and aryl alkyl ethers	1282 (w)
$\nu_{\text{C-O; -OH}}$	Primary alcohols	1097 (m) – 1033 (m)
ν_{CH_2}	Methylene groups	1450 (m)

Note. s — strong; m — medium; w — weak bands.

The investigation of coal samples of the «Karazhyra» field were carried out using an Epsilon X-ray fluorescence spectrometer (Panalytical, Netherlands).

The obtained data are presented in Figure 2 and Table 3. The analysis of XFA showed that the percentage of silicon (5.024 %), aluminum (2.764 %), calcium (2.232 %) exceeds all other indicators. The lowest percentages are zinc (0.008 %), manganese (0.0006 %), chrome (0.011 %). Generally, according to the results revealed 16 elements in the composition of coal.

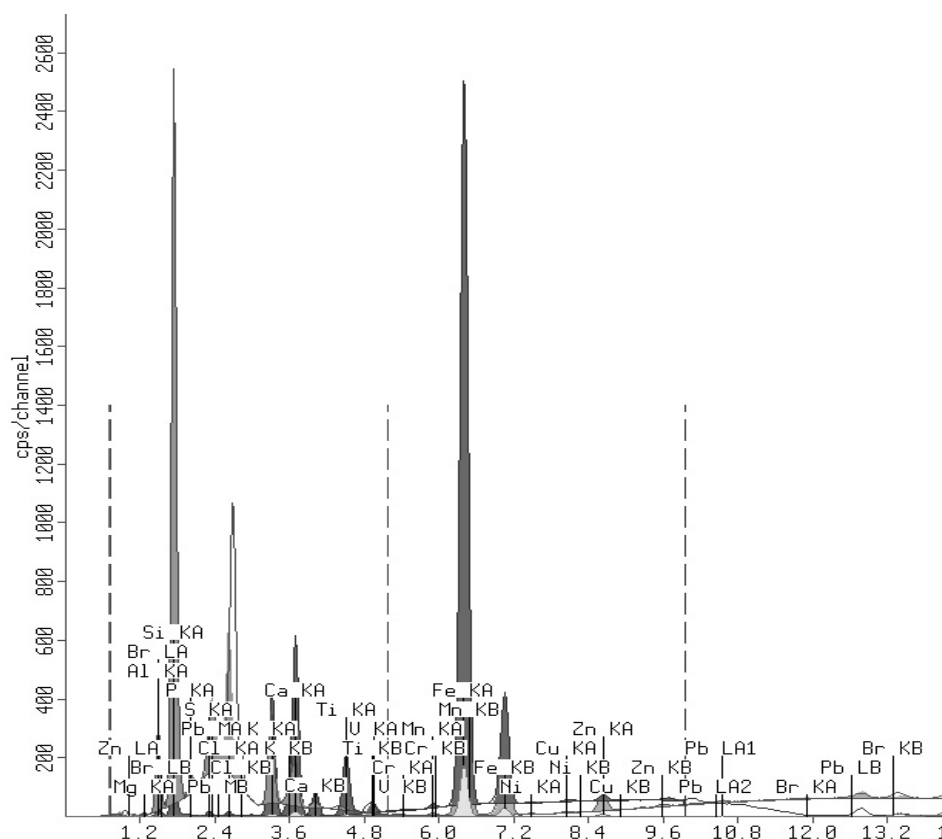


Figure 2. X-ray pattern of the coal sample from the «Karazhyra» field

The morphology and particle size of the coal were determined by scanning electron microscopy (SEM) using a JSM 6390 LM JEOL microscope. Table 4 presents the results of the study. The sample surface is non-uniform with areas characterized by a dense structure and with a porous texture. On the surface also observed clusters with micron size. Areas with a porous texture have a corrugated surface with open slit-like and tunnel-like outcrops forming a pore system with a size of 2–10 μm (Fig. 3, 4).

Table 3

The results of the analysis of the coal sample from the Karazhyra field obtaining by XFA

No.	Element	Sample 1	Sample 2	Sample 3	Average value, %
1	Mg	0.097	0.099	0.095	0.097
2	Al	2.770	2.769	2.755	2.764
3	Si	5.027	5.033	5.012	5.024
4	P	0.432	0.437	0.439	0.436
5	S	1.074	1.070	1.071	1.071
6	Cl	0.445	0.444	0.444	0.444
7	K	0.424	0.426	0.421	0.423
8	Ca	2.235	2.234	2.229	2.232
9	Ti	0.442	0.443	0.441	0.442
10	V	0.021	0.021	0.021	0.021
11	Cr	0.012	0.011	0.011	0.011
12	Mn	0.007	0.006	0.007	0.006
13	Fe	1.469	1.469	1.461	1.466
14	Ni	0.017	0.017	0.017	0.017
15	Cu	0.030	0.030	0.030	0.030
16	Zn	0.008	0.008	0.008	0.008

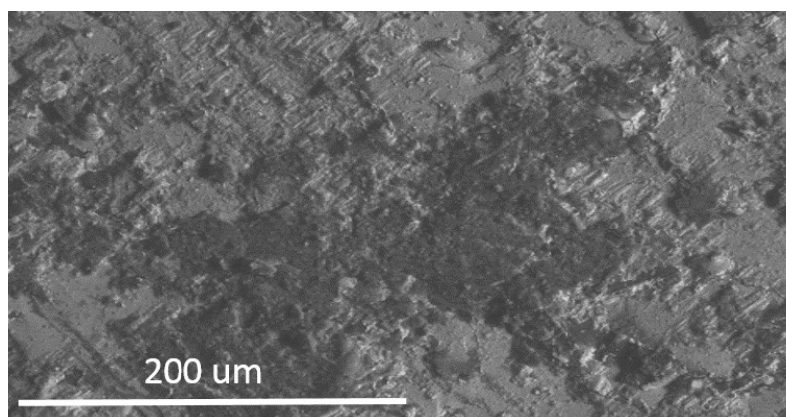


Figure 3. Scanning electron microscope (SEM) image of a sample of coal from the Karazhyra field — a site with a dense morphology of a surface with a porous texture

Based on the data of XFA and SEM, it can be concluded that the results of the analyzes diverge: the use of XFA provides a more accurate and broad list of fixed components in coal composition than SEM. This is due to the fact that XFA allows to explore the entire structure of coal pulverized in powder. A certain section of coal and only the surface are investigated with scanning electron microscopy.

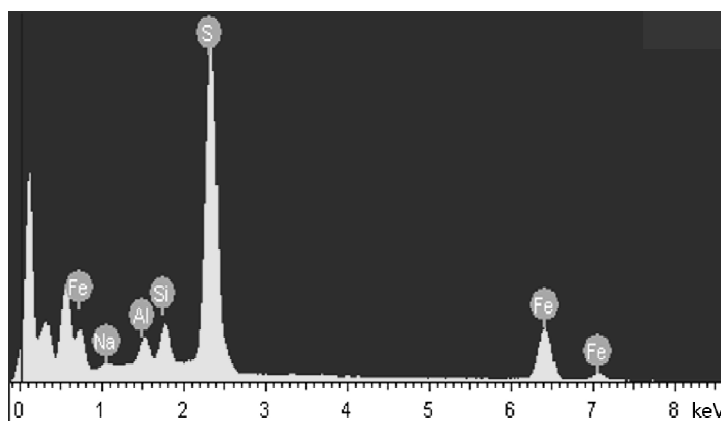


Figure 4. Graph of coal analysis of Karazhyra field by scanning electron microscopy (SEM)

Sample analysis result by SEM, %

No.	Na	Al	Si	S	Fe
Sample 1	2.18	3.39	4.94	49.08	40.42
Sample 2	2.19	3.53	5.09	49.36	39.84
Sample 3	2.06	3.59	5.20	48.91	40.24
Average value	2.14	3.50	5.07	49.12	40.16

Thermal stability of the stone coal samples from the «Karazhyra» field was determined on DSC EVO 131 Setaram by differential scanning calorimetry (DSC) (Research were performed on the basis of the «Institute of Polymeric Materials and Technologies» in Almaty). Based on the analysis given in Figure 5, the moisture of the coal evaporates at temperature 126 °C, and then with further heating of the coal to 750 °C its structure destroyed. In the range 50–75 °C the loss of mass of coal was 67 %.

Heat of combustion is the most important characteristic of thermal properties. The higher heat of combustion for dry ashless state Q_s characterizes the natural type of coal, the degree of its coalification and the material composition. The lowest heat of combustion of the working mass of coal Q_i , expresses the amount of heat that can be practically realized during combustion and directly depends on the ash content and humidity of the coal. On average, the lowest calorific value of coal samples is 4650 kcal/kg, at $A_a = 19.8$ % and $W_a = 14.0$ %.

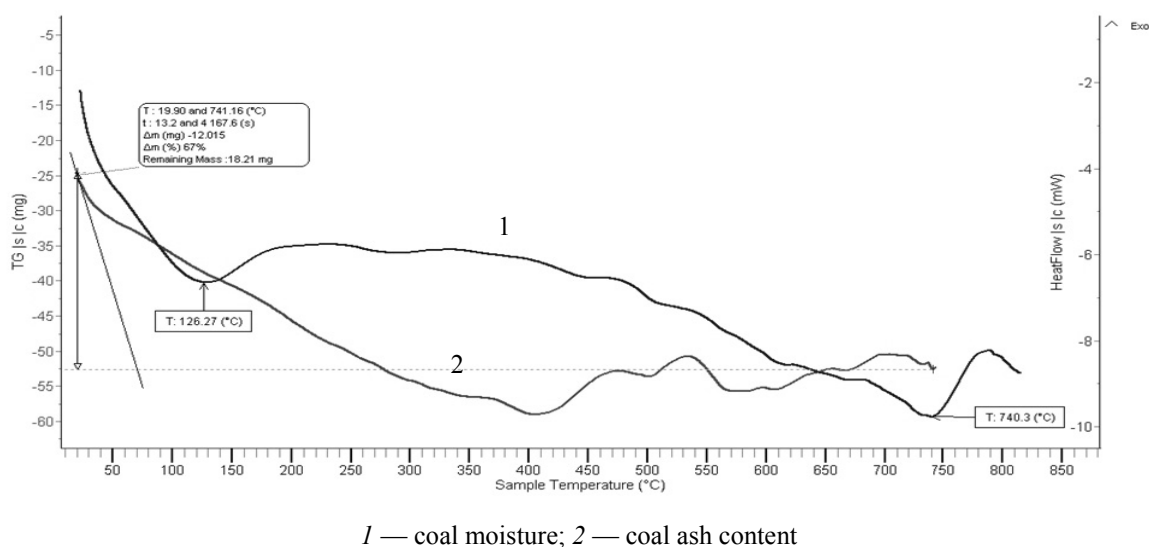


Figure 5. The graph of the interaction of coal from Karazhyra field with heat (with thermal effect)

Conclusion

Thus, the coal of the Karazhyra field belongs to grade D (long-flame), and the fraction size is 0–300 millimeters. Coal has a relatively high heat of combustion, a high yield of volatile compounds, also characterized by a relatively low ash content, and small content of sulfur and nitrogen. Coefficient of grindability of coal is equal to 1.06, so indicates that it is hard coal. With the set of physical methods were identified oxygen and nitrogen containing groups, aromatic compounds, presence of metals. Consequently, the coals of the Karazhyra field are not only good energy fuels, but also an alternative source of raw materials for the chemical industry, and the opportunity to extract it by the open method makes it suitable for use in many areas of the national economy.

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Р.Т. Динжуманова, Б.Б. Баяхметова, Н.Б. Касенова, А.Н. Кливенко

«Қаражыра» кен орны тас көмірін физика-химиялық зерттеу

Мақалада «Қаражыра» кен орны тас көмірінің физика-химиялық зерттеу нәтижелері келтірілген. Көмірдің мына техникалық көрсеткіштері зерттелінді: ылғалдылығы, күлділігі, ұшқыш заттардың шығымы, күкірт мөлшері, элементтік құрамы, жылу сыйымдылығы, бөлшектердің морфологиясы мен өлшемі. Көмірдің техникалық сараптама нәтижелері оның күлділігі мен ылғалдылығы төмен екенін дәлелдеді. Рентгенофлуоресценттік спектрлік талдау көмірдің құрамында сирек кездесетін металдар бар екенін көрсетті. Көмірдің морфологиясы мен өлшемі сканерлеуші электронды микроскопия әдісімен зерттелінді. Көмір үлгісінің беті әртекті, тығыз және кеуекті құрылымды аудандармен сипатталатыны анықталды. «Қаражыра» кен орнының тас көмірі Д (ұзақ жалынды) маркасына жатады. Сондай-ақ беттік ауданда микронды өлшемді кластерлер де байқалды. Фракцияның орташа өлшемі 0–300 миллиметрді құрайды. Кеуекті құрылымды аудандарда, 2–10 мкм өлшемді саңылаулы жүйе түзетін ашық саңылау тәріздес және туннель тәріздес шығуы бар ойықты беттер бар. Термоаналитикалық нәтижелер негізінде тас көмір үлгілері термиялық тұрақты екені, үлгінің бетінде құрамында оттегі және азот бар топтардың болуы спектроскопиялық түрде анықталды. Көмір салыстырмалы түрде жоғары жану жылуына, жоғары шығымды ұшқыш заттарға ие және төмен күлділігімен, ылғалдылығымен, күкірт пен азоттың аз мөлшерде болуымен ерекшеленеді. $A_a = 19,8\%$ және $W_a = 14,0\%$ болғанда, көмір сынамаларының таза каллориялық мәні орташа 4650 ккал/кг құрайды. «Қаражыра» кен орны көмірінің халық шаруашылығының барлық салаларында пайдалану мүмкіндігі көрсетілді.

Кілт сөздер: тас көмір, морфология, спектроскопия, рентгенофлуоресценттік талдау, электронды микроскоп.

Р.Т. Динжуманова, Б.Б. Баяхметова, Н.Б. Касенова, А.Н. Кливенко

Физико-химическое исследование каменных углей месторождения «Қаражыра»

В статье приведены результаты физико-химического исследования каменных углей месторождения «Қаражыра». Изучены следующие технические показатели углей: влажность, зольность, выход летучих компонентов, содержание серы, элементный состав, теплоемкость, морфология и размер частиц. Результаты технического анализа угля свидетельствуют о его низкой зольности и влажности. Рентгенофлуоресцентный спектральный анализ указывает на наличие редкоземельных металлов в составе угля. Морфологию и размер частиц угля определяли методом сканирующей электронной микроскопии. Установлено, что поверхность образца угля неоднородная с участками, характеризующимися

плотной структурой и пористой текстурой. Уголь месторождения «Каражыра» относится к марке Д (длиннопламенных). На поверхности наблюдаются также кластеры микронного размера. Средний размер фракции составляет 0–300 мкм. Участки с пористой текстурой имеют рифленую поверхность с открытыми щелевидными и туннелевидными выходами, образующими систему пор размером 2–10 мкм. На основании термоаналитических результатов установлена термическая устойчивость образцов каменных углей, спектроскопически идентифицированы кислород- и азотсодержащие группы на поверхности образцов. Уголь обладает сравнительно высокой теплотой сгорания, высоким выходом летучих соединений, отличается относительно низкой зольностью, влажностью, небольшим содержанием серы и азота. В среднем низшая теплота сгорания образцов угля составляет 4650 ккал/кг при $A_a = 19,8\%$ и $W_a = 14,0\%$. Показана возможность применения углей месторождения «Каражыра» практически во всех отраслях народного хозяйства.

Ключевые слова: каменные угли, морфология, спектроскопия, рентгенофлуоресцентный анализ, электронная микроскопия.

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Zh.K. Dzhanmuldaeva, R.R. Yakubova, G.M. Seitmagzimova, S.T. Tleuova

*M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
(E-mail: zhanyld@mail.ru)*

About development of a new method of processing of low-quality phosphate raw materials

Kazakhstan has huge reserves of phosphate raw materials. Nowadays high-grade phosphates are almost exhausted, and the ore is mainly represented by run-of-mine and low-grade phosphorites with small phosphorus content. Processing of low-grade phosphate raw materials by traditional methods is hindered. Formed large amounts of solid waste at phosphorus production require searching methods of their recycling or utilization. It also makes an urgent the search for new alternative ways of processing low-quality phosphate raw materials. Obtaining phosphorus oxyfluoride from low-grade phosphorites with its further processing into elemental phosphorus is one of ways of processing such phosphate raw materials, which allows to simplify the process and improve phosphates quality. According to the task, the process of calcium phosphates interaction with ammonium fluoride was investigated; thermodynamic analysis of possible reactions was carried out, which confirmed primary formation of monoammonium phosphate with the following its conversion into phosphorus oxyfluoride. The results of mass spectrometric analysis of samples of dicalcium phosphate and tricalcium phosphate in a mixture with ammonium fluoride confirmed the proposed mechanism of interaction. Based on the results obtained, possibility is shown and optimal parameters for processing low-grade phosphate raw materials into phosphorus were determined.

Keywords: low-grade phosphorites, phosphate raw material processing, phosphorus oxyfluoride, ammonium fluoride, thermodynamic analysis, isobar-isothermal potential.

Introduction

Phosphate raw material base of Kazakhstan is presented by a number of phosphorite deposits. It was primarily proposed to process large fractions of high-grade phosphate raw materials into yellow phosphorus and to direct small fractions for enrichment and further processing by acidic methods. Electrothermal (dry-process) method of phosphorite processing is characterized by physical-chemical process complexity due to phosphate raw material composition, i.e. its quality. High-grade phosphorites are mainly used for phosphorus production. The use of low-grade raw materials results in formation of a large amount of sludge, decrease of phosphorus quality and increasing energy expenses, what causes increasing the production cost. Presently there are large actual reserves of low-grade phosphate raw materials in Kazakhstan. This raw material processing by traditional technological methods is hindered. It is related to the complex mineralogical composition of these phosphorites, which requires the detailed study of initial ore chemical and mineralogical composition, deep investigations of raw material thermal preparation and its processing into a target product. That actualizes a search of new alternative methods of low-grade phosphate raw material processing [1]. Phosphorus oxyfluoride obtaining from low-grade phosphate raw materials with following processing into elemental phosphorus is one of ways of low-grade phosphate raw material processing, allowing to simplify a process and to improve phosphates quality compared to ones produced by dry- and wet-processes. Phosphorus oxyfluoride is colorless gaseous substance with condensation temperature 37 °C, it is hydrolyzed in the moist air or in water [2]. The obtained gas can be processed into phosphates by hydrolysis, and hydrogen fluoride formed as a result of hydrolysis can be used for phosphorus oxyfluoride production. Results of research of phosphorus oxyfluoride production are presented in this work.

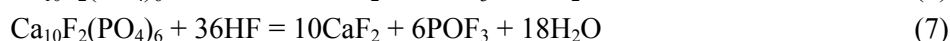
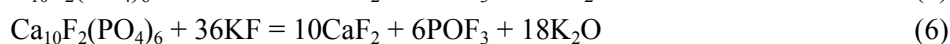
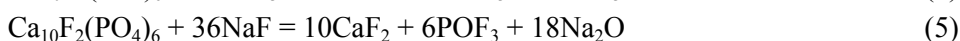
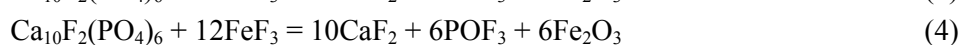
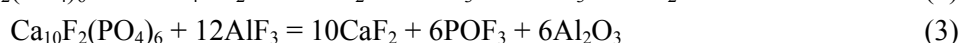
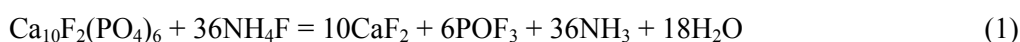
Materials and methods

Dicalcium phosphate, tricalcium phosphate and ammonium fluoride of «chemically pure» grade were used to carry out mass spectrometric analyses, and Karatau low-grade phosphorites for laboratory experiments. A basic procedure of suggested investigation is free associative instrumental method of an experiment which is one of most available and valid procedures. Based on theoretical and applied investigations certain scientifically grounded physical-chemical and technological bases of low-grade phosphate raw material processing can be developed.

An analysis of initial and additional raw materials, target products and materials was performed using up-to-date chemical and physical-chemical research methods. Gas-vapour phase composition when sample thermal processing was studied using mass-spectrometer MCX-3A adjusted to high-temperature investigation performance. The comparative analysis was carried out by means of mathematical treatment of experiment results.

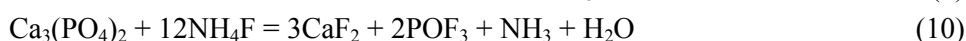
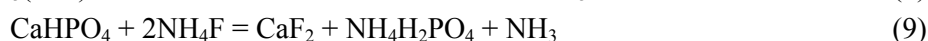
Results and Discussion

In order to define perspectives of new technology development and determine the process thermodynamic probability, the thermodynamic analysis using Temkin-Shwartsman method has been performed for some possible reactions when phosphate raw materials processing by a fluoride treatment [3]. Changes of isobar-isothermal potential in the temperature interval 50–2000 K were calculated for reactions of fluorapatite interaction with ammonium, aluminum, iron, sodium, potassium and hydrogen fluorides forming phosphorus oxyfluoride:

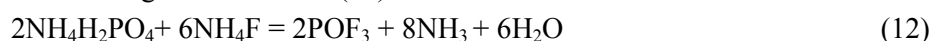


An analysis of performed calculations has shown that (1) and (2) reactions are more probable ones. ΔG_T^0 has positive value for these reactions at temperature 273 K. When temperature increases, ΔG_T^0 decreases and becomes equal to zero at temperatures 532 and 647 K correspondingly, i.e. these reactions become thermodynamically probable at temperatures 532 K and 647 K correspondingly. Reactions of fluorapatite interaction with aluminum, iron, sodium and potassium fluorides become thermodynamically probable at temperatures higher than 2000 K. Therefore these reactions are practically impossible. For reactions of fluorapatite interaction with hydrogen fluoride ΔG_T^0 has negative value at temperatures lower than 257 K. Therefore the chemical reaction at temperatures above 257 K is thermodynamically impossible. From calculation data it is concluded that ammonium fluorides are most effective reagents for fluoride treatment of phosphate raw materials.

Then the possibility of calcium phosphate interaction with ammonium fluoride was investigated according to reactions:



Thermodynamic analysis of these reactions were also conducted by Temkin-Shwartsman method. Results of thermodynamic calculations have shown that reactions (8) and (9) are more thermodynamically probable ones. For these reactions ΔG_T^0 values become negative at temperatures 246 K and 155 K correspondingly whereas reactions (10) and (11) become thermodynamically probable at temperatures 515 K and 533 K correspondingly. Monoammonium phosphate formed in the course of (8) and (9) reactions can also interact with ammonium fluoride according to the reaction (12):



Thermodynamic calculations have shown that reaction (12) becomes thermodynamically probable one at the temperature above 581 K (see Fig.).

Based on performed thermodynamic analysis of possible reactions of calcium phosphates interaction with ammonium fluoride, one can suppose that most probable interaction mechanism is primary monoammonium phosphate formation according to reaction equations (8) and (9) with subsequent phosphorus oxyfluoride formation according to the reaction equation (12).

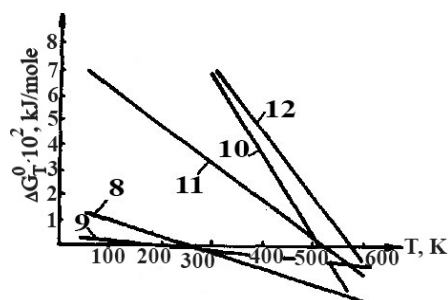


Figure. Dependence of isobar-isothermal potential on the process temperature for reactions 8–12

In order to confirm a conception about mechanism of calcium phosphates interaction with ammonium fluoride, the mass spectrometric analysis was performed for samples #1 (dicalcium phosphate mixed with excess of ammonium fluoride) and #2 (tricalcium phosphate mixed with excess of ammonium fluoride). The temperature interval of investigations is 0–1350 °C. Mass spectra registration in experimental conditions was carried out at step temperature rise with several soakings. A temperature mode was maintained with a block BPT-2.

Sample #1 studying has shown that ion currents with $m/e = 16, 17, 19$ and 20 match to NH_2^+ , NH_3^+ , F^+ and HF^+ ions are registered without furnace block heating up. In experimental conditions apparently there was sufficient heat radiation of ion source cathode of the mass-spectrometer for ammonium fluoride sublimation. The reactor heating up at electric resistance furnace turn-on results in increasing ion current intensity. Therefore ion currents with $m/e = 104, 85$ and 69 interpreted as POF_3^+ , POF_2^+ and PF_2^+ appear in the mass-spectra at temperature above 360 °C. When temperature increasing up to 550 °C ion currents with $m/e = 66, 50$ and 47 are registered in the mass-spectra. The noted ions are identified as POF^+ , PF^+ и PO^+ .

It is established that in experimental conditions the peak intensities and ratios between noted ions are changed depending on temperature and time and attain maximal intensity in temperature interval 650–750 °C. It has been discovered that, when ion currents POF_3^+ , POF_2^+ , POF^+ , PF_2^+ , PF^+ and PO^+ registering in the mass spectra, on one side, the intensity of ion currents HF^+ and F^+ essentially falls, but on the other side, the intensity of background ions with $m/e = 17$ and 18 (ions OH^- and H_2O^+) insignificantly increases. This confirms reactions (10) or (11) proceeding.

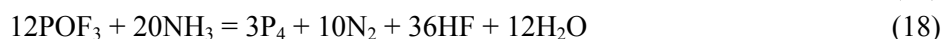
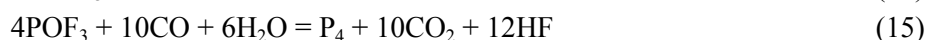
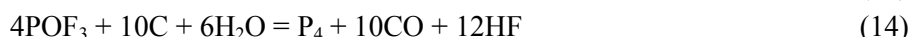
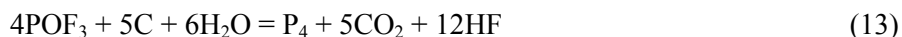
Mass-spectrometer investigation of #2 sample has shown that the qualitative composition of vapour-gas phase corresponds generally to #1 sample. Significant difference is observed in intensity and temperature intervals of registration of ion currents related to phosphorus oxyfluoride formation in vapour-gas phase. So, for #2 sample ions fixation in the mass spectra starts at temperature for 200 °C above and these peaks intensities are of lower order compared to #1 sample. Maximal intensity of ion currents POF_3^+ , POF_2^+ and PF_2^+ in #2 sample mass spectra is registered in the temperature interval 1000–1150 °C. However, it is evident that the fall of intensity of ion currents with $m/e = 19$ and 20 (F^+ and HF^+) for #2 sample is insignificant.

The mechanism of calcium phosphates interaction with ammonium fluoride stated on a basis of thermodynamic analysis of reactions (8)–(12) is confirmed by primary increasing the intensity of ion currents matched to NH_3^+ and NH_2^+ ions at constant background currents OH^- and H_2O^+ and at comparatively low temperatures, which proves the predominant course of the reaction (8) and (9). Increasing the intensity of ion currents matched to phosphorus oxyfluoride and its fractions at temperature higher the 650 °C speaks for primary proceeding the reaction (12).

Performed investigations allow to make a conclusion that calcium phosphates interaction with ammonium fluoride proceeds according to total reactions (10) and (11) through two stages forming ammonium phosphate according to reactions (8) and (9) at the first stage. At the second stage at higher temperatures further formed phosphate interaction with ammonium fluoride takes place forming phosphorus oxyfluoride according to the reaction (12).

We studied kinetics and the mechanism of calcium phosphates interaction with ammonium fluoride. Conducted experimental research has shown that phosphorus sublimation degree in the form of phosphorus oxyfluoride can attain 98 %.

To determine the probability of phosphorus oxyfluoride processing into phosphorus we performed the thermodynamic analysis of following reactions of elementary phosphorus formation from phosphorus oxyfluoride:



Results of thermodynamic calculations have shown that reactions (14) and (18) are more thermodynamically probable ones. These reactions can take place at temperatures 817 °C and 637 °C correspondingly.

Thus the offered method of low-grade phosphate raw materials processing consists of thermal treatment of phosphate raw materials mixed with inorganic reagents with following processing the sublimate into elemental phosphorus. To decrease thermal treatment temperature and to improve product quality the phosphate raw materials is treated with ammonium fluoride excess amount, namely 110–200 % of stoichiometric norm for reactions (1) and (2). At more than 200 % excess of ammonium fluoride the sublimate amount rises sharply. In turn it hinders gases transporting and purification. At less than 110 % norm of ammonium fluoride the sublimation rate of ammonium fluoride is higher than the rate of phosphorus oxyfluoride formation. In addition to that at this norm the phosphorus oxyfluoride output falls sharply.

Thermal treatment is proposed to carry out at the temperature 300–600 °C because temperature increasing above 600 °C insignificantly effects on phosphorus oxyfluoride output. Obtained sublimate is purified from solid impurities and then they are cooled to 100–200 °C and. Thereat phosphorus vapours are condensed, and liquefied phosphorus is formed. At the temperature above 200 °C ammonium fluoride is sublimated.

Then purified gases is suggested to be heated up to 640–1000 °C and then to cool them to 300–250 °C for production phosphorus condensation. When heating lower 640 °C phosphorus reduction rate decreases acutely, and at the temperature above 1000 °C energy expenses increase. Concerning cooling mode at the temperature above 400 °C gaseous phosphorus condensation doesn't practically take place. Ammonium fluoride is precipitated at the temperature lower 250 °C, what can result in production phosphorus pollution.

After phosphorus separation the ammonia is added to the rest gas in the stoichiometric amount for the reaction of ammonium fluoride formation. Gases are cooled to 100–180 °C and ammonium fluoride is separated. It is recycled to the process top. The rest gases are discharged into the atmosphere after sanitary purification.

Conclusion

The possibility of low-grade phosphate raw materials processing into elemental phosphorus is proved on the basis of results of thermodynamic calculations, mass-spectrometer and laboratory investigations. Optimal parameters of the process were determined and the technological scheme of offered technology was developed.

The offered technology of low-grade phosphate raw materials processing gives an opportunity to solve both ecological and economical problems. On one side, the developed technology allows to process low-grade raw materials and to eliminate sludge formation, and from the other side, it results in essential energy consumption decreasing.

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Ж.К. Джанмулдаева, Р.Р. Якубова, Г.М. Сейтмагзимова, С.Т. Глеуова

Төмен сапалы фосфат шикізатын өңдеудің жаңа әдісін әзірлеу туралы

Қазақстан фосфат шикізатының үлкен қорына ие. Қазіргі уақытта бай фосфориттер іс жүзінде таусылған және кен негізінен құрамында фосфор аз қатардағы және төмен сортты фосфориттермен ұсынылған. Төмен сапалы фосфат шикізатын дәстүрлі әдістермен өңдеу қиын. Фосфор өндірісі нәтижесінде пайда болатын қатты қалдықтардың мөлшері оларды өңдеу, пайдаға жарату туралы зерттеуді қажет етеді. Бұл сондай-ақ төмен сапалы фосфат шикізатын қайта өңдеудің жаңа дәстүрлі емес әдістерін іздестіруді өзекті етеді. Процесті жеңілдетуге және фосфаттардың сапасын жақсартуға мүмкіндік беретін төмен сапалы фосфат шикізатын өңдеу жолдарының бірі одан фосфордың оксифторидін алу болып табылады, одан әрі оны қарапайым фосфорға қайта өңдеу болып табылады. Қойылған міндетке сәйкес кальций фосфатының аммоний фторидімен өзара әрекеттесу процесі зерттелді; моноаммонийфосфаттың түзілуінің басымдығын растап, оны кейіннен фосфордың оксифторидіне айналдыра отырып, ықтимал реакцияларға термодинамикалық талдау жүргізілді. Аммоний фторидімен қоспадағы дикальцийфосфат және трикальцийфосфат үлгілерінің масс-спектрометриялық талдауының нәтижелері өзара әрекеттесудің болжамды механизмін растады. Алынған нәтижелердің негізінде төмен сапалы фосфатты шикізатты фосфорға өңдеудің мүмкіндігі және оңтайлы параметрлері анықталды.

Кілт сөздер: төменсұрыпты фосфориттер, фосфатты шикізаттарды өңдеу, фосфор оксифториді, аммоний фториді, термодинамикалық талдау, изобара-изотермиялық потенциал.

Ж.К. Джанмулдаева, Р.Р. Якубова, Г.М. Сейтмагзимова, С.Т. Глеуова

**О разработке нового метода переработки
низкокачественного фосфатного сырья**

Казахстан обладает огромными запасами фосфатного сырья. В настоящее время богатые фосфориты практически исчерпаны, и руда представлена главным образом рядовыми и низкосортными фосфоритами с низким содержанием фосфора. Переработка низкокачественного фосфатного сырья традиционными методами затруднена. Образующиеся объемы твердых отходов производства фосфора требуют проведения исследований по их переработке или утилизации. Это делает также актуальным поиск новых нетрадиционных способов переработки низкокачественного фосфатного сырья. Одним из путей переработки низкокачественного фосфатного сырья, позволяющим упростить процесс и улучшить качество фосфатов, является получение из него оксифторида фосфора с дальнейшей переработкой его на элементарный фосфор. В соответствии с поставленной задачей исследован процесс взаимодействия фосфатов кальция с фторидом аммония; проведен термодинамический анализ возможных реакций, который подтвердил преимущественное образование моноаммонийфосфата с последующим превращением его в оксифторид фосфора. Результаты масс-спектрометрического анализа образцов дикальцийфосфата и трикальцийфосфата в смеси с фторидом аммония подтвердили предполагаемый механизм взаимодействия. На основании полученных результатов показана возможность и определены оптимальные параметры переработки низкокачественного фосфатного сырья в фосфор.

Ключевые слова: низкосортные фосфориты, переработка фосфатного сырья, оксифторид фосфора, фторид аммония, термодинамический анализ, изобарно-изотермический потенциал.

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ХИМИЯНЫ ОҚЫТУ ӘДІСТЕМЕСІ МЕТОДИКА ОБУЧЕНИЯ ХИМИИ METHODS OF TEACHING CHEMISTRY

DOI 10.31489/2019Ch4/110-115

UDC 378.147

L.M. Sugralina, Ye.V. Minayeva, S.G. Karstina, L.K. Salkeeva

*Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: sugralinalm@yandex.ru)*

Engineering Educators Training in Kazakhstan: Situation and Prospects

The article is a brief overview for the current state of engineering education in Kazakhstan and considers the prospects for its further development and implementation, which is due to the need for industrial and innovative development of our state. Kazakhstan, being an industrially developing country, needs qualified engineering personnel, therefore the training of such specialists at a sufficiently high level is a definite problem. It is noted that for its solution it is necessary to modernize existing study programs, train and retrain teaching staff, widely introduce modern educational approaches and technologies. The article discusses various forms of retraining of teachers of engineering disciplines, for example, advanced training courses for university faculty on the basis of additional education departments. Their topics, duration and forms of conducting are very diverse. Nevertheless, existing problems hinder the development of engineering education in our country; for their successful solution, representatives of the Chemistry and Physics & Technics Departments participate in the international project «EngineeriNg educaTors pEdagogical tRaining» (ENTER). This project implements goals aimed at creating an enabling environment in the educational space based on international cooperation between representatives of universities and the organization of Portugal, Estonia, Slovakia, Russia and Kazakhstan. So, it is planned to elaborate three educational programs (i-PETs) for engineering educators with a variable set of modules based on modern technologies (e-learning) and an individual approach. The implementation of the «ENTER» project is a real prospect of improving the status of engineering education and raising the level of engineering educators' training in our country.

Keywords: engineering education, engineering educator, study program, advanced training courses.

Introduction

The economy of Kazakhstan is the largest economy in Central Asia. The country has significant reserves of oil, coal, as well as minerals and metals. The country's industrial sector is based on the extraction and processing of natural resources, as well as on a relatively large machine-constructing sector, specializing in construction equipment, agricultural equipment and some military products. The extractive industries have been and remain the engines of the economy of Kazakhstan and the growth of the country. The training of engineering personnel for the needs of the industrial sector is one of the key factors of state competitiveness and the basis for its technological and economic independence. This causes a social order for the engineering personnel training by the system of higher professional education of the country. The main industrial region of the republic is the Karaganda region which has the largest resources of raw materials of different origins for metallurgy and the construction industry. This defines the foundation for the development of such industries as ferrous and nonferrous metallurgy, coal mining, energy, petrochemical and chemical industry, the food industry, the construction industry. There is sufficient potential in the region for the development of enterprises of machine-constructing and metal-processing branches of industry [1].

The industrial orientation of the region determines the demand for specialists of various manufactories, engineering and teaching personnel. The needs of the region for engineering personnel are consistent with national priorities for the modernization of education.

However despite the significant scale of measures taken in Kazakhstan in recent years to support innovation there are still key problems related to the quality of training engineering professionals, the introduction of advanced technologies and best practices. Domestic universities are still divorced from the real needs of the regions; this is reflected in the discrepancy between the level of graduates and the demand in the local labour market and in distance from the business sector.

These problems lead to the necessity for modernization of existing educational programs at various levels based on a detailed analysis of the needs of the regions, the requirements for key competencies of University graduates defined by employers as well as an assessment of the expectations of Bachelor and Master students and graduates, their career prospects. It is necessary to identify and strengthen relevant and promising areas of training, modernize teaching methods and actively develop distance and online education systems, introduce modern information and communication technologies, improve the electronic infrastructure of universities, elaborate new interactive teaching & learning materials, improve forms, teaching methods and assess trainees' learning outcomes, skills and competencies, create conditions for the development of competence and the skills for faculties involved in the organization and implementation of research projects and programs (engineering and technical personnel, administrative — technical support and support service, etc.), advanced training of teachers.

So the aim of this paper is an analysis of current situation for engineering teachers training and making more precise the prospects for its improvement.

Results and Discussion

The education system in the Republic of Kazakhstan on the basis of the principle of educational training programs continuity includes the following education levels: preschool education and training; primary education; main secondary education; secondary education (general secondary education, technical and professional education); postsecondary education; the higher education; postgraduate education.

Programmes for training of engineering teachers in the Karaganda region include training and professional development of teachers of technical higher educational institutions (HEIs) and technical specialties and also teachers of the multidisciplinary higher education institutions teaching engineering disciplines both on the basis of branches of Institute of professional development of the RK, and at departments of additional education of higher education institutions.

The most common form of the engineering and pedagogical personnel training organization is training at specialized departments in technical, state and pedagogical universities. At the same time, various forms of integration of education, science and production are used: intra-university, when faculties and university research institutes are combined, and external, consisting in creating cooperation with academic institutions and industrial enterprises. The task of engineering and pedagogical education is to provide specialists who are able to organize and carry out fundamental, technological and specialized professional training in the main sectors of the country economy.

The principle of university study programs construction is based on a combination of training based on the fundamental knowledge gained at the university, with practical industrial experience. Educational programs have a modular structure, are based on competence-based, student-centered, subject-activity approaches; are implemented on the basis of a credit system of education, which allows students choosing individual educational tracks. The educational disciplines of related content aggregated for providing meaningful unity are considered as a module. Each module forms specific competencies. The results of training in educational programs are based on the recommendations of potential employers. As applied to engineering education the training programs should be oriented towards the training of engineering educators who are capable of educational activities both in vocational educational institutions and in manufacturing. At the same time the objectives and content of the training are determined by the profile of the industrial potential of the relevant region. In addition, an engineering educator must be an expert in the sector of the national economy for which he/she provides training, to know the peculiarities of industrial branch technology and a separate specialty in it, to have practical professional skills as he/she prepares to conduct both theoretical and practical training. Thus, the system of engineering and pedagogical education should integrate the pedagogical and professional components.

Now the engineering and pedagogical component is available in some Bachelor and Master programs, in particular in the Master degree program of the Academician Ye.A. Buketov Karaganda State University (KSU) 6M072100 — Chemical Engineering of Organic Compounds. Master students study disciplines «Pedagogics of the Higher School», «Psychology of Management», «Concept of Engineering Education for Chemical Technology», pedagogical internship that allows them to realize pedagogical, research and innovative activity in the field of the higher and professional education.

For the training of engineering educators in the universities of Kazakhstan traditional organizational forms of training are implemented. At the same time, peculiar meaning is given to lectures to which the most qualified and experienced teachers are involved (as a rule, professors and associate professors). The lecture lays the foundation of scientific knowledge, seminars allow trainees to expand and detail this knowledge, to develop and consolidate the skills of professional activity. Practical exercises are significant ones in developing students' skills in applying their knowledge to solve practical problems together with a teacher. The experiment plays a large role in the training of engineers who must have research skills from the first steps of their professional activities. In laboratory work the integration of theoretical and methodological knowledge with practical skills of students in a varying degree of proximity to the real professional activity is carrying out. A special attention is paid to trainees' joint group work. The maximum degree of approximation to the future professional activities is achieved during the internship at specific workplaces. Students' self-study under teacher's guidance and students' self-study itself play an important role in training modern specialists.

Karaganda State University developed the practice of opening branches of departments on the basis of partner organizations acting by external experts of educational programs and by potential employers as well. As a rule practical classes are held in the branches of the departments, professional internships are organized, approbation of final qualifying works is conducted. Experienced specialists of enterprises are involved in conducting classes and leading practices. In addition, practitioners are also involved in the final certification of students. The university has a program of attracting foreign specialists to deliver lectures, organize advanced training courses, and provide consulting assistance. Practitioners are involved in the implementation of the educational process. Students have the right to use virtual mobility windows, recruit credits from Kazakhstan or foreign partner universities in the framework of academic mobility, and use various forms of formal education in shaping the educational route. In this case all the results of such training are recognized at the university in accordance with accepted procedures.

The university creates conditions for professional growth as teachers working at KSU, and other educational institutions, including universities, colleges of Kazakhstan. The University has the department of Additional Education, which develops and implements programs for the management of education and modern learning technologies, including professional engineering education. Teachers of educational institutions regularly (at least once every five years) undergo advanced training at courses of various lengths (from 4 days to 3 months), academic load, forms of conducting (contact classes, a combination of online and offline forms, trainings and master-classes, internships in the manufacturing process, courses on open education platforms, online courses). The programs of advanced training courses for scientific and pedagogical staff of universities rely on modern achievements in fundamental and psychological and pedagogical sciences, world and national experience, new educational concepts, systems, technologies, methods and teaching aids, focused on acquaintance and introduction of innovative approaches in training with emphasis to improve the content of the educational program, the formation of a high level of research, the implementation of training using distance learning technologies, development of e-learning materials (multimedia technology, SMART learning technology, case study technology), the use of video materials in the educational process. For example, the result of advanced course «Distance courses «Developing e-learning aids» is learning to clearly formulate the SMART goal of lectures and practical exercises, building a «chain» of logical interrelated actions, as a result of which the student reaches the final goal. The process of advanced training is carried out in the form of a one-time training or several cycles distributed over time — composite modules, allowing ensuring variability with advanced training.

For young teachers the University organizes the «School of lecturing skills» (free of charge), various forms of mentoring by more experienced teachers, and arranges courses for foreign lecturers and practitioners. In addition, university teachers have the opportunity to undergo advanced training courses on the basis of both Kazakhstan and foreign universities organized by JSC «National center for professional development «Orleu» (for example, under the program «Modern Pedagogical Technologies», advanced training programs for teachers of pedagogical specialties of universities in Kazakhstan). University teachers regularly take part

in seminars on the base of Republican organizations; participate in conferences, educational and scientific events of different levels, in scientific and professional internships, etc.

Despite the measures taken for implementation of engineering educators training in Kazakhstan there are some lacks and contradictions between new and old educational media. For overcoming that the representatives of some Kazakhstani universities and organizations succeed in realization of the international project «EngineeriNg educaTors pEdagogical tRaining» (ENTER) which was launched in November, 2018. It is realized in the framework of Erasmus+ Programme; the project reference is 598506-EPP-1-2018-1-PT-EPPKA2-CBHE-JP. The consortium includes Universities and organizations from Europe, Russia and Kazakhstan. Instituto Politécnico do Porto (Portugal), Tallinn University of Technology (Estonia), and Dubnický Technologický Inštitút v Dubníckej nad Vahom (Slovakia) are European partners. Partners implementing the designed project programmes are Agency of Educational Strategies and Initiatives Bologna Club, Russian Association for Engineering Education, Don State Technical University, Tambov State Technical University, Tomsk National Research Polytechnic University, Vyatka State University, and Kazan National Research Technological University from Russia, Academician Ye.A. Buketov Karaganda State University, Al-Farabi Kazakh National University, and Kazakhstan Association of Engineering Education from our country.

The purpose of ENTER project is elaborating a novel multicultural and international approach for formal post-graduate professional and pedagogical education for engineering teachers. As it is focused on low cost and convenience of programmes the e-learning technologies are in the base of them. Whenever feasible, programmes should be designed with the objective of being internationally recognized and accredited. ENTER wants to go further than existing offers, offering the possibility of customization and adaptation to educators and HEIs' needs (e.g. national or regional context) and cover multiple areas of engineering [2].

One of the main objectives of the consortium is to work out multi-level modular system for pedagogical training of engineering educators based on international network cooperation. So the ENTER project participants propose a hierarchy of three well-structured educational programmes for engineering educators, so called iPET programmes which will be designed in the context of the European Qualifications Framework for Lifelong Learning. These educational programs will have various content and duration. They are:

- iPET-1 Short-focused (2 ECTS) — «Qualification Development» Certificate;
- iPET-2 Professional Retraining (e.g. 8 ECTS) — «Higher Education Teacher» Diploma;
- iPET-3 International recognized (e.g. 20 ECTS) — a full programme leading to international accreditation as «Engineering Educator».

Programmes have modular structure, i.e. modules of iPET-1 are included in iPET-2, and both are included in iPET-3. This provides a sustainable improvement path that educators can pass at their own pace. It will also be possible for the educators to combine modules from different ENTER network members [3].

Before starting elaboration of iPET programmes much preparatory work should be done. As project programmes are competence-based some questionnaires were developed aimed to analyze the situation about engineering education in Kazakhstan, to find out concrete expectations of the target audience, i.e. engineers, engineering educators, representatives of stakeholders, etc. much attention will be paid to establishing key competences for engineering educators.

Modern educational programs should include new disciplines reflecting innovative production technologies and giving qualifications that are in demand in the labour market. Educational programs should become practice-oriented. In order to train personnel for the innovation economy, entrepreneurial education will be implemented in the content of educational programs, which means the inclusion of disciplines (modules) that form entrepreneurial knowledge and skills. The authorized body in the field of education is introducing a system of rating educational programs of universities based on a survey of employers on an annual basis and other data. The main indicators will be employment, graduates' salary and characteristics of educational programs used by universities.

As modern forecasts show engineering and natural science specialties related to industrial production take the leading position in Kazakhstan, which should provide the regions with professional engineers, technical specialists and middle and top managers competent in various fields of interdisciplinary knowledge, engineering marketing and management. At the same time, high-quality training should be promoted: modernization of existing educational programs at various levels based on a detailed analysis of regional needs, employers' requirements for graduates' key competencies of from universities by, as well as an assessment of the expectations of applicants, students and graduates of the prospects for their professional activities and career expectations. In accordance with the economic and social transformations taking place in the country,

it is necessary to identify obsolete academic disciplines that lose their relevance, at the same time strengthening the relevant and promising directions, changing the focus and emphasis of educational programs, incorporating practical skills training and getting practical qualifications, entrepreneurial competencies. At the same time, it is necessary to modernize teaching methods and actively develop distance and online education systems, introduce modern information and communication technologies, improve the electronic infrastructure of universities, develop new interactive learning materials that will enhance learning motivation, enhance cognitive activity of students, develop abilities to self-study, develop creativity and thinking outside the box, reveal personality-individual capabilities of each student and determine the conditions for their manifestation and development, develop universal skills.

In the case that the university's curricula do not match current realities, it will not be possible to provide the Kazakhstan's labour market with highly qualified specialists in demand, ensure the competitiveness of educational programs and their recognition by potential consumers, prepare specialists for working in the «digital age», «digital communication», «digital decision making methods». Traditional educational programs and forms of advanced training will not be able to provide contextual learning, within which approaches to the use of professional context in the educational process, the transition from learning tasks to quasi-professional and further to professional tasks should be used. In Academician Y.A. Buketov KSU to solve this problem, the methods of forming educational trajectories are used with the inclusion of elements of professional activity on the basis of branches of departments in the educational process, as part of applied research programs, professional internships and practices, assessment of professional competencies of graduates by representatives of the professional community. The University maintains close contact with employers, analyses feedback on the work of graduates, attracts employers to accredit educational programs, the National Chamber of Entrepreneurs of Kazakhstan «Atameken» participates in competitions to assess the quality of educational programs, creates a register of educational programs based on monitoring the needs of the region in specialists, annually adjustment of learning outcomes based on recommendations of representatives of the relevant professional sphere. The content of educational programs includes elements of formal education with the recognition of their results.

Conclusions

So the modern situation with engineering education in our country was presented based on the analysis of existing study programmes; problems were identified; solutions for them were suggested; one of them is realization of international project «EngineeriNg educaTors pEdagogical tRaining» via elaborating three modular programmes of various academic load and duration. These programmes will be based on modern educational approaches and technologies.

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Л.М. Сугралина, Е.В. Минаева, С.Г. Карстина, Л.К. Селькеева

Қазақстандағы білім беру инженерлерін дайындау: жағдайы және болашағы

Мақалада Қазақстандағы инженерлік білім берудің қазіргі жай-күйіне қысқаша шолу жасалады және мемлекетіміздің индустриалды-инновациялық даму қажеттілігіне байланысты оны одан әрі дамыту мен енгізу перспективалары қарастырылған. Қазақстан өнеркәсіптік дамып келе жатқан ел бола отырып, білікті инженерлік кадрларға мұқтаж, сондықтан мұндай мамандарды жоғары деңгейде даярлау белгілі бір мәселе болып табылады. Оны шешу үшін қазіргі білім беру бағдарламаларын жаңғырту, педагогикалық кадрларды оқыту және қайта оқыту, заманауи білім беру тәсілдері мен технологияларын кеңінен енгізу қажет. Мақалада инженерлік пәндер оқытушыларын қайта дайындаудың әртүрлі түрлері қарастырылған, мысалы, қосымша білім беру факультеттерінің базасында университеттердің профессорлық-оқытушылар құрамы үшін біліктілікті арттыру курстары.

Олардың тақырыбы, ұзақтығы және өткізу түрлері әртүрлі. Осыған қарамастан, қазіргі мәселелер біздің елімізде инженерлік білімнің дамуын тежейді; оларды табысты шешу үшін химия және физика-техникалық факультетінің қызметкерлері «Инженерлік іс оқытушыларын педагогикалық дайындау»/«EngineeriNg educaTors pEdagogical tRaining»(ENTER) халықаралық жобасына қатысады. Бұл жобада жоғары оқу орындары өкілдерінің халықаралық ынтымақтастығы негізінде білім беру кеңістігінде қолайлы орта құруға және Португалия, Эстония, Словакия, Ресей және Қазақстан ұйымдасуына бағытталған мақсаттарды жүзеге асырады. Сонымен, инженерлік мамандықтардың оқытушылары үшін оқытудың заманауи технологиялары (e-learning) және жеке тәсіл негізінде модульдердің ауыспалы жинағы бар үш білім беру бағдарламасын (i-PET) әзірлеу жоспарлануда. «ENTER» жобасын жүзеге асыру инженерлік білім беру жағдайын жақсартудың және біздің елімізде инженер-педагогтардың дайындық деңгейін арттырудың нақты болашағы болып табылады.

Кілт сөздер: инженерлік білім, инженер-оқытушы, білім беру бағдарламасы, біліктілікті арттыру курстары.

Л.М. Сугралина, Е.В. Минаева, С.Г. Карстина, Л.К. Салькеева

Подготовка инженеров-педагогов в Казахстане: состояние и перспективы

Статья представляет собой краткий обзор современного состояния инженерного образования в Казахстане и рассматривает перспективы его дальнейшего развития и внедрения, что обусловлено необходимостью индустриально-инновационного развития нашего государства. Казахстан, будучи промышленно развивающейся страной, нуждается в квалифицированных инженерных кадрах, поэтому подготовка таких специалистов на достаточно высоком уровне является определенной проблемой. Отмечено, что для ее решения необходимо модернизировать существующие образовательные программы, обучить и переобучить педагогические кадры, широко внедрять современные образовательные подходы и технологии. В статье рассмотрены различные формы переподготовки преподавателей инженерных дисциплин, например, курсы повышения квалификации для профессорско-преподавательского состава университетов на базе факультетов дополнительного образования. Их тематика, продолжительность и формы проведения весьма разнообразны. Тем не менее, существующие проблемы сдерживают развитие инженерного образования в нашей стране; для их успешного решения сотрудники химического и физико-технического факультетов участвуют в международном проекте «EngineeriNg educaTors pEdagogical tRaining» (ENTER) /«Педагогическая подготовка преподавателей инженерного дела»/. В данном проекте реализуются цели, направленные на создание благоприятной среды в образовательном пространстве, на базе международного сотрудничества представителей вузов и организаций Португалии, Эстонии, Словакии, России и Казахстана. Так, планируется разработка трех образовательных программ (i-PET) для преподавателей инженерных специальностей с переменным набором модулей на основе современных технологий обучения (e-learning) и индивидуального подхода. Осуществление проекта «ENTER» является реальной перспективой улучшения состояния инженерного образования и повышения уровня подготовки инженеров-педагогов в нашей стране.

Ключевые слова: инженерное образование, инженер-педагог, образовательная программа, курсы повышения квалификации.

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АВТОРЛАР ТУРАЛЫ МӘЛІМЕТТЕР СВЕДЕНИЯ ОБ АВТОРАХ INFORMATION ABOUT AUTHORS

- Ahmedjanov, R.R.** — Doctor of biological sciences, Professor, Tomsk State Pedagogical University, Russia.
- Aibolova, G.K.** — Candidate of technical sciences, Kh.A. Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan.
- Aitbekova, D.E.** — PhD student, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Baikenov, M.I.** — Doctor of chemical sciences, Professor of the department of chemical technology and petrochemistry, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Bakibayev, A.A.** — Doctor of chemical sciences, Professor, Leading Researcher of the Laboratory of Organic Synthesis, National Research Tomsk State University, Russia.
- Bayakhmetova, B.B.** — Candidate of Chemical Sciences, Associate Professor, Department of Biochemistry and Chemical Disciplines, Semey Medical University, Kazakhstan.
- Bayeshov, A.B.** — Professor, Doctor of Chemical Sciences, Academician of the National Academy of the Republic of Kazakhstan, Head of the Laboratory of Electrochemical Technology, D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan.
- Bayeshova, A.K.** — Professor, Doctor of Technical Sciences, Professor of the Department of General and Inorganic Chemistry, Al-Farabi Kazakh National University, Almaty, Kazakhstan.
- Besterekov, U.** — Doctor of technical sciences, Professor, «Chemical technology of inorganic substances» department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Bokova, T.I.** — Professor, Doctor of biological sciences, Novosibirsk State Agricultural University, Russia.
- Burkitbayev, M.M.** — Doctor of chemical sciences, Professor, First vice rector, Al-Farabi Kazakh National University, Almaty, Kazakhstan.
- Bolysbek, A.A.** — Candidate of technical sciences, Associate professor, «Chemical technology of inorganic substances» department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Chertikhina, Yu.A.** — Assistant, Department «Organic chemistry», Ukrainian State University of Chemical Technology, Dnipro, Ukraine.
- Dinzhumanova, R.T.** — Candidate of Chemical Sciences, Associate Professor, Department of Biochemistry and Chemical Disciplines, Semey Medical University, Kazakhstan.
- Dolgov, I.R.** — Postgraduate student, Chemical engineering Department, School of Earth Sciences and Engineering, Tomsk Polytechnic University, Russia.
- Dospayev, M.M.** — Doctor of technical sciences, Head of laboratory «Electrochemical processes», Zh.N. Abishev Chemical-Metallurgical Institute, Karaganda, Kazakhstan.
- Dzhanmuldaeva, Zh.K.** — Candidate of technical sciences, Professor, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Fengyun Ma** — Professor, Xinjiang University, Urumqi, China.
- Govorov, V.A.** — Candidate of chemical sciences, Researcher, A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, Moscow, Russia.
- Guba, G.Ya.** — PhD, Assistant professor, Chemical engineering Department, School of Earth Sciences and Engineering, Tomsk Polytechnic University, Russia.
- Gumennyi, I.V.** — Junior researcher, Graduate student, A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, Moscow, Russia.

- Gusar, A.O.** — Postgraduate student, Engineer, Chemical engineering Department, School of Earth Sciences and Engineering, Tomsk Polytechnic University, Russia.
- Ibishev, K.S.** — Candidate of chemical sciences, Leading researcher, Zh.N. Abishev Chemical-Metallurgical Institute, Karaganda, Kazakhstan.
- Imanbayeva, A.A.** — Candidate of Biological Sciences, General Director, Mangyshlak Experiment Botanical Garden, Aktau, Kazakhstan.
- Ishmuratova, M.Yu.** — Candidate of biological sciences, Senior researcher, Mangyshlak Experiment Botanical Garden, Aktau; Ye.A. Buketov Karaganda State University, Kazakhstan.
- Issabayev, Ye.A.** — PhD, National Center for Expertise of Medicines and Medical Devices, Nur-Sultan, Kazakhstan; Ye.A. Buketov Karaganda State University, Kazakhstan.
- Karstina, S.G.** — Doctor of Physical-Mathematical Sciences, Head of Postgraduate Education Department, Professor, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Kassenova, N.B.** — Junior Researcher, PI «National Laboratory Astana», Nazarbayev University, Nur-Sultan, Kazakhstan.
- Khan, N.V.** — 1st year PhD student of General and inorganic chemistry department, Al-Farabi Kazakh National University, Almaty, Kazakhstan.
- Klivenko, A.N.** — Senior lecturer, Department of Chemistry and Environmental protection, Shakarim State University of Semey, Kazakhstan.
- Kongyratbay, A.M.** — Master student, Department of General and Inorganic Chemistry, Al-Farabi Kazakh National University, Almaty, Kazakhstan.
- Kudaibergenov, S.E.** — Doctor of chemical sciences, Professor, Director, Institute of Polymer Materials and Technology, Head of the Laboratory of Engineering Profile, Satbayev University, Almaty, Kazakhstan.
- Kudasova, D.E.** — Master, Teacher, Department «Biotechnology», M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Kydyraliyeva, A.D.** — PhD third-year student, «Chemical technology of inorganic substances» department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Lebed, O.S.** — Candidate of chemical sciences, Associate professor, Department «Organic chemistry», Ukrainian State University of Chemical Technology, Dnipro, Ukraine.
- Leska, B.** — Professor, Doctor of Science, Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland.
- Makhatova, V.E.** — Candidate of technical sciences, Associate professor, Kh. Dosmukhamedov Atyrau State University, Kazakhstan.
- Malkin, A.Ya.** — Doctor of physical and mathematical sciences, Professor, Chief researcher, A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, Moscow, Russia.
- Mamaeva, E.A.** — PhD, Assistant professor, Chemical engineering Department, School of Earth Sciences and Engineering, Tomsk Polytechnic University, Russia.
- Minayeva, Ye.V.** — Candidate of Chemical Sciences, Head of International Cooperation Department, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Mutaliyeva, B.Zh.** — Candidate of chemical sciences, Associate professor, Department «Biotechnology», M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Naukenov, M.Zh.** — Engineer, «Atyrau oil refinery» LLP, Kazakhstan.
- Petropavlovsky, I.A.** — Doctor of technical sciences, professor, «Technologies of inorganic substances and electrochemical processes» department, D.I. Mendeleev Russian Chemical Technological University, Moscow, Russia.
- Popova, V.A.** — Postgraduate student, Engineer, Chemical engineering Department, School of Earth Sciences and Engineering, Tomsk Polytechnic University, Russia.
- Popp, Ya.I.** — Assistant, Novosibirsk State University of Architecture and Civil Engineering, Russia.
- Prosyaniк, A.V.** — Doctor of chemical sciences, Professor, Department «Organic chemistry», Ukrainian State University of Chemical Technology, Dnipro, Ukraine.

- Pochitalkina, I.A.** — Candidate of technical sciences, Associate professor, «Technologies of inorganic substances and electrochemical processes» department, D.I. Mendeleev Russian Chemical Technological University, Moscow, Russia.
- Sagyndykova, M.S.** — PhD, Head of Scientific Project, Mangyshlak Experiment Botanical Garden, Aktau, Kazakhstan.
- Salkeeva, L.K.** — Doctor of Chemical Sciences, Head of Chair of Organic Chemistry and Polymers, Professor, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Sarsembayev, B.Sh.** — Candidate of chemical sciences, Senior researcher, Karaganda Economic University of Kazpotrebsoyuz, Kazakhstan.
- Seitmagzimova, G.M.** — Candidate of technical sciences, Professor, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Shambilova, G.K.** — Doctor of chemical science, Professor, Kh. Dosmukhamedov Atyrau State University, Kazakhstan.
- Su, E.** — PhD student, Istanbul Technical University, Turkey.
- Sugralina, L.M.** — Candidate of Chemical Sciences, Professor, Chair of Organic Chemistry and Polymers, Associated Professor, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Suleimen, Ye.M.** — Candidate of Chemical Sciences, PhD, Assistant professor, Director of Institute of applied chemistry, L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan.
- Tleuova, C.T.** — Candidate of technical sciences, Associate professor, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Toleutay, G.** — PhD student, Satbayev University, Almaty, Kazakhstan; Institute of Polymer Materials and Technology, Almaty, Kazakhstan.
- Tuleshova, E.Zh.** — Candidate of chemical sciences, Association professor, Kh.A. Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan.
- Tusipkhan, A.** — Doctor PhD, Senior lecturer, Department of chemical technology and petrochemistry, Ye.A. Buketov Karaganda State University, Kazakhstan.
- Urakaev, F.Kh.** — Doctor of chemical sciences, Professor, Leading researcher, V.S. Sobolev Institute of Geology and Mineralogy of the Russian Academy of Sciences, Novosibirsk, Russia.
- Urakov, K.N.** — PhD second-year student, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Xintai Su** — Professor, Xinjiang University, Urumqi, China.
- Yakubova, R.R.** — Candidate of technical sciences, Associate professor, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Yeskendiroya, M.M.** — Senior lecturer, «Chemical technology of inorganic substances» Department, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
- Zhumabay, F.M.** — Doctoral student, Department of General and Inorganic Chemistry, Al-Farabi Kazakh National University, Almaty, Kazakhstan.

**2019 жылғы «Қарағанды университетінің хабаршысында»
жарияланған мақалалардың көрсеткіші.
«Химия» сериясы**

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**Указатель статей, опубликованных
в «Вестнике Карагандинского университета» в 2019 году.
Серия «Химия»**

№ с.

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«Bulletin of the Karaganda University» in 2019.
«Chemistry» Series**

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