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SURFACTANT ADSORPTION PARAMETERS DETERMINED FROM SURFACE TENSION DATA AS MEASURED BY DROP AND BUBBLE PROFILE ANALYSIS TENSIOMETRY

Abstract: Drop and bubble profile analysis tensiometry is the most frequently used methodology for studies of surfactant adsorption at liquid interfaces. However, there is depletion of surfactant molecules caused by adsorption when drop profile analysis tensiometry is applied for surface tension measurements at low surfactant bulk concentration. This depletion can lead to wrong characteristic adsorption parameters when not quantitatively corrected in the data analysis. We show for the two surfactants CTAB and Tween 20, that particularly the values for the adsorption activity coefficient and the molar area of adsorbed molecules are largely overestimated when using drop profile analysis data. It is shown that bubble profile analysis data provide correct values of the adsorption characteristics. The data analysis presented here is based on the Frumkin adsorption model.

Keywords: Adsorption of surfactant, bubble and drop profile analysis tensiometry, depletion effects due to adsorption, Frumkin adsorption model.

1. Introduction

Surface active molecules – surfactants – are omnipresent in our daily life and applied in many modern technologies. The optimum use of surfactants requires good knowledge of their surface properties. The surface tension isotherms measured for aqueous solutions of surfactants as a function of bulk concentration give access to the most important fundamental information about the properties of the surfactant adsorption layers, such as surface activity, molar area at the surface and critical micelle concentration [1].

Among the various surface tension methods, the bubble and drop profile analysis tensiometry is the most frequently used one to day. The pioneer for this methodology was A.W. Neumannwho published a number of fundamental papers about this method which he called ADSA (Axisymmetric Drop Shape Analysis) [1,2,3,4].Recently, the state of the art of this methodology was described with details referring to the Profile Analysis Tensiometer PAT1 (SINTERFACE Technologies, Berlin, Germany) [6].

It was discussed in [6] that in studies with protein solutionsa depletion happens due to the adsorption of part of the protein molecules at the drop surface. In contrast, when using an air bubble immersed in the protein solution, the depletion due to protein adsorption at the bubble surface is negligible. From the difference between the obtained data the adsorbed amount of protein can be estimated [7].

The mentioned depletion effects in protein adsorption experiments appear as the used bulk concentrations are very low. However, also studies of solutions of strongly surface-active moleculescan be affected by this phenomenon. Thus, it is important to know from what surface activity and surfactant bulk concentration on the mentioned depletion effects become important and have to be quantitatively considered.

In a recent work, we presented experimental data for the surface tension isotherms of three different surfactants: sodium dodecyl sulphate (SDS), hexadecyl trimethyl ammonium bromide (CTAB) and the non-ionic surfactant Polyoxyethylene(20)sorbitanmonolaurate (Tween20) [1]. In this work a protocol was proposed thattakes into account the mass balance of the amount of surfactant adsorbed at the drop surface

and remaining in the drop bulk. It is the purpose of this short communication to show how the erroneous use of surface tension isotherm data can lead to large errors in the determination of characteristic adsorption data for the studied surfactants.

2. Adsorption model for describing the experimental isotherm data

The Frumkin adsorption model is one of the most frequently used one for many surfactant systems although it had been proposed already almost 100 years ago [1]. The equation of state for this model reads

$$-\frac{\Pi\omega_0}{RT} = \ln(1-\theta) + a\theta^2 \tag{1}$$

while the adsorption isotherm has the form

$$bc = \frac{\theta}{1-\theta}\exp(-2a\theta) \tag{2}$$

Here $\theta = \Gamma\omega$ *is the surface coverage,* Γ *is the adsorption,* ω is the molar area, $\Pi = \gamma_0 - \gamma$ is the surface pressure with γ_0 and γ being the surface tension of the solvent and solution, respectively, a is the interaction parameter, R is the gas law constant, T is the temperature, and b is the adsorption activity coefficient. In [8] it was assumed that the intrinsic compressibility coefficient ε depends on the surface coverage, however, for the discussion here, we will assume that this coefficient is negligible in order to simplify the discussion of the adsorption parameters.

To quantify the depletion effects appearing during the adsorption of surfactants at the surface of a single drop, we have to make a quantitatively mass balance. In [8] it was shown that the final concentration inside a drop is given by

$$c = c_0 - (A/V)\Gamma \tag{3}$$

While c_0 is the initial surfactant concentration in the drop having the volume V and the surface area A. Introducing this final bulk concentration c into the adsorption isotherm given by Eq. (2) we obtain:

$$b\left(c_0 - \frac{A}{V}\Gamma\right) = \frac{\theta}{1-\theta}\exp(-2a\theta) \tag{4}$$

The set of Eqs. (1) and (2) can be used for the analysis of data obtained from experiments without any depletion effects, as it is the case for bubble profile analysis tensiometry. In contrast, using isotherm data measured with drop profile analysis tensiometry, a depletion appears and Eqs. (1) and (4) have to be used to correct the evident loss of molecules in the drop volume caused by adsorption at the drop surface.

The question we want to answer here is now, what happens when we apply the original Frumkin model, as given by Eqs. (1) and (2), to data measured by drop profile analysis without considering depletion effects. Note, this was the well accepted procedure done before we discussed the depletion effects due to adsorption.

The amount of lost surfactant molecules due to adsorption can be estimated by Eq. (3) and is mainly given by the ratio of drop area over drop volume A/V. In routine experiments, the drop surface area is about 0.35 cm² while the volume is about 0.02 cm³, so that the ratio is A/V=17.5 cm⁻¹, i.e. A/V » 1 cm. For bubbles of the same size like the drop, immersed into a surfactant solution of say 20 cm³ volume, the ratio is A/V=0.0175 cm⁻¹, i.e. three orders of magnitude less. Note, for smaller drops the ration A/V is even larger, which is less favourable and the loss of surfactant determined via Eq. (3).

3. Materials and experimental methods

The experimental data we want to reinterpret here were obtained in [8] by using the drop and bubble profile analysis tensiometer PAT-1 (SINTERFACE Technologies, Germany) [10].The surfactants studiedin [8] were SDS, decanol, CTAB and Tween20.As the data obtained for SDS did not show any measurable depletion effects, and for decanol only very little effects, we will not discuss them here. Note, for all surfactants having a surface activity less than that of decanol or SDS any depletion effects can be neglected. We do not want to present an extensive discussion on how the surface activity of a surfactant is defined, but we just use the value of the adsorption activity coefficient b in Eq. (2) as a useful parameter. The larger the value of b is, the higher is the surface activity of the corresponding surfactant.

4. Results and Discussion

The experimental results presented in Figs. 1 and 2 are replotted from [8]. There are two sets of data in the given isotherms, one measured with drop profile (black squares) and one measured with bubble

profile analysis tensiometry (red circles). As expected for the two rather strong surface-active surfactants, the data points obtained from bubble experiments are further left at lower concentrations than those measured with single drops. This was expected because to reach the same surface tension with a single drop, we need a higher initial bulk concentration. During the experiment, the concentration inside the single drops decreases due to the loss of surfactant molecules adsorbed at the drop surface.

Following the target of this work, the experimental data were fitted by the Frumkin adsorption model given by Eqs. (1) and (2). As mentioned already further above, we used the Frumkin adsorption model in its classical form as derived in [9] and did not add the dependence of the molar area of adsorbed surfactant molecules as function of the surface coverage θ, as it was made in [8], i.e. assuming a so-called intrinsic compressibility coefficient which allows a qualitatively better reflection of the experimental findings by the model. In the data analysis performed here, we also did not consider the obviously happening depletion due to adsorption. This "wrong" approach on purpose was made in order to demonstrate the impact of depletion effects on the adsorption parameter values. The results of fitting are summarized in Table 1.

Table1 - Model parameters used for fitting of experimental data
by the classical Frumkin adsorption model given by Eqs. (1) and (2)

Surfactant	Experimental mode	$\omega,$ $10^5\,\mathrm{m^2/mol}$	$b,$ $\mathrm{m^3/mol}$	a	Line in the figure
CTAB,					Fig. 1
	Drop	2.36	40	0.95	dashed line
	Bubble	2.1	14.7	1.8	solid line
Tween 20					Fig. 2
	Drop	2.27	300	0.7	dashed line
	Bubble	1.6	170	0.6	solid line

As we can see, in particular the value of the adsorption activity coefficient obtained for the drop data as much larger than that for the bubble data. For CTAB this value for the coefficient b is almost three times larger, which means the isotherm is shifted to larger concentrations by a factor of almost 3, a shift of half an order of magnitude. The molar area obtained from the drop data is also larger (by more than 10%) as compared to the bubble data. This would mean that the molecules require more area at the interface, or in other words are less close packed, as we would conclude from the data obtained from bubble experiments.

For the second surfactant discussed here, the non-ionic surfactant Tween 20, the situation is quite similar. The surface activity coefficient is decreased by a factor of about 2 (larger value of b for the drop data), while the area per adsorbed molecule is larger by even 30%. These changes can be evaluated as dramatic and reflect a strongly different adsorption behaviour.
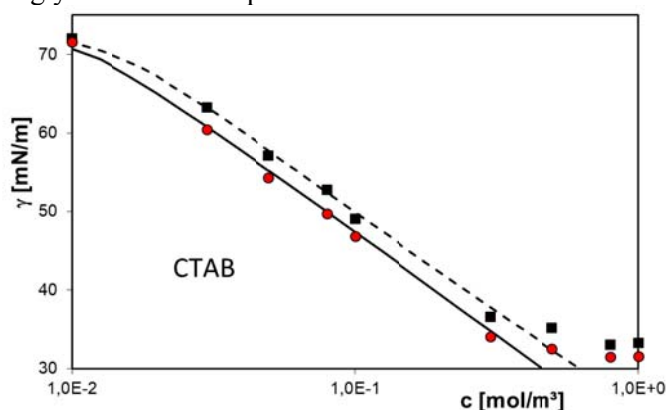

Figure 1 - Equilibrium surface tension isotherm for aqueous solutions of CTAB plotted as a function of the initial solution concentration, as measured by bubble profile (●) and drop profile analysis tensiometry (■); lines represent the results of fitting the adsorption model to the experimental data
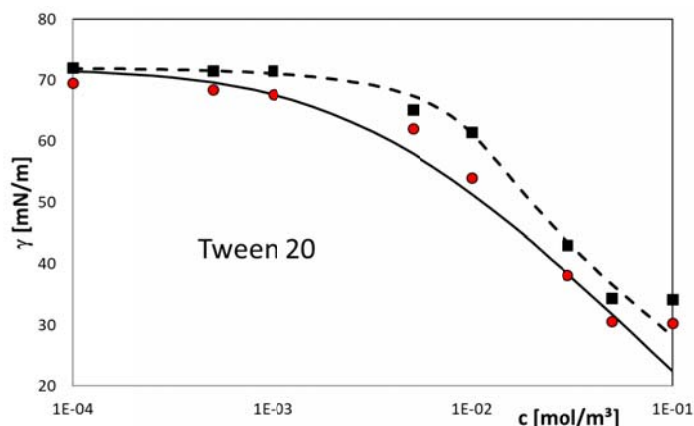
Figure 2 - Equilibrium surface tension isotherm for aqueous solutions of Tween 20 plotted as a function of the initial solution concentration, as measured by bubble profile (●) and drop profile analysis tensiometry (■); lines represent the results of fitting the adsorption model to the experimental data

Let us somehow generalize the findings so that we can apply them to other surfactant systems. It was shown that for the given experimental conditions the ratio of A/V for drops (17.5 cm^{-1}) is much larger than 1 cm^{-1}, while it is much smaller than 1 cm^{-1} for bubble data. Assuming that typical values of the adsorbed amount Γ are between 10^{-11}mol/cm² and 10^{-9}mol/cm², we obtain for the second term $(A/V)\Gamma$ on the right-hand side of Eq. (3) values of roughly 10^{-10} to 10^{-8}mol/cm³, i.e. 10^{-4} to 10^{-2}mol/m³. This is exactly the concentration range in which the two studied surfactants adsorb (see Figs. 1 and 2). Their surface activity, expressed by the adsorption activity coefficient b, let us expect this. We know that at a bulk concentration of c≈1/b the surface layer is covered by approximately 50%, i.e. the parameter 1/b refers to a concentration which tells us where we must expect serious depletion effects. For all concentrations below 1/b, these depletion effects must be essential. For CTAB this means for concentrations below about 10^{-1}mol/m³ and for Tween 20 below 10^{-2}mol/m³ the depletion effects are remarkable. Comparing this finding with experiments for the various surfactants studied and applied in surface science and technology (cf. the isotherms given in [1] for many surfactants), we can conclude that for example for Triton X100 or the oxyethylated alcohols like $C_{12}EO_5$ or $C_{14}EO_5$ the depletion effects are substantial, while for SDS and shorter chain alkyl sulphates, DeTAB (decyl trimethyl ammonium bromide) or $C_{10}EO_8$the depletion effects are negligible and errors will not appear when drop profile data are analysed and interpreted with the classical version of the Frumkin or any other adsorption model.

Finally, we should compare the parameter values in Table 1 with those published in [8] using a more refined adsorption model. The absolute values deviate from those presented in the table. This is clear as the parameters are not completely independent of each other. During the fitting process, any change in one parameter value causes changes in the optimum values of any other parameter. This is particularly true for the technical surfactant Tween 20, which is obviously a large mixture of many surface-active compounds. Thus, only the complete set of parameter values describes the adsorption behaviour of a surfactant sufficiently well. Note, however, the parameter values given in Table 1 are based on fitting drop and bubble data by exactly the same adsorption model and all discussed differences originate from the depletion effects, which were neglected on purpose when fitting the drop data (although these effects are essential).

5. Conclusions

As discussed recently in [8], a specialcorrection and fitting algorithm has to be applied to determine the characteristic adsorption parameters from experimental data obtained from drop profile analysis tensiometry. This algorithm is based on the balance between the surfactant mass in the drop bulk and the amount adsorbed at the drop surface. Exact knowledge about the surface area and volume of the drop is required for these corrections as shown above.When ignoring the mentioned effects, the error made by this erroneous procedure is significant and can lead to wrong conclusions.

Similar mistakes are sometimes made in studies on emulsions. When supporting emulsion properties, often interfacial tension studies are performed in order to determine the number of surfactants adsorbed at drop surfaces. In the case, however, when the emulsion drops are rather small (much smaller than the drops used in tensiometry so that the ratio A/V becomes even much larger than here), the amount of adsorbed surfactant is enormous and data measured at macroscopic interfaces are not relevant. As shown here, errors in the determined coefficient b used to estimate the order of magnitude for the required concentration c>1/b for covering the emulsion drop surfaces sufficiently by surfactant molecules, can lead to wrong values, too loweven by several orders of magnitude.

It could be recommended to use only bubble profile tensiometry in order to avoid errors in the determination of adsorption characteristics for surfactants. Experimentalists know, however, that experiments with single drops are much easier performed than with bubbles immersed in a solution container. In addition, some specific samples can be provided only in extremely small quantities so that drop profile analysis with single drops (typically with volumes of 20 μl) is the method of choice while for bubble experiments a much larger amount of solution (typically 10-25 ml) would be required required.

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ТАМШЫЛАР МЕН КӨПІРШІКТЕР СҰЛБАСЫН ТАЛДАУ АРҚЫЛЫ БЕТТІК КЕРІЛУДІ ӨЛШЕУ ӘДІСІМЕН БЕТТІК-АКТИВТІ ЗАТТАРДЫҢ АДСОРБЦИЯЛЫҚ ПАРАМЕТРЛЕРІН АНЫҚТАУ

Аннотация: Тамшылар мен көпіршіктер сұлбасын талдау тензиометриясы беттік-активті заттардың сұйық беттердегі адсорбциясын зерттеуде жиі қолданылады. Алайда, бұл әдісті беттік-активті заттардың (БАЗ) төмен концентрациясында қолдану БАЗ-дардың көлемдегі мөлшерінің азаюына апарады. Бұл өзгеріс беттік-активті заттардың адсорбциялық параметрлерін анықтау барысында ауытқулар беруі мүмкін, сол

себепті алынған сандық нәтижелерге түзетпелер енгізу қажет. Осыған орай адсорбциялық белсендігі мен мольдік ауданы жоғары болған СТАВ және Tween 20 сияқты екі БАЗ үшін адсорбциялық мәліметтер берілген. Көпіршіктер сұлбасын талдау арқылы алынған мәліметтер адсорбцияны дұрыс сипаттайтындығы көрсетілген. Талдау Фрумкиннің адсорбция моделінде жасалған.

Тірек сөздер: Беттік-активті заттардың адсорбциясы, тамшылар мен көпіршіктер сұлбасын талдау тензиометриясы, адсорбция барысында зат мөлшерінің азаюы, Фрумкиннің адсорбция моделі.

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АДСОРБЦИОННЫЕ ПАРАМЕТРЫ ПАВ (ПОВЕРХНОСТНО-АКТИВНОГО ВЕЩЕСТВА), УСТАНОВЛЕННЫЕ ИЗМЕРЕНИЕМ ДАННЫХ ПОВЕРХНОСТНОГО НАТЯЖЕНИЯ МЕТОДОМ АНАЛИЗА ПРОФИЛЯ КАПЕЛЬ И ПУЗЫРЬКОВ

Аннотация. Тензиометрия анализа профиля капель и пузырьков является наиболее часто используемой методикой для исследования адсорбции поверхностно-активного вещества на жидких межфазных границах. Однако, происходит уменьшение поверхностно-активных молекул в объемной концентрации в связи с их адсорбцией при использовании тензиометрического метода анализа, применяемого при измерении поверхностного натяжения ПАВ при малых концентрациях. Это уменьшение в объеме может привести к неправильным характеристикам параметров адсорбции, если не ввести количественные поправки при анализе данных. Представлены данные для двух поверхностно-активных веществ: СТАВ и Tween 20, в частности, для которых значительно завышены данные коэффициента адсорбционной активности и молярной площади адсорбированных молекул при анализе данных профиля капли. Показано, что данные анализа профиля пузырьков представляют правильные значения адсорбционных характеристик. Анализ данных основан на модели адсорбции Фрумкина.

Ключевые слова: Адсорбция ПАВ, тензиометрия анализа профиля капель и пузырьков, эффект обеднения раствора при адсорбции, модель адсорбции Фрумкина.

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RESEARCH OF THE CONTENT OF ZINC AND LEAD IN THE LIGHT-CHESTNUT SOILS ON THE TERRITORY OF ISLANDS "POLKOVNICHII" (KAZAKHSTAN)

Abstract. The aim of the work was to study and evaluate the main regularities of distribution of zinc and lead compounds in light chestnut soils. The study was carried out to assess the impact of man-made pollution on the environment and monitoring of soil pollution. The objects of research were the natural typical light chestnut soils of "Polkovnichii" island, located in the city of Semipalatinsk (Semey), Kazakhstan. For the monitoring, samples of all available genetic horizons of the soil section were applied. It is established that with increase in content of physical clay in the soil the maintenance of a bulk form of lead increases. With increase in maintenance of a humus in the soil the tendency to increase in maintenance of a bulk form of Zn is observed. The total lead content varies from 4.91 to 12.24 mg/kg; the total content of zinc is in the range of 14.84-23.67 mg/kg. It has been revealed that, according to the level of the average content of the mobile form of zinc, the researched soils are related to the average soils provided by these elements. The authors conclude that it is necessary to study the effect of the physical and chemical properties of the region's soils on the effectiveness of zinc fertilizers and to continue research in this direction.

Keywords: light chestnut soils, zinc, lead, "Polkovnochii" island, Semipalatinsk.

Introduction

The soil produces minerals from the substances which are contained in it, the introduced fertilizers, pollinators. The minerals which are contained in them pass into plants. Therefore the plants going to food reflect features of microelement structure of this soil and its geological structure. Emissions of industrial plants also contain harmful impurities deposited on the soil. So, in the soil around the enterprises of non-ferrous metallurgy there are oxides of lead, tin, molybdenum, arsenic, etc.; around factories of ferrous metallurgy contain zinc, lead, phenol, arsenic, sulfur [1-3]. Excess of minerals, such as mercury, lead, cadmium or selenium, obtained from vegetable or animal food, can cause the human body poisoning, whereas copper deficiency, iron, manganese, zinc, iodine, fluorine, cobalt and molybdenum cause a variety of problems related to nutrition [4, 5-8]. In natural, uncontaminated reservoirs and in places where there are no enterprises for production and processing of minerals and where mineral substances are not brought in the soil as fertilizers or growth factors of plants, minerals contain, as a rule, in thousand or ten-thousand shares of milligram on water liter.

At the solution of practical questions of environmental protection from anthropogenic pollution the important place is taken by data on the content of toxiferous ingredients in soils of the concrete region. At pollution level assessment as background usually take uncontaminated territories with a similar soil cover for which concentration of heavy metals are known. The way of analogy in this case is very difficult to observe, since city soils are urban soils, strictly speaking there are no analogues in natural conditions. In this regard, there is an urgent problem of finding a local urbanized background that could be used to assess the level of soil contamination.

The aim of the work was to study and evaluate the main regularities of distribution of zinc and lead compounds in light chestnut soils.

The natural typical light chestnut soils of "Polkovnichii" island (fig. 1), located in the city of Semipalatinsk (Semey), Kazakhstan, were chosen as objects of research. The city of Semey is divided by the Irtysh River on left-bank and right-bank. In the middle of the Irtysh River there is an island "Polkovnichii" (fig.2). The original and present name of the island is associated with the name of Matvei Ivanovich Geytsig, the lieutenant colonel (later Colonel), who was appointed commandant of the Semipalat fortress in 1787. The name of the island "Polkovnichii" is mentioned in plans from the 19th century [8]. The island "Polkovnichii" is one of the main sights of Semey. During its long history, it experienced different periods. To restore the island to its former glory, it is necessary, first of all, to change its consumer attitude to natural resources. Today, the fate of the Polkovnichii's Island is also worried about environmentalists, public figures, and law enforcement agencies.

Figure 1 – An island"Polkovnichii", Semey, Kazakhstan, 070000

Figure 2 – General view of the island location map

For tests were taken samples of all of the genetic horizons of the soil profile. Definition of macrocomposition of all tests of soils (pH, a humus, CO_2 of carbonates, granulometric composition) was carried out by standard methods [9].

Among the heavy metals as studying objects lead and zinc have been taken. The choice of these elements is due to two factors: firstly, the physiological importance of zinc in living organisms and in particular for plants, and second - the lack of information on the biogeochemistry of these elements on the island "Polkovnichii" needed to solve a number of scientific and practical issues [10, 11].

Lead (Pb) is a metal that has long been extracted and used by man in various spheres of economic activity. Just as long ago, the negative impact of lead on human health is known: already in the II century of BC signs of "saturnism", lead poisoning of the organism, were described. In urban conditions, the most studied is lead contamination: it is more where there is more humus (the soil of the city is parks, gardens, squares, transport arteries). In the soils of transport highways lead is detected even at great depths.

Zinc (Zn) is one of the most important trace elements: it is part of the enzymes that lead and regulate many vital processes. Zinc increases the heat and frost resistance of plants. With its lack in the soil, the inorganic phosphates are slowed down into organic plant compounds. On the other hand, a significant increase in the content of zinc in the components of the environment and foodstuffs negatively affects living organisms, accompanied by a deterioration in human health. Plants have a different ability to absorb zinc from the soil. Of all heavy metals, zinc is the most mobile element and is well absorbed by plants.

The content of heavy metals in the explored soils was determined on the KFK-3 device by a photocolorimetric dithizone method by G.Ya.Rin'kis's recipe [9, 12, 13]. The reproducibility of the method was equal to $\pm 4.2\%$. Selection of fractions of Pb and Zn was carried out by method of parallel extraction. All analytical data were processed by mathematical analysis and mathematical statistics in soil science according to E.A.Dmitriev [14].

Results and discussion

Results of the performed researches (table) show that the average total content of lead in the general set of soil samples of the investigated territory in 1.2 time, of zinc – is 2.4 times lower than their clark contents in soils.

Table - The total content of lead and zinc in the light chestnut soils of "Polkovnichii" island (in mg/ kg)

Metal	K_v,	M±m,	V, %	Clark in a soil [15]	Clark in the lithosphere [15]	Maximum concentra-tion limit in the soil [5]
Pb	4.91 – 12.24	8.32 ± 1.05	34.0	10.00	16.0	100
Zn	14.84-23.67	20.86± 1.37	17.0	50.00	83.0	300

Note: K_v - a range of a variation, M±m – an arithmetic average and its mistake, V – variation coefficient.

The studied heavy metals on magnitude of the average total content are arranged in such a way: Zn>Pb. On value of coefficient of a variation (in %) heavy metals in the researched soils are located in the following decreasing order: Pb (34)>Zn (17).

It was found that the content of total forms of heavy metals on a profile of soils is distributed unevenly. The maximal content of lead is characteristic of the illuvial horizon of B_1, minimum – of the humic horizon A. The maximal content of a total form of Zn is characteristic of the humic horizon of A_n and the humic and accumulative horizon of A_1, minimum – of the transitional horizon of BC. The increased content of a total form of Zn in the humic and humic and accumulative horizons is explained by the increased contents in them of the maximum quantity of a humus, and also higher value pH. In turn, the increased content of a total form of lead in the illuvial horizon B_1 is explained by the increased contents in this horizon of the maximum quantity of physical clay (<0.01 mm), possible carbonaceous and alkaline geochemical barriers.

According to numerous researches, organic matter and its components form various complex compounds with heavy metals [6, 11], and the fine-grained mineral phase is the strong adsorbent of heavy metals [7]. Results of the carried out researches show that with increase in content of physical clay in the soil the content of a bulk form of lead increases, and also with increase in content of a humus in the soil the tendency to increase in content of a bulk form of Zn takes place. Reaction of aqueous soil slurries in the humic and humic and accumulative horizons is neutral. Namely at values pH, the close to neutral, the maximum of absorption of heavy metals by organic matter and clay minerals is reached [7, 16]

Amplitude of fluctuation of content of elements in the soil is a little various: for lead accumulation in the top horizon of the soil sharply increases with a depth, on the contrary, accumulation in the humic and accumulative horizon which gradually decreases is characteristic of Zn. It indicates that lead in the researched soils is less mobile metal, is capable to form steady compounds with finely dispersed mineral phase of the soil. It should be noted that zinc in these investigated soils relates to metals less mobile in the soil; a key role in this belongs to an organic substance capable of forming stable complexes with zinc, which is very important and has great practical significance for the management of migration and bioavailability of this element in the soil. The research of the work showed that the observed the unequal correlation between the total content of heavy metals and indicators of humus, soil pH and physical clay. A positive reliable correlative dependence of content of a total form of lead only on availability of physical clay is revealed. In the investigated light chestnut sandy loam soils reliable positive correlative dependence between the total content of Zn and existence of a humus, and also value pH is found. The established level of total contents in soils of the studied urbanized background is much lower than the recommended maximum permissible limits. V.V.Kovalsky established the threshold concentrations of some elements in soils according to their possible pathological influences on farm animals [17]. When compared with these threshold concentrations total zinc content is within the lower threshold boundary. The investigated light chestnut soils of "Polkovnichii" island are characterized by low total zinc content in comparison with soils of different regions [12, 13, 16, 17]. According to gradation to Ya.V.Peyv and G.Ya.Rin'kis [9, 12-14], by the level of average content of the mobile form of Zn the researched soils belong to the medium soils accordingly presence of this element.

Data on the background content of zinc and lead in the studied soils are very valuable, give the possibility of systematic observations in this natural region and improve the objectivity of the evaluation of the emerging environmental conditions. In recent years farmers to the soil introduce Zn-containing fertilizers therefore carrying out a research of influence of physical and chemical properties of soils of the region on effectiveness of zinc fertilizers has applied value. Thus, as a result of the research it was found that the studied soils are characterized by deficiency of zinc content and by the level of the average content of mobile forms of zinc belong to the medium soils by the presence of this element. This must be considered when using zinc-containing fertilizers into the soil. It is necessary to carry out detailed investigation of the influence of physical and chemical properties of the soil in the region on the effectiveness of zinc fertilizers, and to continue research in this direction.

Conclusion

The researches on the soils of the territory of the island "Polkovnichii" (Kazakhstan) for an assessment of the main regularities of distribution of forms of finding of Zn, Pb in light chestnut soils were carried out. It is found that the total content of lead fluctuates from 4.91 to 12.24 mg/kg, the average value is equal to 8.32 mg/kg, the coefficient of a variation is equal to 34.0%; the total content of zinc is in limits of 14.84-23.67 mg/kg, the average value is equal to 20.86 mg/kg, the coefficient of a variation is twice less, than for lead and amounts 17%. Average total content of lead in 1.2 times, zinc - 2.4 times lower than their clark contents in soils. The total content of zinc in the soils of investigated area is located within the lower threshold limits. Migration of forms of finding of lead and zincum on a profile of the soil happens nonuniformly: accumulation of zinc is noted in the top horizons of the soil – humic A_n and the humic accumulative horizon of A_1. It indicates the leading role of soil organic matter in accumulation of this element. Lead accumulation occurs in the illuvial horizon B_1 of the investigated soils, due to the increased content of physical clay in this horizon.

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ӘОЖ: 543.5

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«ПОЛКОВНИЧИЙ» АРАЛЫНДАҒЫ АШЫҚКАШТАНДЫ ТОПЫРАҚ ҚҰРАМЫНАН МЫРЫШ ЖӘНЕ ҚОРҒАСЫН МӨЛШЕРІН ЗЕРТТЕУ

Тірек сөздер: ашыққаштанды топырақ, мырыш, қорғасын, мониторинг, «Полковничий» аралы, Семей.

Аннотация. Жұмыстың мақсаты ашыққаштанды топырақ құрамынан мырыш және қорғасын қосылыстарының таралуының негізгі заңдылықтарын бағалау мен зерттеу болып табылады. Зерттеу қоршаған ортаға техногенді ластаушыларды бағалау мен топырақтың ластануына мониторинг жасау үшін жүргізілді. Зерттеу нысаны ретінде Семей қаласының маңында орналасқан «Полковничий» аралының табиғи ашыққаштанды топырағы алынды. Мониторинг жасау үшін генетикалық горизонталды топырақтың барлық үлгісі қолданылды. Топырақ құрамында физикалық саздың мөлшері артқан сайын қорғасынның валдық түрінің үлесі де артады. Топырақ құрамында гумус мөлшері артқанда мырыштың валдық түрі артатыны байқалды. Қорғасынның валдық мөлшері 4,91-ден 12,24 мг/кг, ал мырыш мөлшері 14,84-23,67 мг/кг болады. Зерттелген топырақта мырыштың орташа қозғалмалы түрі топырақты осы элементпен қамтамасыз етудің орташа деңгейіне жататыны анықталды. Аймақтың топырағының физикалық-химиялық қасиетіне мырыштың тыңайтқышының тиімділігіне жеткілікті зерттеу қажет деген тұжырымға келіп, бұл бағыттағы зерттеуді жалғастыру керек.

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ИССЛЕДОВАНИЕ СОДЕРЖАНИЯ ЦИНКА И СВИНЦА В СВЕТЛО-КАШТАНОВЫХ ПОЧВАХ НА ТЕРРИТОРИИ ОСТРОВА «ПОЛКОВНИЧИЙ» (КАЗАХСТАН)

Аннотация. Целью работы является изучение и оценка основных закономерностей распределения соединений цинка и свинца в светло-каштановых почвах. Исследование проводилось для оценки влияния техногенного загрязнения на окружающую среду и мониторинг загрязнения почв. Объекты исследований – это естественные типичные светло-каштановые почвы острова Полковничий, находящегося в черте города Семипалатинск (Казахстан). Для мониторинга были использованы образцы всех имеющихся генетических горизонтов почвенного разреза. Установлено, что с увеличением содержания физической глины в почве увеличивается содержание валовой формы свинца. С повышением содержания гумуса в почве наблюдается тенденция к увеличению содержания валовой формы цинка. Валовое содержание свинца колеблется от 4,91 до 12,24 мг/кг; валовое содержание цинка находится в пределах 14,84-23,67 мг/кг. Выявлено, что по уровню среднего содержания подвижной формы цинка исследуемые почвы относятся к средним по обеспеченности этими элементами почвам. Авторы делают вывод, что необходимо провести исследования влияния физико-химических свойств почв региона на эффективность цинковых удобрений и продолжить исследования в этом направлении.

Ключевые слова: светло-каштановые почвы, цинк, свинец, мониторинг, остров «Полковничий», Семипалатинск.

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CATALYSTS OF CRACKING ON THE BASIS OF HETEROPOLYACIDS

Abstract. Heteropolyacids (HPA) are strong Bronsted acids. The heteropolyacids of the 12 series the most value for catalytic reactions are. The purpose of the work was to develop the composition of cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan). Modification of the catalysts was carried out with mineral acids, organic acids and HPA. The catalysts have been extensively studied by a complex of physicochemical methods. According to IR spectroscopy data, after decationation and dealumination, the natural zeolite does not change its crystal structure. Presumably, the formation of the bond of HPA with the zeolite occurs when the zeolite of the HPA is modified. Electron microscopy data indicate high degrees of dispersion and particle distribution of PW_{12}-HPA on the surface of clinoptilolite. A detailed study of the zeolite surface by the TEM-BP method has shown the formation of stable cluster structures 1-2 nm in size, which are partially embedded in the zeolite volume. These clusters are evenly distributed over the surface of the zeolite and are available for reacting substances.

Keywords: catalytic cracking, heteropolyacids, zeolite of the Shankanay deposit, electron microscopy.

Introduction
Catalysis using heteropolycompounds is one of the important directions in modern catalysis. In acid catalysis, predominantly heteropolyacids are used. The compounds of a proton with a complex anion of inorganic polyoxometallates - molybdenum, tungsten, less frequently vanadium are called heteropolyacids (HPA) [1-3]. HPA are ionic crystals in the solid state, they consist of a large heteropolyanion, a cation, crystallization water, in some cases they also contain additional molecules. The unique physicochemical properties of HPA, providing great potential for the preparation of catalysts with controlled acidity, dispersity of the modifier metal, increased thermal stability, have led to their use as modifiers of heterogeneous catalysts in catalysis[7-11]. The highest value for catalysis is HPA of 12 row. They contain heteropolyanions - the structures of the most common heteropolyanion Keggin $X^x M_{12}^{vi} O_{40}^{x-8}$ or $X^x M_{12-n}^{vi} O_{40}^{x-n-8}$, where X is a central atom (Si^{vi}, P^v, As^{vi}), x is its oxidation degree, M is metal (molybdenum, tungsten or vanadium)[12-15]. HPA of tungsten row PW_{12}-HPA ($H_3PW_{12}O_{40} \cdot 6H_2O$) or of molybdenum row PMo_{12}-HPA ($H_3PMo_{12}O_{40} \cdot 6H_2O$) are well studied[4-7, 16-19]. In the Keggin anion $H_3PW_{12}O_{40}$, for example, the tungsten atom is located in the center of the oxygen octahedron. The phosphorus atom is surrounded by $12WO_6$ octahedra, forming PO_4 tetrahedron. This structure is retained in concentrated solutions of HPA even after the loss of several oxygen atoms. For this reason, HPA has, like zeolites, a high adsorption capacity. For example, polar molecules such as water and alcohols easily penetrate the pores of the HPA and leave the volume of the catalyst, expanding and compressing the distances between the keggin anions, while nonpolar molecules (eg, hydrocarbons) do not give such an effect. This model allows to successfully explain the characteristic behavior of HPA, for example, high catalytic activity at low temperatures, the Keggin structure has a sufficiently high strength[21]. Acid-catalytic liquid-phase

processes based on HPA catalysts were carried out on an industrial scale, for example, hydration of propylene, isobutylene, butenes, polymerization of tetrahydrofuran[22-26]. HPA are strong Bronsted acids and surpass the strength of many mineral acids. HPA have stronger acid sites than the zeolites HX, HY and amorphous aluminosilicates. The acidity of the solid acidity of HPA close to acidity of superacids. This determines the prospects of their use as acidic homogeneous and heterogeneous catalysts. HPA can be applied to the surface of such carriers as SiO_2, TiO_2. The main carriers-Al_2O_3, MgO, - tend to decompose HPA. The practical use of HPA is mainly due to their use as catalysts for the oxidation of unsaturated hydrocarbons, olefin polymerization, epoxidation. Solid HPA, including applied, are used as catalysts in the alkylation of aromatic compounds, hydration of olefins and in other acid-type reactions. Heteropolycompounds of molybdenum find application as flame delayers[27]. An even wider area is their use in reactions where it is necessary to combine acid-base and oxidation-reduction properties of the catalyst[28]. It is known that the acid nature of the catalyst plays a fundamental role in the cracking of hydrocarbon feedstocks. However, the information on the use of HPA in cracking is not numerous, and the cracking properties of HPA-modified natural zeolites have not been practically investigated[8, 29,30].

The aim of the work is the synthesis of cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan), modified with mineral acids, organic acids and HPA and the study of the qualitative and quantitative compositions of the working surface of the catalysts by physical and chemical methods of investigation.

Materials and methods

For preparation of long-chain α-olefins from paraffins, cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan) were prepared by modifying the natural zeolite with mineral acids, organic acids and HPA. Samples were also synthesized on the basis of industrial γ-Al_2O_3 with bulk density 0.68 g/cm^3 modified by HPA. For removal various metals from the cation surface (mainly alkaline and alkaline earth), the zeolite was treated with mineral acids. Natural zeolite (NZ) and previously decationed with hydrochloric acid samples of natural zeolite (H-NZ) were processed with complexons. For example, using one-, two- and three-fold modification of the natural zeolite with 1.75 N HCl samples of cracking catalysts: H-NZ-1, H-NZ-2 and H-NZ-3 were synthesized. For the selective removal of Fe^{3+} iron ions, facilitating the carburization process, a chosen zeolite was treated with organic acids. For this aim, chelating agents (for example, sulfosalicylic acid and citric acid with 10% or 20% concentration), ethylenediamine-tetraacetic acid and its disodium salt of EDTA (Trilon B, aqueous 10% strength solution) were used. All these listed compounds with iron ions form stable water-soluble complexonates.

Treatment of zeolites with HPA was carried out for strengthening of force of the acid centers on which cracking reaction proceeds. For this aim the new catalysts for the cracking of decationized natural zeolite and industrial aluminum oxide have been synthesized and have been modified by the heteropolyacids of the molybdenum and tungsten series: PMo_{12}-HPA/H-NZ, PMo_{12}-HPA/Al_2O_3, PW_{12}-HPA/H- NZ and PW_{12}-HPA/Al_2O_3. HPA were used in an amount of 1.0% to 10% by impregnation on the surface of a decationized natural zeolite (H- NZ) by a known technique[7,9,15,19].

Results and discussion

By IR spectroscopy and X-ray diffraction analysis were studied the structure and phase composition of the catalysts synthesized on the basis of the natural zeolite of the Shankanay deposit (NZ-1) and industrial alumina, modified by the HPA of the molybdenum and tungsten series (PW_{12}-HPA/H-NZ-1 and PW_{12}-HPA/Al_2O_3 (the content of the HPA was 1% , 3%, 5%, and 10%), 10% of PMO_{12}-HPA/H-NZ-1 and 10% of PMO_{12}-HPA/Al_2O_3). The IR spectra (fig. 1, 2) of the starting PMO_{12}-HPA and PW_{12}-HPA contain the following main absorption bands: 510; 594; 789; 867; 962; 1,065; 1,400; 1,618; 2,850; 2,925; 3,210; 3,419 cm^{-1} , which are typical for the compound of the composition $H_3PMo_{12}O_{40} \cdot 6H_2O$ and $H_3PW_{12}O_{40} \cdot 6H_2O$, respectively (fig. 1, a; fig. 2, a). The results of the investigation of the samples of H-NZ-1, PMo_{12}-HPA/H-NZ-1, PW_{12}-HPA/H-NZ-1 by IR spectroscopy and their comparative analysis show that their spectra contain characteristic absorption bands of the clinoptilolite type zeolite in the region of 465; 615; 780; 1,060; 1,635; 3,460 cm^{-1}. In the IR spectra of the zeolite sample of the Shankanay field activated by acid, these absorption bands are very clearly manifested (fig. 1, b, c; fig. 2b, c); at decationization and dealumination, the natural zeolite retains its crystalline structure. Figures 1, 2 show that the modification of the HPC of an acid-activated sample of zeolite of the Shankanay deposit is unambiguously manifested in the IR spectra of the resulting catalysts. For example, when PMo_{12}-HPA is introduced into the zeolite

composition on the IR spectra of the catalyst, some absorption bands characteristic of zeolites are shifted and new bands appear.
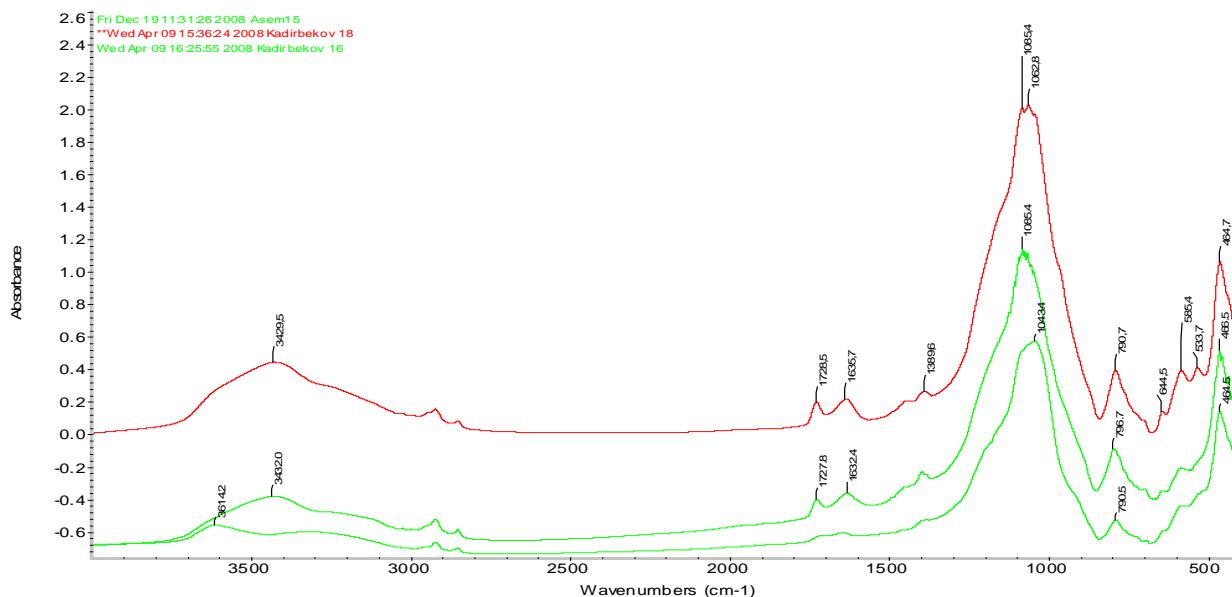

Figure 1-IR spectra of the catalyst 10% PW_{12}-HPA/H-NZ-1 and its components:
a) lower green curve- initial tungsten HPA - PW_{12}-HPA ($H_3PW_{12}O_{40} \cdot 6H_2O$),
b) upper green curve - H-NZ-1, c) red curve - the catalyst 10% PW_{12}-HPA/H-NZ-1
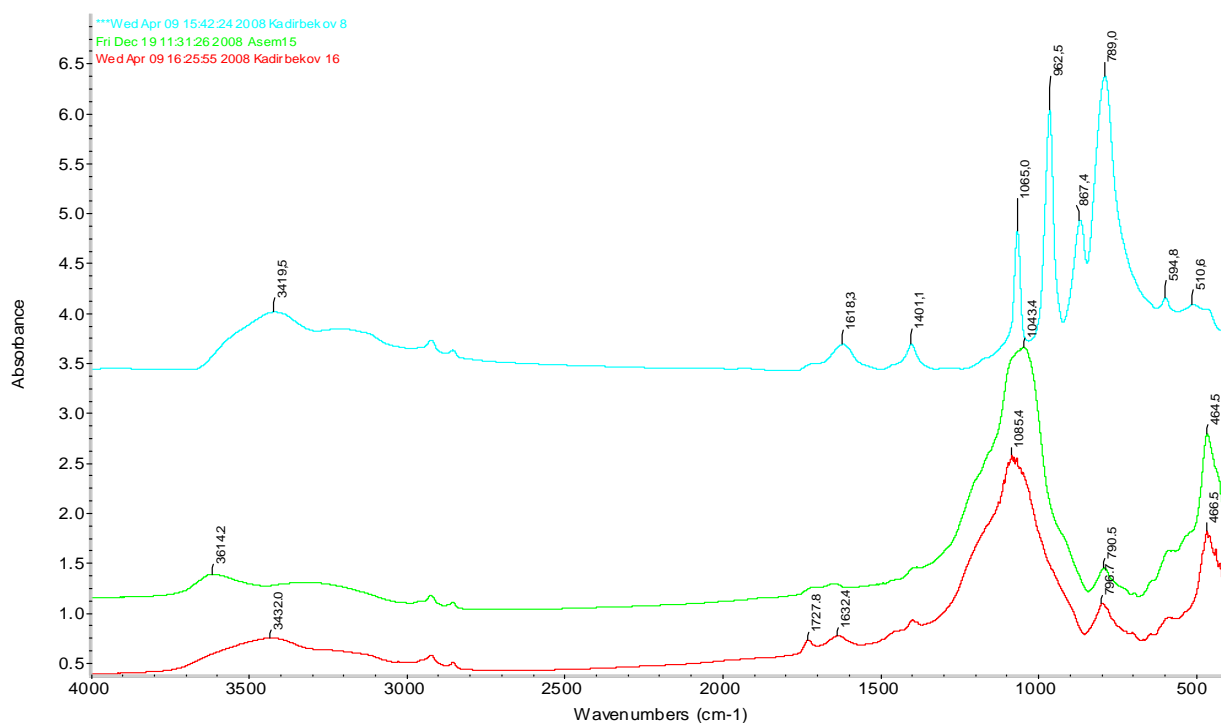

Figure 2-IR spectra of the catalyst 10% PMo_{12}-HPA/H-NZ-1 and its components:
a) red curve- initial molybdenum HPA-PMo_{12}-HPA ($H_3PMo_{12}O_{40} \cdot 6H_2O$),
b) green curve- H-NZ-1, c) blue curve - 10% PMo_{12}-HPA/H-NZ-1 catalyst

So, a shift of the band in the region of 1,060 cm^{-1} to 1,097 cm^{-1} and 1,108 cm^{-1} is found. The absorption band of 780 cm^{-1} disappears, and in the 800 cm^{-1} area a new band appears, which is typical for

valence vibrations of the Si-O bond. This indicates the formation of a bond of HPA with a zeolite. If take into account the appearance of a shift in the band in the range of 1,065 to 1,100 cm^{-1}, it can be concluded that Al-O-Si-bonds are broken in the zeolite structure and Si-O-Si bonds are formed, and aluminum goes into the ion exchange position. Dealumination of the clinoptilolite framework is also indicated by the appearance and growth of the intensity of the shoulder at 1,210 cm^{-1} on the IR spectra of this sample, referring to the asymmetric valence vibrations of the Si-O end groups. Inspite of it a complete destruction of the crystalline skeleton of the zeolite is not revealed and only its partial amorphization is observed.

The EM-image and the elemental composition of the scanned section of the catalyst PW$_{12}$-HPA/H-NZ-1 (fig.3) show that the content of its basic elements predominates on the surface of the zeolite, at the same time, the intensities of the spectra of the components of the HPA (tungsten and phosphorus) are clearly manifested. Apparently, this is due to the high degrees of dispersion and distribution of PW$_{12}$-HPA particles over the surface of clinoptilolite.
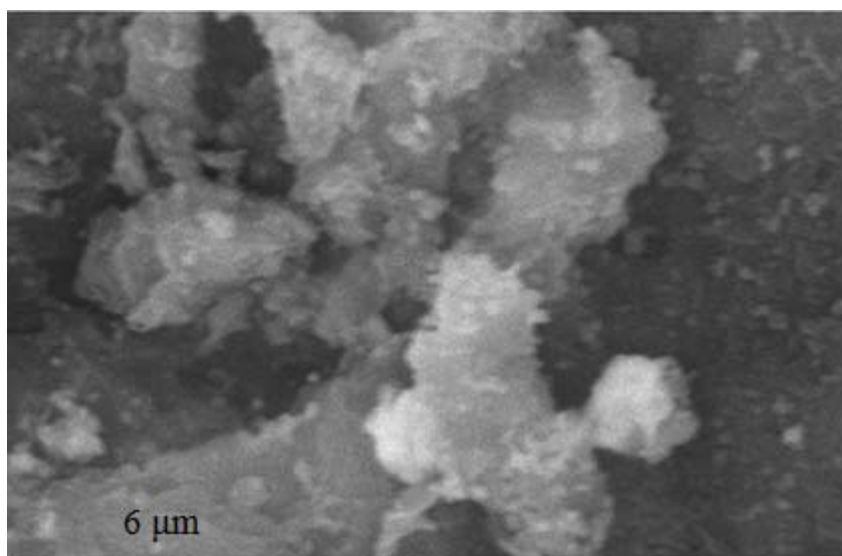
a
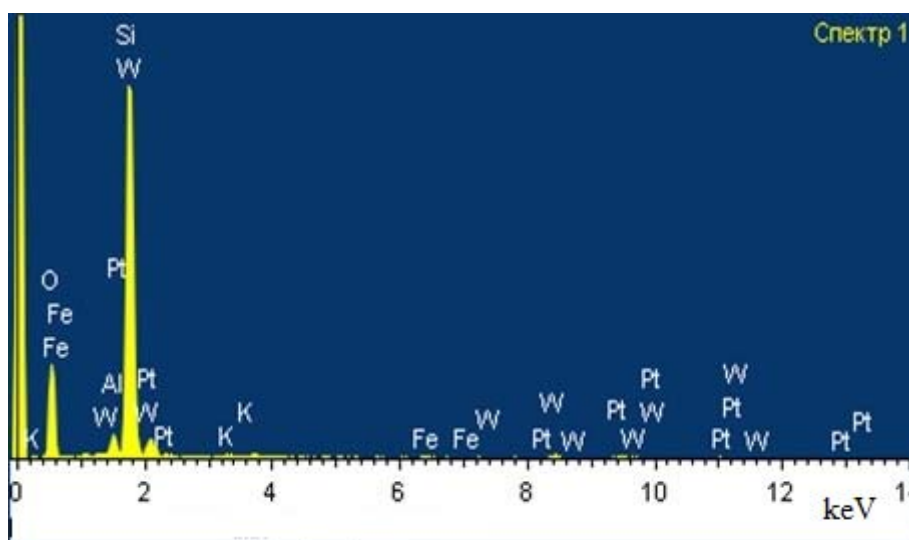
b

Figure 3- Electron microscopic image(a) and elemental composition (b) of the scanned section
of the catalyst PW$_{12}$-HPA/H-NZ-1, obtained by SEM

X-ray patterns of the samples also indicate a change in the structure of the natural zeolite when modifiying its by HPA (fig.4). Thus, a decrease in the intensity of one of the main peaks and the disappearance of several peaks characteristic of the mineral clinoptilolite on X-ray patterns of 10% PMo_{12}-HPA/ H-NZ-1 and 10% PW_{12}-HPA / H-NZ-1 were clearly detected, which is apparently related to partial amorphization of the structure and a change in the cation composition of the zeolite surface.
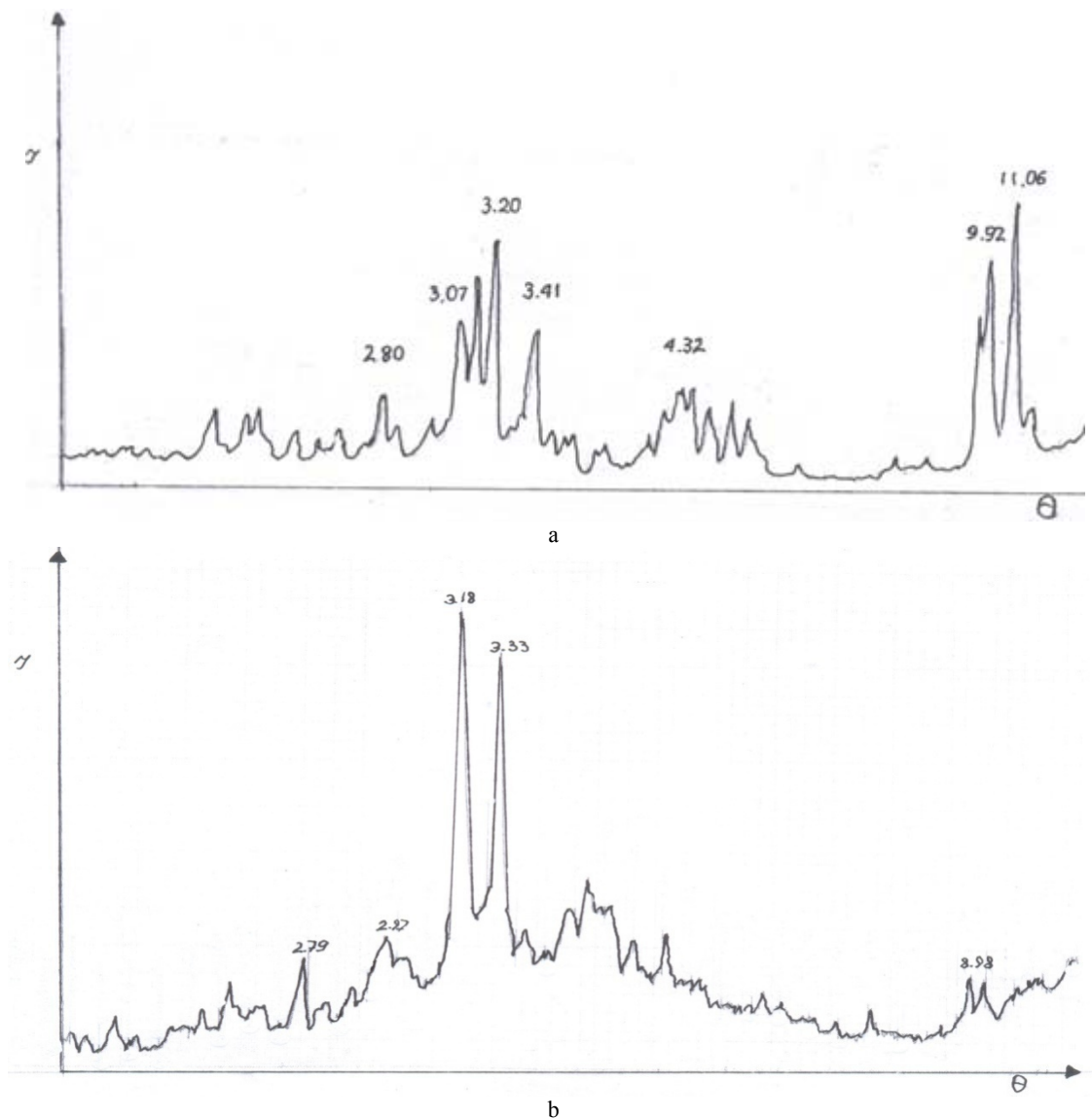

Figure 4 - The XRD pattern of the catalyst 10% PMo_{12}-HPA / H-NZ-1:
a) X-ray diffraction pattern of the initial HPA: $H_3PMo_{12}O_{40} \cdot 6H_2O$,
b) X-ray diffraction pattern of the catalyst 10% PMo_{12}-HPA / H-NZ-1

It was found in electron microscopic images of a thin layer of catalyst PW_{12}-HPA/H-NZ-1, obtained by TEM (translucent electronic microscopy), it is possible to see spots of different sizes with different shapes and contrasts. The microanalytical experiments on the EDAX-spectrometer showed that the above-mentioned spots have the similar compositions, identical to the PW_{12}-HPA (fig. 5).

It is considered[11, 20, 24, 29] that during the deposition and as a result of calcination of the catalyst, PW_{12}-HPA is converted to a highly dispersed state, in which PW_{12}-HPA particles exhibit special adsorption and catalytic properties. It is obvious that the emergence of nanostructures and the presence of a large number of strong acidic centers lead to an increase in the cracking activity of the catalyst of 10% PW_{12}-HPA/H-NZ during the cracking of paraffins.

A detailed study of the zeolite surface by the TEM-BP method has shown the formation of stable cluster structures 1-2 nm in a size, which are partially embedded in the zeolite volume (fig.5). These clusters are evenly distributed over the surface of the zeolite and are available for reacting substances.

In some places on the surface of clinoptilolite, the fine particles of the HPA are located in layers in the form of associates - they appear in the images as contra-sections, while the particle sizes clearly appear (0.78 - 1.32 nm) (fig. 6). Compositions of nanostructures according to the EDX-spectrometer are also identical with PW_{12}-HPA.
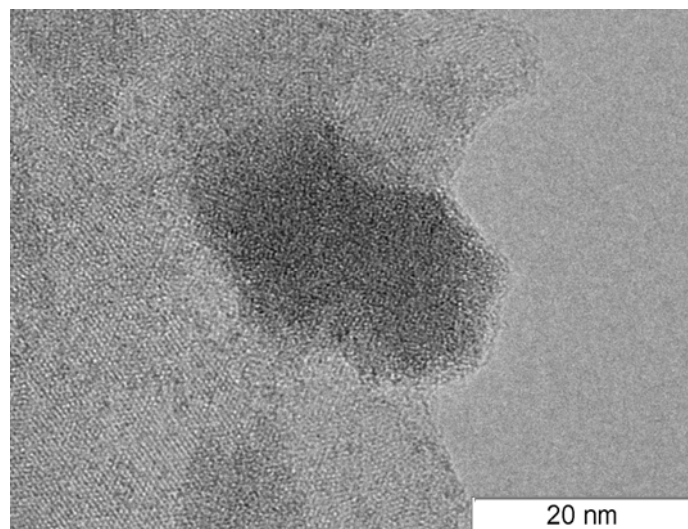
Figure 5 - Electron microscopic image of the catalyst PW_{12}-HPA / H-NZ-1, obtained by TEM BP.
Degree of resolution 1cm = 20nm
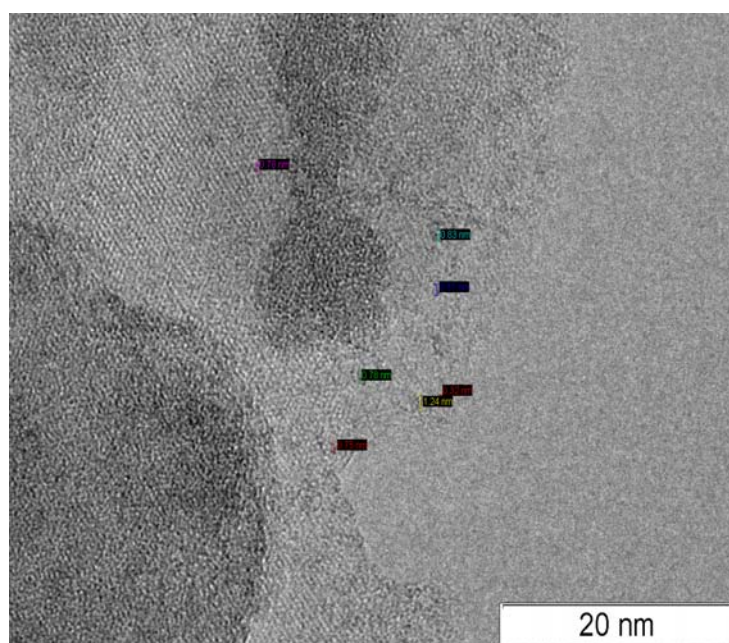
Figure 6- Electron microscopic image of the catalyst PW_{12}-HPA / H-NZ-1, obtained by the TEM-BP method.
Degree of resolution 1cm = 20nm

Conclusion

In the work catalysts for cracking on the basis of natural zeolite of the Shankanay field (Kazakhstan) modified by mineral acids, organic acids and HPA were synthesized. Investigations of the working surface of catalysts by physical and chemical methods of a research were carried out. By IR data during

decathionization and dealumination the natural zeolite retains its crystalline structure. It is possible to assume formation of a bond of HPA with a zeolite at modifying of the zeolite by HPA. Possibly because of the shift of the band in the region of 1,065 to 1,100 cm^{-1} the Al-O-Si- bonds are broken in the zeolite structure and Si-O-Si- bonds are formed, and the aluminum goes into the ion exchange position. The complete destruction of the crystalline skeleton of the zeolite is not revealed, only partial amorphization is observed. X-ray patterns of the samples also indicate a change in the structure of the natural zeolite when its is modified by HPA. By EM data there are high degrees of dispersion and particle distribution of PW12-HPA on the surface of clinoptilolite.

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ГЕТЕРОПОЛИҚЫШҚЫЛДАР НЕГІЗІНДЕГІ КРЕКИНГ КАТАЛИЗАТОРЫ

Аннотация. Гетерополиқышқылдар (ГПҚ) күшті бренстедті қышқылдар болып табылады. ГПҚ 12 қатардағының катализ үшін маңызы өте зор. Жұмыстың мақсаты – Шанханай кен орыны табиғи цеолиті

негізінде крекинг катализаторының құрамын жасау. Катализаторды модифицирлеу минералды, органикалық қышқылдармен және ГПҚ жргізілді. Дайындалған катализатор физикалық-химиялық әдістермен зерттелді. ИҚ-спектроскопия нәтижелеріне сәйкес табиғи цеолит декатионирлеу мен деалюминирлеуден кейін өзінің кристалдық құрылымын өзгертпейді. Модифицирлеу кезінде ГПҚ мен цеолит арасында байланыс түзілетіні болжанды. Электронды микроскопия мәліметі бойынша PW$_{12}$-ГПҚ бөлшектері клиноптилолит бетінде жоғары дисперстілік дәрежесінде таралады. Цеолит бетін ПЭМ ВР әдісімен зерттегенде өлшемі 1-2 нм тұрақты кластерлі құрылымның түзілгенін көрсетті. Бұл кластерлер цеолит бетінде тепе-теңдікте таралған және әрекеттесуші заттарға қолайлы.

Тірек сөздер: катализдік крекинг, гетерополиқышқылдар, Шанханай кенорынының цеолиті, электронды микроскоп.

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КАТАЛИЗАТОРЫ КРЕКИНГА НА ОСНОВЕ ГЕТЕРОПОЛИКИСЛОТ

Аннотация. Гетерополикислоты (ГПК) являются сильными бренстедовскими кислотами. ГПК 12 ряда имеют наибольшее значение для катализа. Цель работы – разработка состава катализаторов крекинга на основе природного цеолита Шанканайского месторождения (Казахстан). Модифицирование катализаторов проводилось минеральными кислотами, органическими кислотами и ГПК. Катализаторы всесторонне исследованы комплексом физико-химических методов. По данным ИК-спектроскопии после декатиониро-вания и деалюминирования природный цеолит не изменяет свою кристаллическую структуру. Предполо-жительно, происходит образование связи ГПК с цеолитом при модифицировании цеолита ГПК. Данные электронной микроскопии говорят о высоких степенях дисперсности и распределения частиц PW$_{12}$-ГПК по поверхности клиноптилолита. Детальное изучение поверхности цеолита методом ПЭМ ВР показало образо-вание устойчивых структур кластеров размером 1-2 нм, которые частично внедрены в объем цеолита. Эти кластеры равномерно распределены по поверхности цеолита и доступны для реагирующих веществ.

Ключевые слова: каталитический крекинг, гетерополикислоты, цеолит Шанканайского месторож-дения, электронная микроскопия.

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INVESTIGATION OF CHEMICAL CONSTITUENTS
OF *BERGENIA CRASSIFOLIA*

Abstract. The roots of *Bergenia crassifolia* collected in Kazakhstan, were investigated for chemical constituent. The quantitative and qualitative analysis of the medicinal plant have been made. Biological active constituents such as organic acid (1.49 %), flavonoids (0.14%), and polysaccharides (1.74 %) together with moisture content (8.6%), total ash (8.4%), and extractives content (34.8%) of plant *B. crassifolia* were determined. In The Institute of Combustion Problems using the method of multi-element atomic emission spectral analysis in the ash of the plantwas identified 7 macro-micro elements, in which the main contents were calcium (2054.10 mg/ml) and potassium (1050 mg/ml). In addition, twenty amino and eight fatty acids were analyzed from *B. crassifolia*extract. The results showed that the major contents of amino acids were glutamate (2705 mg/100g), aspartate (1216 mg/100g) and alanine (958 mg/100g), as well as fatty acids were linoleic (56.8%) and oleic acids (28.4%), respectively.

Key words: *Bergenia crassifolia,* bioactive constituents, macro-micro elements, amino-, fatty acids, GC-MS.

Introduction

Bergenia is flowering plant of the family Saxifragaceae which named in commonly as elephant-eared saxifrage, or elephant's ears. This genus contain of 10 species, which is widespread in area of Siberia regions (including Altai) andcentral Asia, from vastness's of Afghanistan to north-west in China and the Himalayan mountains [1].In territory of Kazakhstan can be found two species *Bergenia crassifolia* and *Bergenia ugamica*, where second is listed in the Red Book of Republic of Kazakhstan [2]. *Bergenia crassifolia*(L.) is commonly known as badan, Siberian tea, Mongolian tea, leather bergenia. In Altai, *B. crassifolia* is popular as a subtea and called as "Chigir Tea". Brew the overwintered leaves that have undergone natural fermentation, taking dark colored drink with taste remotely like black tea, and has a number of beneficial properties and a tonic effect [3]. *B. crassifolia* has been used for treatments of bronchitis, gastroenteritis, diarrhea, hemostasia, and metrorrhagia in Kazakh Medicine [4].The phytochemical constituents including bergenin, tannins, flavonoids, phenols, polysaccharide, amino acids and coumarins with some pharmacological actions such as antioxidant, antimicrobial, antiviral, anti-inflammatory, diuretic, immunostimulating, and lipase inhibiting activities have also been reported [5-10].

Proteins are large, complex molecules that are critical for the normal functioning of the human body. They are essential for the structure, function, and regulation of the body's tissues and organs. Proteins are made up of hundreds of smaller units called amino acids that are attached to one another by peptide bonds, forming a long chain. First point of investigation was on amino acids, which is organic (carboxylic) acids, the molecules of them contain one or more amino groups (NH_2-groups), the basic structural elements of protein molecules. In recent years, individual amino acids, their salts and mixtures have been increasingly used as highly effective, low-toxic drugs for children and adults. Drugs containing amino acids are used for a variety of diseases.So, glutamic acid is used to treat diseases of the central nervous system, methionine and histidine - the treatment and prevention of liver diseases, cysteine - eye diseases [11].

It is known that fatty acids - components of lipids exist in plants, animals, and microorganisms. Lipids are necessary for our body, because without them, metabolism cannot be carried out normally, and toxins and toxins accumulate in cells and tissues, as purification processes are slowed down. Many of fatty acids cannot be synthesize in human organism. Those fatty acids are required, however, for cellular processes and the production of other necessary omega-3 and omega-6 fatty acids. In addition fatty acids have a wide range of commercial applications, for example, they are used not only in the production of numerous food products but also in soaps, detergents, and cosmetics. Soaps are the sodium and potassium salts of fatty acids [12].

In the present study, the quantitative and qualitative analysis of bioactive constituents such as moisture, total ash, and extractives contents of *B. crassifolia*have been carried out, as well as amino-fatty acid contents were determined. In all this study, the quantitative and qualitative analysis of bioactive constituents and fatty acid contents of*B. crassifolia*which growing in Altay region of Kazakhstan were reported for the first time.

Materials and Methods

The root of plant material *Bergenia Crassifolia* was collected at Altay region Kazakhstan in July, 2015.The botanical identification was made by pharmacist Bahargul Konirhan, Institute of Medicine Inspection Department of Altay City, Xinjiang, China.The air dried roots of *B. crassifolia* were cut into small pieces and stored at room temperature.

The quantitative and qualitative analysis of biologically active constituents of the plant were made according to methods reported in the State Pharmacopeia XI edition techniques.

In the "Center of Physico-Chemical methods of research and analysis", Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *B. crassifolia* was analyzed elemental constituents. To determine the mineral composition of ashes was used Shimadzu 6200 series spectrometer.

To determine the amino acid composition was made erenow [13] of the raw material used GC/MS device.GC-MS analysis: the aerial part of *B. crassifolia* were analyzed byGas Chromatograph coupled to Mass Spectrometer using polar mixiture of 0.31% carbowax 20 m, 0.28%silar 5CP and 0.06% lexan in chromosorb WA-W-120-140 mesh.,column (400 x 3mm). The column temperature was programmed from 110°C (held for 20min), at 6°C/min from 110°C to 180°C, at 32°C /min from 185°C to 290°C. when it reaches to 250°C, it should stay constant till finishing of exit of all amino acids.

Results and discussion

The quantitative and qualitative analysis of biologically active constituents together with moisture content, total ash, extractives contents were determined from roots of *B. crassifolia.* The results shown in Table-1.

The ash of plant raw materials is the balance of inorganic substances obtained after burning the raw material and then calcining the residue to a constant mass. The ash of plants consists of a mixture of various inorganic substances characteristic of the plant, and mineral impurities that can get into the raw material during collection and drying. The moisture of plant materials is the loss in the mass due to hygroscopic moisture and volatile substances detecting when plant material is dried till constant weight. The moisture content in medicinal plant raw materials serves as one of the numerical indicators characterizing its quality. Medicinal plant raw materials should not contain moisture above the permissible standards, because with high humidity, during storage conditions are created that contribute to a decrease in its quality. For most types of medicinal plant raw materials, the permissible moisture limit is usually 12-15%.

Table 1 - Quantitative and qualitative analysis of *Bergenia Crassifolia*

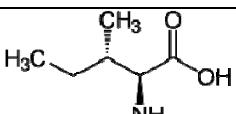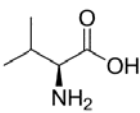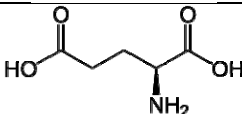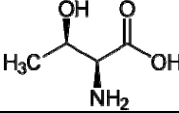| Content, %					
Moisture content	**Ash**	**Extractives**	**Organic acids**	**Flavonoids**	**Polysac-charides**
8.6	8.4	34.8	1.49	0.14	1.74
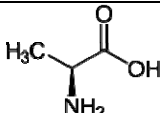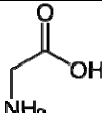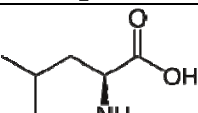
In The Institute of Combustion Problems using the method of multi-element atomic emission spectral analysis in the ash of *B. crassifolia* were determined seven macro- and microelements, showed in Table-2 and major of them are Calcium (2054.10 mg/ml) and Potassium (1050.10mg/ml). One of the main factors of nutrition, affecting health, working capacity and active longevity, are micronutrients - macro- and microelements. The body does not produce microcircuits and should receive them in ready form, for example, with food. The ability to store these substances in the body is absent. Calcium is participating on formation of bone tissue, the formation of teeth, the process of blood coagulation, neuromuscular conduction. Potassium is the most important component of intracellular fluid, controlling acid-base balance, muscular activity, and synthesis of proteins and glycogen [14].
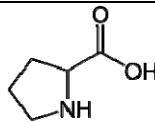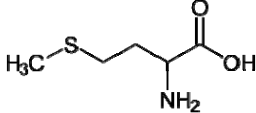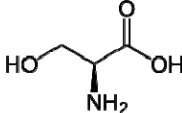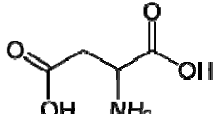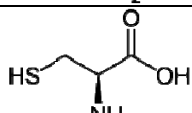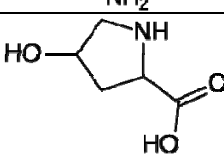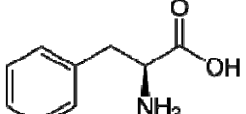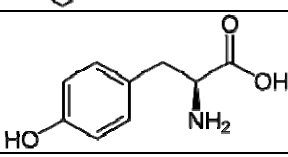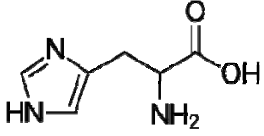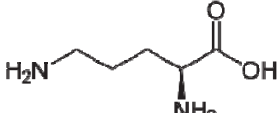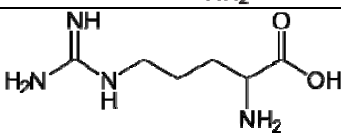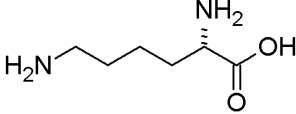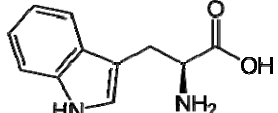
Table 2 - Composition of macro-micro elements in ash of*Bergenia crassifolia*

Element	K	Mg	Ca	Mn	Fe	Zn	Cu
µg/ml	794.5750	107.73	440.63	1.3556	4.5005	1.6911	0.6098

Determination of fatty acid composition of raw material, and dried plant *B. crassifolia* extracted with a chloroform-methanol mixture (2: 1) for 5 minutes, the extract is filtered through a paper filter and concentrated to dryness. Then, to taked extract add 10 ml of methanol and 2-3 drops of acetyl chloride and further methylation at 60-70° C in a special system for 30 minutes. The methanol is removed by rotary evaporation and the samples are extracted with 5 ml of hexane and analyzed using a gas chromatograph "CARLO-ERBA-420" allocated the Kazakh Academy of Nutrition for 1 hour. As a result, chromatograms of methyl esters of fatty acids were obtained. By comparison with reliable samples by the time of exit from the column, eight fatty acids were identified.

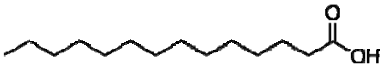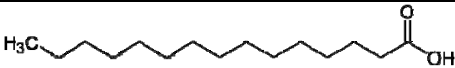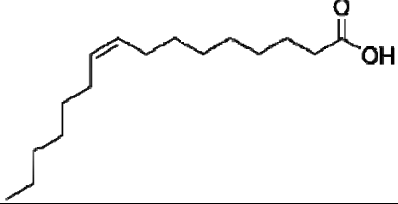Table 3 - Amino acids contents of *B. crassifolia*
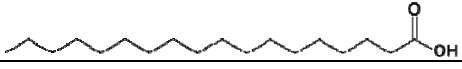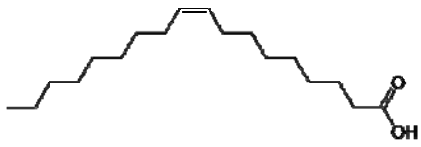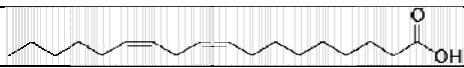
№	Amino acids	Molecular formula	Structure	MW	Amount in plant, mg/100g
1	Alanine	$C_3H_7NO_2$		89	958
2	Glycine	$C_2H_5NO_2$		75	405
3	Leucine	$C_6H_{13}NO_2$		131	462
4	Isoleucine	$C_6H_{13}NO_2$		131	344
5	Valine	$C_5H_{11}NO_2$		117	220
6	Glutamate	$C_5H_9NO_4$		147	2705
7	Threonine	$C_4H_9NO_3$		119	232

8	Proline	$C_5H_9NO_2$		115	806
9	Methionine	$C_5H_{11}NO_2S$		149	125
10	Serine	$C_3H_7NO_3$		105	502
11	Aspartate	$C_4H_7NO_4$		133	1216
12	Cysteine	$C_3H_7NO_2S$		121	46
13	Oxyproline	$C_5H_9NO_3$		131	3
14	Phenylalanine	$C_9H_{11}NO_2$		165	382
15	Tyrosine	$C_9H_{11}NO_3$		181	394
16	Histidine	$C_6H_9N_3O_2$		155	248
17	Ornithine	$C_5H_{12}N_2O_2$		132	3
18	Arginine	$C_6H_{14}N_4O_2$		174	365
19	Lysine	$C_6H_{14}N_2O_2$		146	260
20	Tryptophan	$C_{11}H_{12}N_2O_2$		204	92

Quantitative composition of fatty acids in *B. crassifolia* mostly contained in linoleic acid (56.8%) and Oleic acid (28.4%). Linoleic acid has received much attention in recent years because of its interesting

biological benefits. The main health effects described for linoleic acid include reduction of carcinogenesis, atherosclerosis, inflammation, obesity, diabetes, as well as growth promoting and bone formation-promoting properties [15]. Oleic acid can inhibit the progression of diseases affecting the brain and adrenal glands, as well as improve memory and reduce blood pressure, but there is evidence that the substance can provoke cancer, in particular breast cancer [16].

Table 4 - Fatty acids contents of *Bergenia crassifolia*

№	Fatty acids	Molecular formula	Structure	MW	Amount in plant, %
1	Meristic acid $C_{14:0}$	$C_{14}H_{28}O_2$		228	1.2
2	Pentadecanoic acid $C_{15:0}$	$C_{15}H_{30}O_2$		242	0.4
3	Palmitic acid $C_{16:0}$	$C_{16}H_{32}O_2$		256	7.2
4	Palmitoleic acid $C_{16:1}$	$C_{16}H_{30}O_2$		254	1.5
5	Stearin acid $C_{18:0}$	$C_{18}H_{36}O_2$		284	3.4
6	Oleic acid $C_{18:1}$	$C_{18}H_{34}O_2$		282	28.4
7	Linoleic acid $C_{18:2}$	$C_{18}H_{32}O_2$		280	56.8
8	Linolenic acid $C_{18:3}$	$C_{18}H_{30}O_2$		278	1.1

In the composition of amino acids mainly were glutamate (2705 mg/100g), aspartate (1216 mg/100g) and alanine (958 mg/100g). Glutamate is replaceable amino acid, which plays the role of a neurotransmitter with high metabolic activity in the brain, stimulates redox processes in the brain, the exchange of proteins. Normalizes the metabolism, changing the functional state of the nervous and endocrine systems [17]. Aspartic acid increases immunity, metabolism, deactivates ammonia, participates in the formation of ribonucleic acids, promotes the removal of chemicals, including drugs, restores working capacity. Studies conducted by scientists have proved the effectiveness of taking asparaginic acid preparations for increasing testosterone levels. Aspartic acid is taken as an additive by bodybuilding athletes to improve strength, increase libido and testosterone in the blood [18]. Alanine plays a significant role in metabolic processes, as well as to regulate the level of sugar in the bloodstream. This amino acid protects against the development of cancer of the pancreas and prostate gland, it is an important part of sports nutrition, increases physical endurance and allows to build muscle mass [19].

Conclusion

Quantitative and qualitative analysis of bioactive constituents and the moisture, total ash,and extractivescontents of roots *B. crassifolia* were determined. Besides, macro-micro elementsin the ash of the medicinal plant were investigated, and total sevenmacro-micro elements were identified by the method of multi-element atomic emission spectral analysis.Meanwhile, twenty amino and eight fatty acids were

determined from *B. crassifolia*. The results showed that the major contents of amino acids were glutamate (2705 mg/100g), aspartate (1216 mg/100g) and alanine (958 mg/100g, and fatty acids were linoleic (56.8%) and oleic acid acids (28.4%), respectively.

The main health effects described for *B. crassifolia*constituents include reduction of carcinogenesis, atherosclerosis, inflammation, obesity, diabetes, as well as growth promoting and bone formation-promoting properties, allows to build muscle mass, normalizing the metabolism, changing the functional state of the nervous and endocrine systems regulate the level of sugar in the bloodstream. The research work on investigation of chemical constituents of the medicinal plant to be continuing.

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BERGENIA CRASSIFOLIA ХИМИЯЛЫҚ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Қазақстанда жиналған *Bergenia crassifolia* тамырының химиялық құрамы зерттелді. Дәрілік өсімдіктің сандық және сапалық талдауы жүргізілді. Өсімдіктің ылғалдылығы (8.6%), жалпы күлділігі (8.4%) және экстрактивтілігі (34.8%), сонымен бірге органикалық қышқыл (1.49%), флавоноидтар (0.14%) және полисахаридтер (1.74%) сияқты биологиялық активті компоненттер құрамы анықталды. Жану проблемалары институтында, атомдық эмиссия спектральды талдау әдісін қолдана отырып, өсімдіктің күліндегі 7 микро және макро элементері анықталды және оның негізгі құрамы кальций (2054.10 мг / мл) және калий (1050 мг / л) элементтерінен тұратыны анықталды. Бұдан басқа, *B. crassifolia*-ден жиырма амин және сегіз майлы қышқыл анықталды. Алынған нәтижелер бойынша амин қышқылдардың негізгі құрамы глутамат (2705 мг / 100 г), аспартат (1216 мг / 100 г) және аланин (958 мг / 100 г) және май құрамында линол (56.8%) және олеин қышқылдары (28.4%).

Тірек сөздер: Bergenia crassifolia, биоактивті құрамдастар, макро-микроэлементтер, амино-майлықыш-қылдар, GC-MS.

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ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА *BERGENIACRASSIFOLIA*

Аннотация. Был исследован химический состав корней *Bergeniacrassifolia*, собранного в Казахстане. Сделан количественный и качественный анализ лекарственного растения. Определены биологически активные компоненты, такие как органические кислоты (1.49%), флавоноиды (0.14%) и полисахариды (1.74%), а также содержание влаги (8.6%), общяя зольность (8.4%) и экстрагенты (34.8%) растения *B. crassifolia*. В Институте проблем сжигания с использованием метода многоэлементного атомно-эмиссионного спектрального анализа в золе растения было найдено 7 макро-микроэлементов, основными веществами из которых были кальций (2054.10 мг / мл) и калий (1050 мг / мл). Кроме того, из корней *B. crassifolia* были идентифицированы двадцать аминокислот и восемь жирных кислот. Результаты показали, что основным содержанием аминокислот являются глутамат (2705 мг / 100 г), аспартат (1216 мг / 100 г) и аланин (958 мг / 100 г), а среди жирных кислот - линолевые (56.8%) и олеиновые кислоты (28.4%) соответственно.

Ключевые слова: Bergeniacrassifolia, биоактивные компоненты, макро-микроэлементы, амино-, жирные кислоты, GC-MS.

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ORIGINAL TECHNOLOGY OF SYNTHESIS POLYMER SULFUR COMPOSITES ON THE BASE OF BY-PRODUCT SULFUR OF THE PETROLEUM DESULFURIZATION

Abstract. Technological methods for obtaining of polymer sulfur composites by redox copolymerization on the basis of by-product sulfur with electrically conductive copolymers (pyrrole, aniline) have been developed. The conditions for carrying out the reaction are established, which allow varying the sulfur content of the obtained materials. The electrochemical activity and efficiency of the use of sulfurous polymeric compositions of aniline and pyrrole as active electrode materials of lithium-sulfur batteries have been studied. It was established by physical-chemical methods that the obtained high-sulfur polymers possess electroconductive properties, oxidation-reduction activity and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

The developed technology of sol-gel synthesis of copolymers of aniline and pyrrole based on nanoscale sulfur by the method of redox copolymerization to produce electrically conductive high-sulfur polymers can be recommended for use in the creation of domestic production of cathode materials for lithium-sulfur batteries.

Key words: polymer sulfur composites, polypyrrole, polyaniline, cathode materials, lithium-sulfur batteries.

Introduction. The annual growth in hydrocarbon production in Kazakhstan and the environmental requirements for the quality of petroleum products resulted in the accumulation of more than 10 million tons of sulfur at the sulfur storage site as it is a large-scale by-product of oil and gas processing. In this regard, there is an excess of world production of sulfur - the product of desulfurization of hydrocarbon raw materials over consumption.The inevitable consequence of this is the technogenic impact on the objects of the environment. The actual task is the development of modern utilization ways into new polymeric sulfur composites, possessing a number of valuable properties , which will increase the world demand for elemental sulfur.

In recent decades, special development has been given to a new direction in polymer sulfur technology: the development of electroconductive, electrochemically active polymeric sulfur composites for their use in modern lithium-sulfur batteries. Prospectivity of lithium-sulfur batteries is due to high values of their theoretical specific energy (2500 Wh / kg), low cost and environmental safety. In terms of their energy intensity, they outperform other chemical sources of current 2.5-5 times. Using rechargeable lithium cells allows to solve a purely economic problem, because their use is much cheaper than the use of relatively expensive elements of a one-time action. In this regard, particular interest is due to the peculiarities of the properties of polymeric sulfur [3-10]. Lithium-sulfur batteries were first shown to the world public by Sion Power in 2004. Even then, such batteries were much more efficient than current lithium-ion batteries. The main distinguishing features of these drives can be called a less expensive production, as well as more than double the capacity in comparison with analogues. This type of battery is called Li/S.

Despite intensive research in this field, up to the present there was practically no information on synthesis and properties high-sulfur polycondensed heterocyclic systems with oxidation-reduction

functions (S-S, S-H and C = S), which have redox activity and are promising as active cathode materials of rechargeable lithium current sources. In connection with this, the synthesis and study of new high-sulfur materials that combine in the molecule condensed aromatic heterocyclic fragments and redox-active functions are relevant.

There are various methods for obtaining polymeric sulfur [3-13], including the direct sulphuration of industrial polymers [4,7], the reverse vulcanization method [14]. Polymer sulfur with improved electrically conductive and redox activity properties for use as cathode materials of lithium-sulfur batteries is formed by using the initial nanostructured colloidal sulfur [15].

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), are very interesting materials for using in Li/S batteries. Polymer modification of the carbon surface facilitates a more complete reaction by providing a chemical gradient that retards diffusion of the polysulfides into the electrolyte. Reversible capacities up to 1320 mAh/g are attained with no shuttle phenomenon on the first cycle, indicating the shuttle mechanism is fully suppressed. This polymer modified composite clearly exhibits better morphological control than the unmodified composite during cycling [16]. Therefore, the development of new methods for the preparation of the sulfur-polypyrrole and sulfur- polyaniline composite by the method of redox copolymerization of elemental sulfur with aniline / pyrrole is actual.

Materials and methods. Used reagents: Petroleum-based sulfur was supported by TengizChevrOil LLP - S_{TCO} (sulfur granulated), T_{melt} 122 $^{\circ}$C, as well as the block sulfur of the Shymkent Petroleum Refinery (**PetroKazakhstan Oil Products** LLP) S_{SPR}, T_{melt} 113 $^{\circ}$C. Other chemical ingredients, namely, aniline were purchased from Sigma-Aldrich Chemie GmbH, 99.5(registration number is Beilstein 605631, density is 1,022 g / ml at 25 °C); pyrrole from Sigma - Aldrich GmbH, 98% (registration number is Beilstein 1159, density 0.967 g / ml at 25 °C); Iron trilogy six water (FeCl$_3$ · 6H$_2$O) - chemically pure, GOST (TU) 4147-74; Sodium sulfurous nine (Na$_2$S·9H$_2$O) - chemically pure for analysis, GOST (TU) 2053-77.

 Method of redox copolymerization of sulfur with aniline or pyrrole. Colloidal cross-linked copolymers were synthesized by redox copolymerization of sulfur with monomer (aniline or pyrrole). The sulfur was introduced into the reaction mixture in a colloidal form. Colloidal activated sulfur was prepared by *in situ* from sodium polysulphides Na$_2$S$_x$ (x = 4.0-4.5). Sodium polysulphide was synthesized from sodium sulfide Na$_2$S·9H$_2$O (8.3 g, 34.7 mmol), preheated to 80-90 °C, to which 4.2 g (130 mmol) of powdered sulfur S_{TCO} or S_{SPR} (for 30-40 minutes) was added in portions. The reaction mixture was stirred at 80-90 °C for 40 minutes, then diluted with 6.7 ml of hot water (80-90 °C), left over night at room temperature and then filtered from unreacted sulfur. The resulting sodium polysulfide Na$_2$S$_x$ was used subsequently for the synthesis of new high-sulfur copolymers based on aniline/or pyrrole and sulfur. The synthesis was carried out in the presence of the oxidation system H$_2$O$_2$ / FeCl$_3$ / HCl, which is 7 ml of a 33% solution of H$_2$O$_2$, 0.2 g of FeCl$_3$·6H$_2$O and 50 ml of 2 N HCl solution. In the second stage, a mixture of a water-alcohol solution of sodium polysulphide and monomer was prepared. This mixture was added with vigorous stirring to a H$_2$O$_2$ / FeCl$_3$ / HCl oxidation system containing 1-5 wt % gelatin, and stirring was continued for 3 hours. As a result, the high sulfur copolymers on the base of aniline or pyrrole were obtained in the form of powders of dark brown color.

Results and discussion. Polyaniline is among the most studied conductive polymers, mainly due to the combination of high conductivity, various different oxidations and protonation states each one exhibiting different color and electronic properties, light weight, easy preparation and low cost. Its ability to form ultra-small nanostructures, including nanowires, nanoneedles and nanofibers has been proven particularly useful in the application of the polymer in sensors applications since their extremely high specific area enables the fast detection of small molecules that can cause immediate changes in the oxidation states and as it is expected to the conductivity values and the optical absorption spectrum, the latter can exhibit from one to three absorbance bands depending on the polymer form [8-11].

Colloidal activated sulfur was prepared by in situ from sodium polysulphides in the first stage. Synthesis of new sulfur and aniline copolymers was carried out in the presence of oxidation systems: H$_2$O$_2$ /FeCl$_3$/HCl, and K$_2$Cr$_2$O$_7$ (H$_2$O$_2$)/HCl. In the second stage, the above oxidation system was prepared. The effect of surfactant and gelatin on the reaction process and the yield of the desired product were investigated. Gelatin (or surfactant, 0.25 g in 5 ml H$_2$O) was placed in the flask and stirred vigorously for 15 minutes, a solution of HCl (or H$_2$SO$_4$) was added to the emulsion and stirring was

continued for 0.4-2 hours. Next, $FeCl_3 \cdot 6H_2O$ and the emulsion was stirred for 15 minutes before the formation of the oxidation system H_2O_2 / $FeCl_3$ / HCl as a white foam. The product was filtered off, washed with water to pH ~ 6 and a negative reaction to chlorine ions, dried in vacuo at 40 °C to constant weight (Table 1).

Table 1 - Conditions for the synthesis and yield of polymers based on aniline and elemental sulfur

Copolymer cipher	Reaction conditions			Yield, %
	Composition of the reaction mixture	Temperature, °C	Time, h	
SPAN-1	polysulphide, aniline, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, surfactants	25-42 (self-heating)	4.0	61.2
SPAN-2	polysulphide, aniline, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, gelatin	25-45 (self-heating)	2.5	54.6

As a result of redox copolymerization of aniline with sulfur, sulfur-aniline polymers are synthesized in the form of powders from light brown to black. The composition of the obtained copolymers was determined by the methods of elemental analysis (Table 2).

Table 2 - Element composition and melting temperature of polymers based on aniline and elemental sulfur

Sample cipher	Elemental analysis					T_{melt}, °C
	C	H	N	S	Cl	
SPAN-1	9.7	0.4	1.3	80.4	-	190-240
SPAN-2	8.5	0.4	1.4	89.2	0.8	165-260

Depending on the reaction conditions, the nature of the oxidation system, the addition of gelatin or surfactant to the reaction mixture, sulfur-aniline polymers with a high sulfur content were obtained: from 80.4 to 89.4 %.

The main synthesis conditions and properties of the copolymers obtained are shown in Table 3.

Table 3 - Composition of the obtained copolymers

Copolymer cipher	Composition of the reaction mixture	Yield, %	Sulfur content, %	T_{melt}, °C	σ, S / cm
SPAN-1	polysulphide, aniline, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, surfactants	81.0	80.4	190-240 (partially)	$2.1 \cdot 10^{-5}$
SPAN-2	polysulphide, aniline, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, gelatin	73.4	80.2	165-260 (partially)	$1.2 \cdot 10^{-7}$
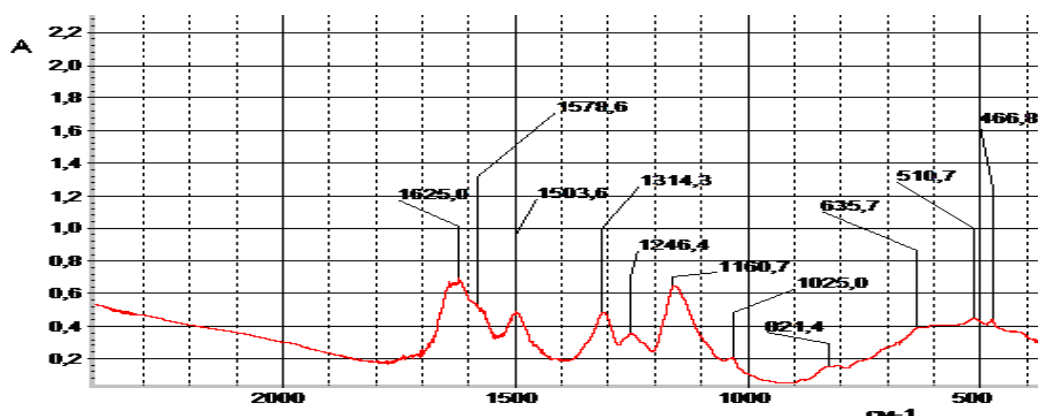
Figure 1 - IR spectra of a high-sulfur polymer based on Tengiz sulfur and aniline

Synthesized copolymers are characterized by high sulfur content (80-89 %). In the IR spectra of copolymers there are characteristic absorption bands (cm^{-1}): 1625, 1503 (ν, C = C of the polyaniline chain); 1314 (ν, C = C-H); 1301 (ν, O = S = O); 1246 (ν, C = S, ν, C-N); 1160 (ν, O = S = O); 1025 (ν, O = S); 824 (ν, C = C-H); 635, 510 (ν, C-S); 467 (ν, S-S).

The composition of the obtained copolymers was determined by elemental analysis. IR spectra were recorded for all the samples, specific electrical conductivity (σ) was determined, and oxidative thermal destruction was studied by thermogravimetric analysis.

Copolymers have a high resistance to thermal oxidative degradation (up to 210-230 °C) and electrical conductivity of the order of 10^{-5}-10^{-13} S / cm. Figure 1 shows the IR spectrum of a synthesized high-sulfur polymer based on Tengiz sulfur and aniline.

The redox copolymerization of elemental sulfur with pyrrole. In contrast with polyaniline that is a slightly hydrophilic polymer and can be solubilized in water upon high dilution, polypyrrole is a completely insoluble polymer in any solvent either organic or water. With respect to the above, the interfacial polymerization seems an excellent candidate for the synthesis of a thin film in the boundary of the two phases. This thin film can be easily extracted and purified. The poor solubility of polypyrrole in any solvent has been assigned to an extensive cross-linking 20 between the polymer chains. Oligomers however, tend to be easily dispersible. The polymerization of pyrrole involves oxidation of the monomer with metal cations.

For the synthesis of high-sulfur pyrrole-based polymers, the method of co-oxidation of pyrrole and polysulfone, previously generated *in situ* from an aqueous solution of sodium polysulphide in the presence of an oxidizing system and a colloidal stabilizer (gelatin), was used. The stabilizer was used as a pre-prepared aqueous solution. The oxidation system H_2O_2 / $FeCl_3$ / HCl includes 7 ml of a 33 % solution of H_2O_2, 0.2 g of $FeCl_3 \cdot 6H_2O$ and 50 ml of a 2 N solution of HCl.

The resulting filtrate was used subsequently to prepare colloidal sulfur-pyrrole copolymers. In the same way, colloidal activated sulfur was obtained from the associated sulfur of Shymkent refinery S_{SPR}. As a result of the variation in the nature of the initial sulfur (S_{TSO} or S_{CPR}), sulfur-pyrrole copolymers are obtained in the form of powders of a dark brown color with a different sulfur content (Tables 4, 5).

Table 4 - Synthetic conditions and polymers yield based on pyrrole and the desulphurization product of TSP (SPPy $_{TSO}$) and (SPPy $_{SPR}$)

Copolymer cipher	Composition of the reaction mixture	Reaction temperature, °C	Reaction time, h	Yield, %
SPPy $_{TSO}$	polysulfide, pyrrole, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, gelatin	25-47 (self-heating)	4.0	80.3
SPPy $_{SPR}$	polysulfide, pyrrole, HCl, $FeCl_3 \cdot 6H_2O$, H_2O_2, gelatin	25-53 (self-heating)	4.5	79.2

Table 5- Elemental composition and melting point of polymers based on pyrrole and sulfur

Sample cipher	Elemental analysis					T_{melt}, °C
	C	H	N	Cl	S	
SPPy $_{TSO}$	6.2	0.6	1.1	0.58	72.0	170-255
SPPy $_{SPR}$	10.6	1.5	1.8	0.38	80.0	167-210

Thus, as a result of redox synthesis of high-sulfur polypyrrole, sol-gel copolymerization of pyrrole with associated S_{TSO} or S_{SPR} sulfur, with other equal process conditions, depending on its origin, the sulfur content of sulfur - polipyrrole is higher than in case of succumbing associated Tengiz sulfur.

In the IR spectra of high-sulfur pyrrole-based polymers (Fig. 2 a, b), there are characteristic absorption bands (cm^{-1}): 1714, 1718 (ν, C-O); 1557, 1457, 1414, (ν, C=C a polypyrrole fragment); 1328, 1235 1225, 791 (δ, C=C-H); 1236, 1047, 1025 (12), 1225, 1138, 1051, 1032 (13) (ν, O=S); 791, 771, 800(δ, C=C-H); 628, 632(ν, C-S); 467, 464 (ν, S-S).
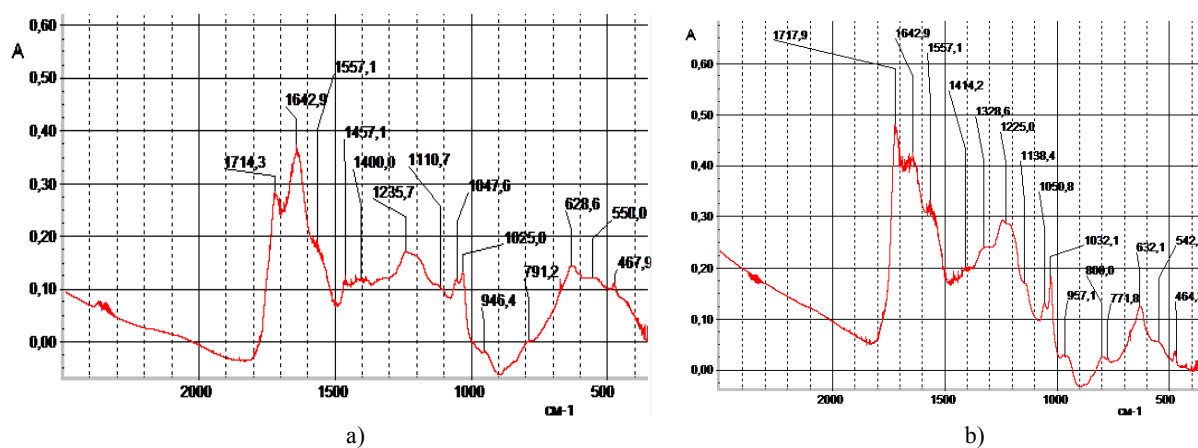
a) $S_{TCO \text{ and}}$ pyrrole; b) S_{SPR} and pyrrole
Figure 2 - IR spectra of high-sulfur polymer based on:

When studying the electrical conductivity of the obtained high-sulfur aniline-based polymers and also on the basis of pyrrole, they have a specific electric conductivity of the order of 10^{-5} - 10^{-7} S/cm, corresponding to high-resistance organic semiconductors (Table 6).

Table 6 - Specific electric conductivity (σ) and thermogravimetric analysis of high-sulfur polymers based on aniline SPAN (№ 1, № 2) and pyrrole SPPy (№ 3, № 4)

№ п/п	Sample cipher	Content S, %	The temperature of the onset of thermooxidative degradation,°C	σ, S/cm
1	SPAN-1	80.4	~210	$2.1 \cdot 10^{-5}$
2	SPAN-2	89.2	~210	$1.2 \cdot 10^{-7}$
3	SPPy -1	72.0	~220	$8.1 \cdot 10^{-7}$
4	SPPy -2	80.0	~210	$4.3 \cdot 10^{-7}$

According to the results of thermogravimetric analysis, the polymers obtained are highly resistant to thermal-oxidative degradation (up to 210 -220 °C).

Microstructure of synthesized polymers based on elemental sulfur and aniline. For the purpose of conducting comparative studies of the microstructure of synthesized high-sulfur polymers based on aniline, and also on the basis of pyrrole, X-ray dispersive spectral microanalysis was used. Typical micrographs of synthesized sulfonated copolymers SPAN (№ 1) and SPPy (№ 2) are presented in figure 3.
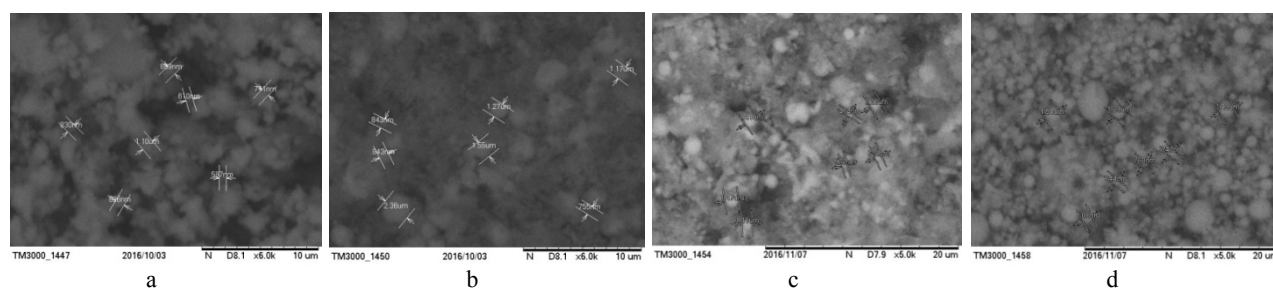
a) SPAN -1 (587 nm – 1.10 μm); b) SPAN -2 (755 nm – 2.36 μm);   c) SPPy (474 nm – 1.47 μm); d) SPPy (644 nm – 1.54 μm)
Figure 3 – Micrographs of synthesized sulfonated copolymers

The obtained results indicate that the synthesized copolymers have a developed microstructure, with sufficiently small microparticles of narrow polydispersity. The SPAN-1 copolymer has the smallest

particle sizes in the range of 587 nm to 1.10 μm, in the case of SPPy-1 in the range 474 nm - 1.54 μm. A somewhat larger particle (up to 755 nm - 2.36 μm) is formed in the synthesis of an aniline-sulfur copolymer SPAN-2, also slightly larger than the particle in the case of SPPy - 2 (up to 644 nm - 1.54 μm) using the H_2O_2 / $FeCl_3$ / HCl oxidation system and adding gelatin to the reaction mixture.

The oxidation-reduction properties and the electrochemical activity of the synthesized products, as well as the possibility of their use as active cathode material in lithium batteries, were investigated by cyclic voltammetry and charge-discharge processes of cathodes.

Electrochemical properties of synthesized cathode samples № 1 SPAN-1 and № 2 SPPy-2 (Table 6) were studied in lithium batteries. Galvanostatic measurements were carried out on a multichannel tester (BT-2000, Arbin Instruments) in the range of potentials from 0.1 to 2 V. The values of current intensity and specific capacitance were calculated taking into account the weight content of sulfur in the SPAN-1 electrode composite (80.4 %) and SPPy - 2 (80 %) (Figure 4).
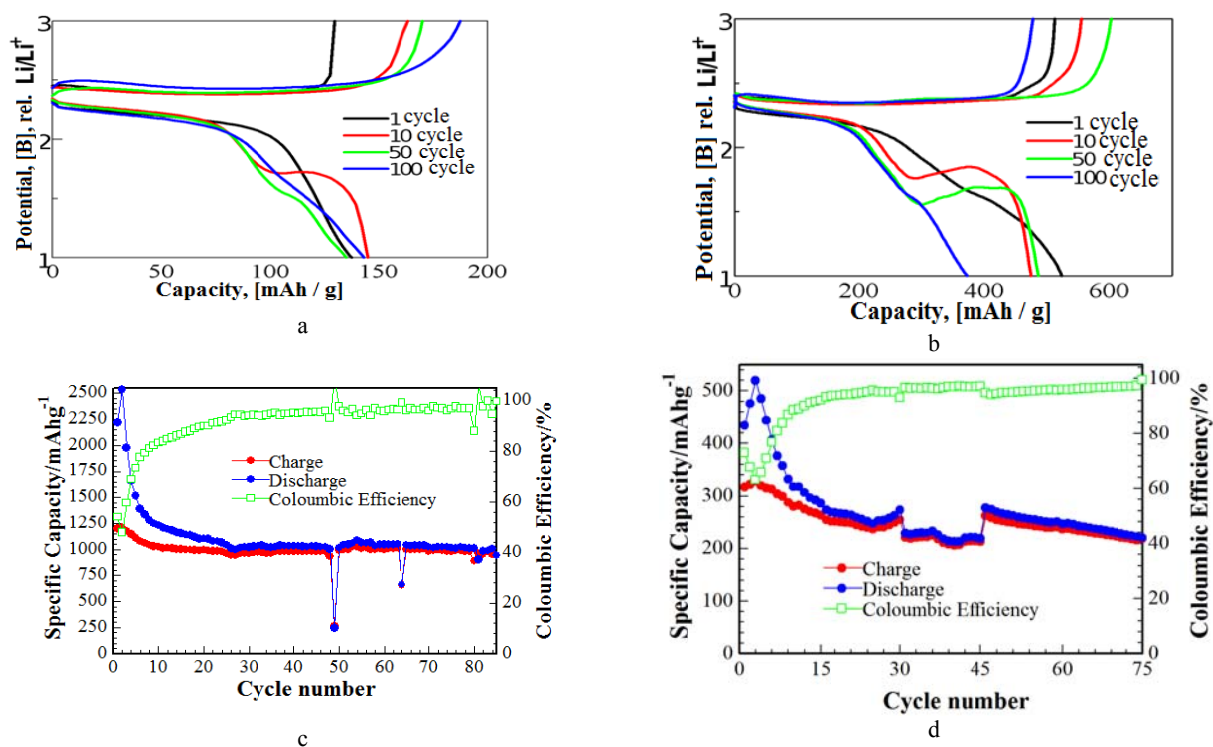
Figure 4 - Charging-discharge curves (a, c) and cycling curves (b, d)
at a current density of 0.2 C of an aniline-based SPAN-1 (a, b) based aniline based polymer based on SPPy-2 (b, d)

The results of the electrochemical cycling of the SPAN-1 sample deposited on the aluminum current collector showed a low capacitance, but when deposited on carbon paper (TGP-H-030), showed a high capacitance (Fig. 4 a, b), the test samples of button batteries were high the initial discharge capacity is 2500 mAh^{-1} at a current density of 0.2 C, it can be seen that the battery gradually loses its original discharge capacitance to 50 % within 15 cycles. However, the charging capacity is more stable for 15 cycles (the battery continues to cycle).

The specimen of the SPPy-2 sample was also electrochemically tested, showed a smaller charge capacity within 430-320 mAh^{-1} and a maximum discharge capacitance of 520 mAh^{-1}. Figure 4 c, d shows charge-discharge curves and cycling at a current density of 0.2 C.

On cyclic voltammograms one anode peak is observed at 2.5 V and two cathode at 2.4 and 1.9 B, which indicates the multistage nature of the reduction process in polymers. The electrochemical behavior of a polymer with polysulfide blocks is determined by two fundamentally different parts of it.

The first is polysulfide blocks, which give peaks of oxidation and reduction, in position close to the peaks of sulfur, and are not very dependent on the structure of the polymer. The second part is fragments

remaining on the cathode (organic or heteroorganic thiolates), which modify the cathode matrix in a certain way, accelerating or slowing down the intermediate stages of the redox process. It is possible to learn how to control this process in order to achieve its maximum reversibility and speed, by searching for the optimal structure and combination of the two specified parts of the electroactive sulfur-organic polymer.

Thus, technological methods for the synthesis of high-sulfur polymers have been developed, based on the redox copolymerization of elemental sulfur with aniline and pyrrole. Conditions for carrying out the reaction have been found, which make it possible to vary the sulfur content of the obtained materials. It has been established that synthesized high-sulfur polymers have thermal stability, semiconductor properties, developed surface morphology and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

Conclusion. Technological methods for obtaining polymeric sulfur composites and an original sol-gel technology for the synthesis of nanoscale polymer sulfur and its composites with electrically conductive polymers (polypyrrole, polyaniline) have been developed. Conditions for carrying out the reaction have been found, allowing to vary the sulfur content in the obtained materials. The electrochemical activity and efficiency of the use of aniline and pyrrole-based gray polymer compositions as active electrode materials of lithium-sulfur batteries have been studied. It has been established by physico-chemical methods that the obtained high-sulfur polymers possess semiconductor properties, redox activity and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

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МҰНАЙДЫ КҮКІРТСІЗДЕНДІРУДЕ АЛЫНҒАН ІЛЕСПЕЛІ КҮКІРТ НЕГІЗІНДЕ КҮКІРТ-ПОЛИМЕРЛІ КОМПОЗИТТЕРДІҢ СИНТЕЗІНІҢ ӨЗІНДІК ТЕХНОЛОГИЯСЫ

Аннотация. Полимерлі күкірт композиттерін электрлік өткізгіш сополимерлермен (пиррол, анилин) ілеспелі күкірт негізінде тотығу-тотықсыздану сополимерлеу арқылы технологиялық әдістер жасалынды. Алынған материалдардағы күкірттің мөлшерін өзгертуге мүмкіндік беретін реакцияны жүргізу шарттары белгіленді. Литий-күкірт аккумуляторларының белсенді электродтық материалдары ретінде анилин мен пирролдың күкіртті полимерлі композицияларының электрохимиялық белсенділігі мен тиімділігі зерттелді. Физико-химиялық әдістер бойынша алынған жоғары күкірт полимерлерінің электр өткізгіш қасиеттерімен, тотығу-тотықсыздану белсенділігімен және қазіргі заманғы қайта зарядталатын литийлі ток көздерінің белсенді катодты материалдарын әзірлеу үшін перспективалы болып табылатыны анықталды.

Литий-күкірт аккумуляторлары үшін катодты материалдарды өндіретін отандық өндірісті құру кезінде электр өткізетін жоғары күкірт полимерлерін шығаруға арналған тотығу-тотықсыздану сополимеризация арқылы наномөлшерлі күкірт негізінде анилин мен пирол сополимерлерін золь-гель синтезінің дамыған технологиясын ұсынуға болады.

Түйін сөздер: полимерлі күкірт композиттері, полипрырол, полианилин, катодты материалдар, литий-күкірт батареялары.

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ОРИГИНАЛЬНАЯ ТЕХНОЛОГИЯ СИНТЕЗА СЕРОПОЛИМЕРНЫХ КОМПОЗИТОВ НА ОСНОВЕ ПОПУТНОЙ СЕРЫ ОБЕССЕРИВАНИЯ НЕФТИ

Аннотация. Разработаны технологические методы получения полимерных серных композитов путем окислительно-восстановительной сополимеризации на основе попутной серы с электропроводящими сополимерами (пиррол, анилин). Установлены условия проведения реакции, которые позволяют варьировать содержание серы в полученных материалах. Изучена электрохимическая активность и эффективность использования сернистых полимерных композиций анилина и пиррола в качестве активных электродных материалов литий-серных батарей. Физико-химическими методами установлено, что полученные высокосернистые полимеры обладают электропроводящими свойствами, окислительно-восстановительной активностью и перспективны для разработки активных катодных материалов современных перезаряжаемых источников тока лития.

Разработанная технология золь-гель синтеза сополимеров анилина и пиррола на основе наноразмерной серы методом окислительно-восстановительной сополимеризации для получения электропроводящих высокосернистых полимеров может быть рекомендована для использования при создании отечественного производства катодных материалов для литий-серных аккумуляторов.

Ключевые слова: полимерные серные композиты, полипиррол, полианилин, катодные материалы, литий-серные батареи.

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POTENTIAL OF USE THE MODIFIED POLYMERIC SULFUR BASED ON THE BY- PRODUCT PETROLEUM SULFUR IN THE RUBBER PRODUCTION

Abstract. Technological methods have been developed for the production of new polymer sulfur composites based on activated by-product sulfur and polystyrene for their use as a vulcanizing agent with improved binding and astringent properties. Optimum process conditions have been worked out, allowing to vary the sulfur content in the obtained materials. An experimental laboratory batch of new sulfur-polymer composites for testing in extended laboratory conditions as a vulcanizing agent has been gained.

Formulations, optimal conditions for mixing and vulcanization of rubber compounds have been developed. Tests of physical- mechanical and operational properties of rubbers on their basis showed the effectiveness and prospects of their application in the production of tires and rubber products.

The developed technology for the production of new sulfur-based vulcanizing agents based on activated by-product sulfur and polystyrene is promising and can be recommended for use in the production of rubber products with improved performance properties.

Key words: modified polymeric sulfur, polystyrene, rubber, caoutchouc, vulcanization.

Introduction. Vulcanization plays an important role on rubber industry by offering the rubber products containing three-dimensional net work of rubber molecules. By this mean, the significant improvement innumerous properties including tensile and tear properties, set, resilience and abrasion of rubber vulcanizates is resulted. The vulcanization could generally be divided into 3 main systems, i.e., sulfur, peroxide, and metal oxide systems [1-4]. The sulfur vulcanization system is generally preferential because of its superiority in mechanical properties and ease of cure behavior adjustment [5, 6]. Typically, the sulfur used in rubber industry originates from 2 main resources, i.e., natural resource and petroleum refinery. Basically, the sulfur from natural resource is more prefer able because of its certain chemical structure in conjunction with its high sulfur content (99 %). The petroleum-based sulfur is taken as a by-product from petroleum refinery. The annual growth in hydrocarbon production in Kazakhstan and the environmental requirements for the quality of petroleum products resulted in the accumulation of more than 10 million tons of sulfur in the Tengiz field at the sulfur storage site. Our main goal of this work is to make full use of such sulfur by investigating the modification technique for enhancing the petroleum-based sulfur to match the requirement of rubber industry. Thus, the most promising direction for the creation of large-scale production of associated sulfur utilization is the production of polymer compositions of modified sulfur with improved properties for use as vulcanizers and hardeners, as well as a plasticizer of rubber compounds and bases for soft rubbers and elastomers.

This article presents the results of studies on the production of high-sulfur polymers based on the by-produced Tengiz sulfur and polystyrene (PS) and the use of the polymers obtained as the vulcanizing agent of rubber compounds.

Results and discussion. Studies of the using possibility a by-product of oil processing-by-sulfur as a vulcanizing agent of unsaturated rubbers compared to commercially available rhombic sulfur offer several advantages. In contrast to conventional polymeric sulfur has a complex of unique properties: high resistance to aggressive media, high impact strength, the absence of thermal shrinkage deformations in the compositions, insolubility in organic solvents and rubbers, does not "bloom" on the surface of rubbers and vulcanizates, which stabilizes the properties of the product in for long periods of storage and can be widely used as a vulcanizing agent in the tire and rubber industries [7-10].

At this study, the production of polymer sulfur was carried out by direct catalytic sulphurization of polystyrene (PS) using by-product sulfur. In order to obtain high-sulfur polymers, deep sulfurization of granular polystyrene by Tengiz sulfur was carried out, and the physical-chemical properties of the products obtained were studied. In the synthesis, activated colloidal nanosized sulfur was used, obtained by acid decomposition of calcium polysulphides [8].

The reaction was studied in the temperature range 240-330 °C at a molar ratio of PS and sulfur (16 grams of sulfur atoms per unit PC), calculated on partial or exhaustive sulfurization. The synthesized samples are powders of dark gray and black color with metallic sheen, insoluble in water and organic solvents.

The synthesized samples were analyzed for the content of S (C, H). According to the thermogravimetric analysis, the polymers obtained are heat-resistant up to 220-240 °C.

Copolymer sulfur modified with polystyrene (SPSM-PS) is formed by the catalytic copolymerization of colloidal sulfur, obtained on the basis of by-product sulfur (by using diphenylguanidine, DPHG, as a catalyst). It was expected that the reaction would proceed according to figure 1 [11-13].
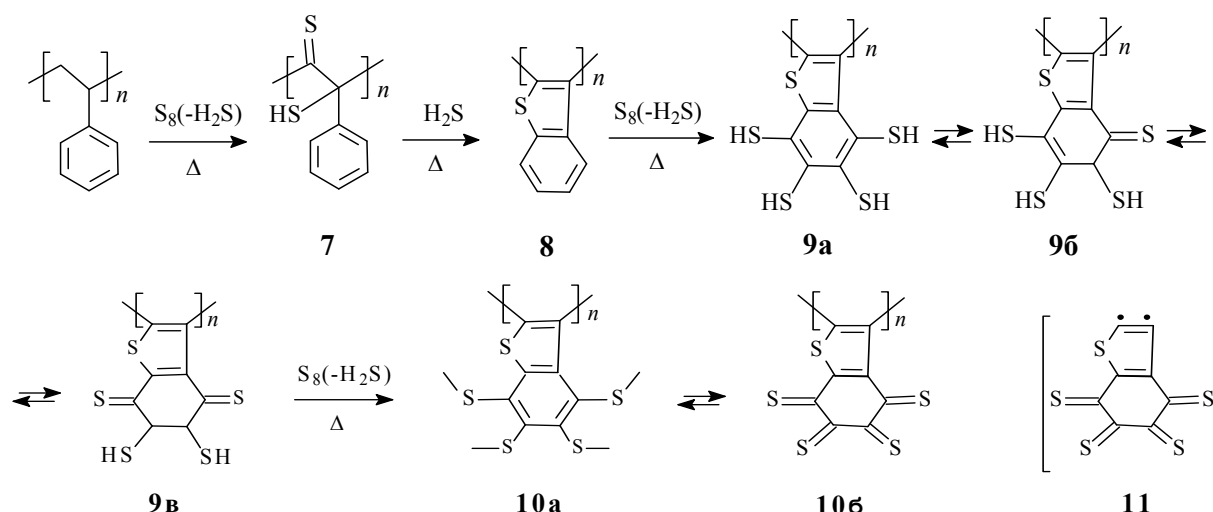
Figure 1 – Reaction scheme of copolymer sulfur modified with polystyrene

As can be seen from the scheme, in the copolymerization products there are condensed benzothiophenes linear and partially cross linked polymers with sulfide units. Under the studied conditions, high-sulfur polymers are formed from PS and colloidal sulfur (content S = 65.7-73.0%) (table 1).

Table 1 - Results of catalytic sedimentation of PS by elemental sulfur

Experi-ence	PS:S, mol	T_a, °C	Time, h	Catalyst, wt. %	Yield	S, %
1	1:8	240	2	DPHG(1)	47.0	42.1
2	1:16	240	2	DPHG (1)	78.1	66.5
3	1:16	240	3	DPHG (1)	98.1	73
4	1:16	300	3	no	96.5	65.7

Analysis of the data given in table 1 shows that the molar ratio of polystyrene to sulfur of 1:16 is optimal, because the molar ratio of PS:S = 1:8 shows a low yield of the product and a low sulfur content in it (runs 1-4). It should be noted that the catalytic synthesis of the sulfurized polystyrene with activated colloidal by-product sulfur shows the best yields (98.1 %) and sulfur content   (73 %, experiment 3) compared to elemental sulfur (experiments 1, 2).

In the IR spectra of the compounds obtained (figure 2), the absorption peak with a maximum at 471 cm^{-1} refers to the ν (S-S). Absorption in the 1700-1000 cm^{-1} region (maxima of 1639-1403 cm^{-1}) is apparently due to the vibrations of the skeleton of the exhausted sulfurized benzothiophene skeleton 10a (figure 1). The peak of 1108 cm^{-1} can be attributed to the oscillations of $\nu(C = S)$ in structures   9 b, c and 10 b. The triplet 757, 729, 707 cm^{-1} may be due to the mixed vibrations of the aromatic bonds C-C and C-S, in this case in the structure 10 a.
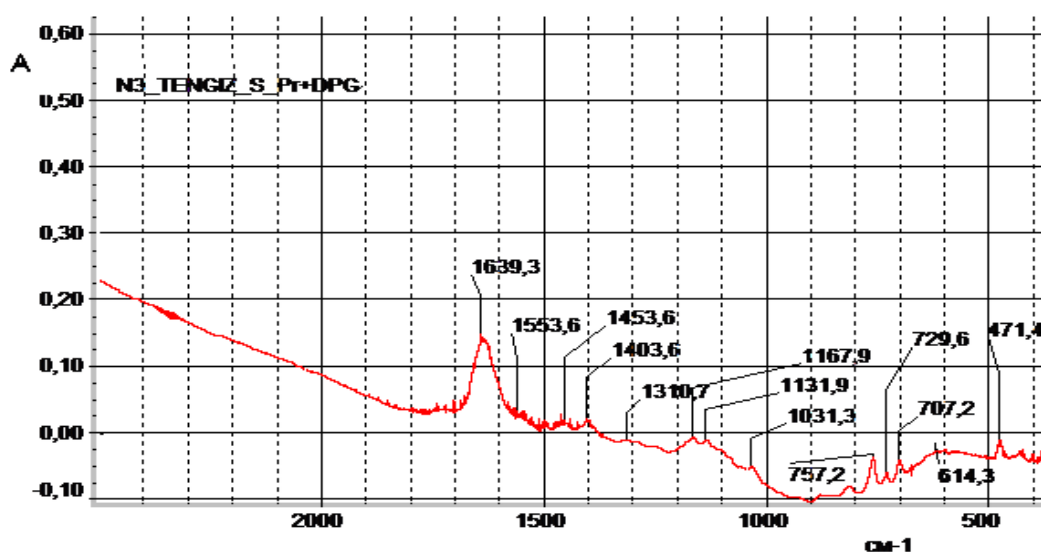
Figure 2 – IR spectrum of sulfurized polystyrene

Development of formulations, optimal conditions for mixing and vulcanization of rubber compounds. The resulting high-sulfur polymers on the basis of associated sulfur and polystyrene were tested during vulcanization of rubbers.

The tests were carried out in the enlarged laboratory conditions on the serial formulations of rubber compounds for the insulation of the bead wire of truck tires containing various amounts of high-sulfur polymer.

The necessary amount of colloidal sulfur preparation depends to a large extent on the compounding formula. As a rule, with an increase in its content for the same composition in the rest of the mixture, the degree of vulcanization increases to a certain optimum. With a further increase in the sulfur dosage, hardness continuously increases, but the overall technological properties deteriorate. For the production of rubber products, 0.2-5.0 wt. h. sulfur (based on 100 parts by weight of rubber); Conversely, for ebonite mixtures, the sulfur content must be increased to 25-40 wt.h. The dosage sulfur in rubber mixtures depends on the rubber type and the number of vulcanization accelerators taken. In mixtures based on sodium-divinyl rubbers, sulfur is taken in an amount of up to 2.5 %, in mixtures with divinyl-styrene rubbers up to 2 %. Rubber is a complex multicomponent system, consisting of 10-15 or more ingredients.

SKMS-30 ARKM-15 (GOST 11138-78 E) - synthetic methylstyrene rubber with a methylstyrene content of 30 %. This rubber refers to the "oil" with an average content of highly aromatic oil. Properties of butadiene-methylstyrene rubbers SKMS largely depend on the content of α-methylstyrene in them.

To establish the curing activity of the obtained SPSM-PS, laboratory samples of copolymer sulfur were tested on model filled rubber compounds based on SKMS-30 ARK rubber of insulation of the bead wire in comparison with the standard (table 2), where a different content of the modified polymer sulfur SPSM- PS (2, 3, 4, 6 mph).

Table 2 - Formulation card. Cipher 3 - 111. Assignment: Insulation of the bead wire

	At 100 m.ch. rubber, m.ch.				
	Standard	1 var	2 var	3 var	4 var
SKMS-30 ARC	70,0	100,0	100,0	100,0	100,0
SKI-3 2 gr.	30,0				
Technicalsulfur	4,0				
Sulfur modified polymeric		2 m.ch.			
Sulfur modified polymeric			3 m.ch.		
Sulfur modified polymeric				4 m.ch.	
Sulfur modified polymeric					6 m.ch.
Sulfenamide M	1,2	1,2	1,2	1,2	1,2
Santograd	0,2	0,2	0,2	0,2	0,2
ZincWhite	4,0	4,0	4,0	4,0	4,0
Stearicacid	2,0	2,0	2,0	2,0	2,0
Pinerosin	6,0	6,0	6,0	6,0	6,0
Softener ASMG	7,0	7,0	7,0	7,0	7,0
Oil PN - 6SH	4,0	4,0	4,0	4,0	4,0
Technical carbon P-514	70,0	70,0	70,0	70,0	70,0
Total	198,4	197,4	195,4	198,4	200,4

As the temperature and degree of vulcanization increase, the solubility of sulfur in rubber increases significantly. In natural rubber, during the mixing process at a temperature of 55-56 °C, its solubility reaches 3-4 % of the mass of the rubber.

In the production of soft rubber, where the sulfur content usually does not exceed 3%, during the mixing of the rubber compound, all sulfur can dissolve in the rubber. At the vulcanization temperature, the solubility of sulfur reaches 10%.

When the rubber mixture is cooled, supersaturated solutions can form, from which, due to diffusion, excess sulfur partially crystallizes onto the surface of the rubber mixture. Such a crystallization of sulfur on the surface of a rubber compound or vulcanizate is called "blooming" of sulfur.

Crystallization of sulfur on the surface of rubber unvulcanized parts reduces stickiness, which causes difficulties in assembling rubber products. Reduction of sulfur fading is observed when:

1) introduction of some softeners (stearic acid and pine resin into the rubber mixture, obviously, because these softeners are sulfur dispersants that promote a more even distribution of it in the rubber compound;

2) introduction of a regenerate and carbon black into the rubber mixture, which is explained by the high solubility of sulfur in the regenerate and the adsorption of sulfur by a gas black;

3) conducting the mixing process at the lowest possible temperatures, at which part of the sulfur remains in the undissolved state;

4) the use of small amounts of sulfur during vulcanization, as well as the use of mixtures of sulfur with selenium. The fading of sulfur in rubber is one of the signs of the rubber's lack of vulcanization, and also the consequence of the excess content of free sulfur in rubber. Mixing of rubber compounds was carried out in two stages on laboratory rollers PD 320 160/160. The temperature of the front rollers is 50-60 °C, the rear temperature is 60-70 °C. Duration 25 minutes in the first stage; on the second - 6 min. Vulcanization of the samples was carried out on a vulcanizing press RDE 800x800, at a temperature of 1550 °C, for 20 minutes (table 3). Difficulties were not observed during the mixing process, high-sulfur polymers are easily introduced into the rubber mixture. The distribution of polymer sulfur in rubber is satisfactory, which does not require a change in the rolling and vulcanization regime. The production of a rubber compound for the insulation of the bead wire of trucks was carried out in the following mode (table 3):

Equipment: Laboratory rollers PD 320 160/160

Roller temperature: Front 50-60 °C; Rear 60-70 °C

Table 3 - Mode of manufacturing of a rubber compound for insulation of the bead wire of truck tires

Name of operation	Time, min	
	Beginning of operation	End of operation
1 mixing stage		
Loading of rubbers, SKMS-30, ARC, SKI-3, plasticization	0	3
Load loose ingredients (zinc white, pine rosin, stearic acid, santograd, softener ACMG) and 1 / part of the carbon tetrachloride P-514, mix, rolling rolls on both sides 8 times (4 times on the left side, 4 times on the right)	3	8
Cut 1/3 part of the mixture, load 1/2 part of technical sulfur P-514, insert the cut 1/3 part of the mixture, mix, rolling rolls on both sides 8 times (4 times on the left side, 4 times on the right)	8	12
Cut 1/3 part of the mixture, load the plasticizer PN-6SH, load 1/2 part of the technical sulfur P-245, insert the cut 1/3 part of the mixture, mix, roll rolls on both sides 8 times (4 times on the left side, 4 times with the right)	12	17
Table 3 continue		
Cut 1/3 part of the mixture, load 1/2 part of technical sulfur P-245, add cut 1/3 of the mixture, mix, roll rolls on both sides 8 times (4 times on the left side, 4 times on the right)	17	23
Remove the mixture from the rollers	23	25
Total		25
2 mixing stage		
Load the mixture of the first stage, heat	0	2
Cut 1/3 part of the mixture, load the Sulfenamide M acce-lerator, insert the cut 1/3 part of the mixture, mix, rolling rolls on both sides 4 times (2 times on the left side, 2 times on the right side)	2	4
Cut 1/3 part of the mixture, load the modified sulfur, insert the cut 1/3 part of the mixture, mix, rolling rolls on both sides 4 times (2 times on the left side, 2 times on the right)	4	5
Remove the mixture from the rollers	5	6
Total		6

After the first operation, the rubber mixture was aged for at least 2 hours, the mixture was cooled to room temperature not higher than 250 °C. Vulcanization of the plates was carried out at a temperature of 1550 °C for 20 minutes. At the same time the equipment was used: vulcanization press RDE 800x800.

Thus, as a result of the research, new high-sulfur polymers based on colloidal Tengiz sulfur and polystyrene have been synthesized.

Technological parameters of obtaining sulfur-enriched polymeric composites have been worked out.

It is shown that polystyrene is sulfurized by excess sulfur at temperatures of 240-330 °C. Conditions for carrying out the reaction have been found, which make it possible to vary the sulfur content of the obtained materials. At the same time, the product contains 63.7-73% sulfur.

The resulting composites have been studied as a vulcanizing agent for rubber compounds. Developed recipes, the optimal conditions for mixing and vulcanizing rubber compounds.

In accordance with the developed prescription map (table 3), high-sulfur polymer compositions based on associated sulfur and polystyrene on the physico-mechanical properties of rubbers as a result of vulcanization were also studied.

To establish the curing activity of copolymer sulfur modified with polystyrene-SPCM-PS, laboratory samples of copolymer sulfur were tested on model filled rubber compounds based on SKMS-30 ARK rubber on board wire insulation in comparison with the reference (table 2), where different technical contents were used instead of technical sulfur modified polymer sulfur SPSM-PS (2, 3, 4, 6 m.ch).

Properties of rubber compounds and vulcanizates based on rubbers of general purpose for manufacturing insulation of bead wire of truck tires with additives of polymer sulfur are given in table 4.

Calculation of rheometric curves recorded on a Monsanto rheometer given in table 5.

Table 4 - Physical and mechanical properties of rubbers using modified sulfur

Name of indicators	Control standards	Standard of sulfur tech-4m.ch.	Modified sulfur				
			1 var 2 m.ch	2 var 3 m.ch.	3 var 4 m.ch.	4 var 5 m.ch.	5 var 6 m.ch.
Plasticity, conv. units	0,23-0,33	0,30	0,37	0,34	0,31	0,30	0,34
Breaking strength, kgf / cm^2	n/m 112	140	120	120	135	140	140
Relative elongation,%	180-350	345	367	367	350	355	335
Tear resistance, n / cm	n/m 60	65	55	55	62	63	63
Hardness, conv. units	65-75	71	65	65	67	68	70

Table 5 - Calculation of rheometric curves recorded on a Monsanto rheometer. Mode: 1550C x 20 minutes

Indicator name	Standart	1 variant	2 variant	3 variant	4 variant	5 variant
M_1 τ_1	10 units 1'22"	damp	10,5 units 1'35"	11units 1'25"	11 units 1'25"	12 units 1'22"
M_2 τ_2	12 units 2'15"	-	11,5 units 2'20"	11,5 units 2'20"	11,5 units 2'20"	12 units 2'15"
M_3 τ_3	35,2 units 18'00"	-	36,1 units 17'30"	36,2 units 17'20"	36,2 units 17'20"	37,2 units 17'10"
M_4 τ_4	38 units 19'15"	-	39 units 19'20"	39 units 19'20"	39 units 19'20"	40 units 19'27"

The positive influence of the investigated high-sulfur polymers on the technological properties of the obtained rubber mixtures was established. The results given in Table 4 indicate that the use of polymer-modified polymeric sulfur as the vulcanizing agent improves such physico-mechanical characteristics of rubber products as plasticity, elongation and hardness.

The tests carried out showed that, compared to the standard sample, the plasticity index at a polymer sulfur content of 3 parts by weight are improved by 23 %, a further increase in the content of polymeric sulfur to 6 m.ch. leads to a decrease in this indicator. The value of the relative elongation is maximum at a content of 3 m.p. polymeric sulfur, an improvement of 22 % of the standard sample. The optimum sulfur content is 3-4 parts by weight by 100 parts by mass. rubber.

Conclusion. Thus, based on the results of the conducted studies, it can be concluded that the use of polymeric sulfur as a curative agent has a positive effect on the properties of rubbers based on SKI-3, SKMS-30, ARKM-15.

Based on the results of enlarged laboratory tests on the use of polymer sulfur obtained during the vulcanization of rubber compounds, optimum amounts of polymer sulfur were determined to produce vulcanizates with the best performance properties.

The developed technology for the production of new sulfur-based vulcanizing agents based on activated by-pass sulfur and polystyrene is promising and can be recommended for use in the production of rubber products with improved performance properties.

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СОДЕРЖАНИЕ

CONTENTS

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