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Нұралы мұнайының құрамын және қасиеттерін зерттеу

Физика-химиялық талдау әдістерін қолдану арқылы Нұралы кеніші мұнайының физика-химиялық қасиеттері, шығу тегі (пристанның фитанға қатынасы арқылы) және фракциялық құрамы зерттелді. Хромато-масс-спектрометрия әдісімен мұнайдың толық құрамы анықталып, ондағы қосылыстардың мөлшері ішкі нормализация тәсілімен есептелді. Масс-спектрлердің кітапханасы ретінде NIST-08 базасы қолданылды. Алынған хроматограммадағы 2,6,10,14-тетраметилпентадеканның 2,6,10,14-тетраметилгексадеканға қатынасы арқылы зерттелген мұнайдың шығу тегі табылды. Зерттелген мұнай шығу тегі бойынша жағалауға жақын теңіз табанында түзілген. Мұнай және одан алынған өнімдердің фракциялық құрамы имитациялық дистилляция әдісі арқылы зерттелді. Алынған өнімдердің жану жылулары және мұнайдан алынған бензиннің октан саны анықталды. Зерттеу нәтижесінде алынған нәтижелер мұнайды өңдеуде қолданыс табуы мүмкін.

Кілт сөздер: Нұралы кеніші, мұнай, хроматография, имитациялық дистилляция, пристан, фитан, мұнай өнімдері, октан саны, калориметрия.

Кіріспе

Мұнай адамзат үшін энергия, ал химиялық өнеркәсіп үшін көмірсутекті шикізат көзі болып табылатын табиғи объект. Қазіргі мұнай химиясы физикалық, органикалық және аналитикалық химияның әдістемелік негіздері базасында қалыптасты. Мұнайлардың құрамынан қазіргі таңда C_1–C_{40} құрамды 1000-ға жуық көмірсутектер идентификацияланған [1, 2].

Мұнайлардың химиялық және фракциялық құрамын зерттеу мұнай өңдеудің барынша тиімді кешенін таңдауға, оларды модельдеуге, мұнай өңдеу қондырғыларының қуатын негіздеуге, мұнай генезисі жайлы ұғымды дамытуға және мұнай геологиясының мәселелерін шешу үшін өте маңызды.

Осы мақсат үшін біз бұл мақалада Нұралы кеніші мұнайының құрамын және қасиеттерін зерттеу нысаны ретінде алдық. Нұралы кеніші — Оңтүстік Торғай ойысында орналасқан мұнай кеніштерінің бірі, ол 1987 жылдан игеріліп келеді және қазіргі таңда Қызылорда облысы экономикасының негізгі тіректерінің бірі болып табылады.

Эксперимент

Зерттеулер жүргізбестен бұрын мұнай құрамындағы асфальтендер мен шайырлардан адсорбциялық бағаналы хроматография көмегімен тазартылды. Ол үшін шыны бағананы силикагельмен толтырып, үстіне аз мөлшерде Al_2O_3 ұнтағын салып, зерттелетін мұнай құйылып гексанмен элюирленді.

Фракциялық құрам Varian 450 GC газды хроматографы (Нидерланды) көмегімен имитациялық дистилляция арқылы анықталды. Хроматографиялау жағдайы: буландырғыш температурасы 100-ден 350 °С-ға дейін минутына 15 °С-ге көтеріледі, 350 °С-де 23,33 мин тұрады, жалпы уақыт 40 мин, колонка термостатының температурасы 35-тен 350 °С-ге дейін, минутына 10 °С-ге көтеріледі, 350 °С-де 8,50 мин тұрады, жалпы уақыт 40 мин, детектордың температурасы 350 °С. Детектор ретінде жалынды-ионизациялық детектор қолданылды. Хроматографиялық колонка ұзындығы 10 м (SimDist).

Мұнайдың толық құрамы Agilent 7890A/5975C хромато-масс-спектрометрі (АҚШ) көмегімен анықталды. Хроматографиялау жағдайы: буландырғыш температурасы 350 °С, колонка термостаты 70-тен 290 °С-ге дейін минутына 4 °С-ге көтеріледі, 290 °С-де 30 мин тұрады, жалпы талдау уақыты 80 мин. Детектор ретінде масс-спектрометр қолданылды, масс-спектрлер Scan режимінде алынды. Хроматографиялық бөлу «Hewlett Packard» фирмасының HP-5MS капиллярлы колонкасында іске асырылды, колонка ұзындығы 30 м, ішкі диаметрі 0,25 мм, қозғалмайтын фаза қабатының қалыңдығы 0,25 мкм.

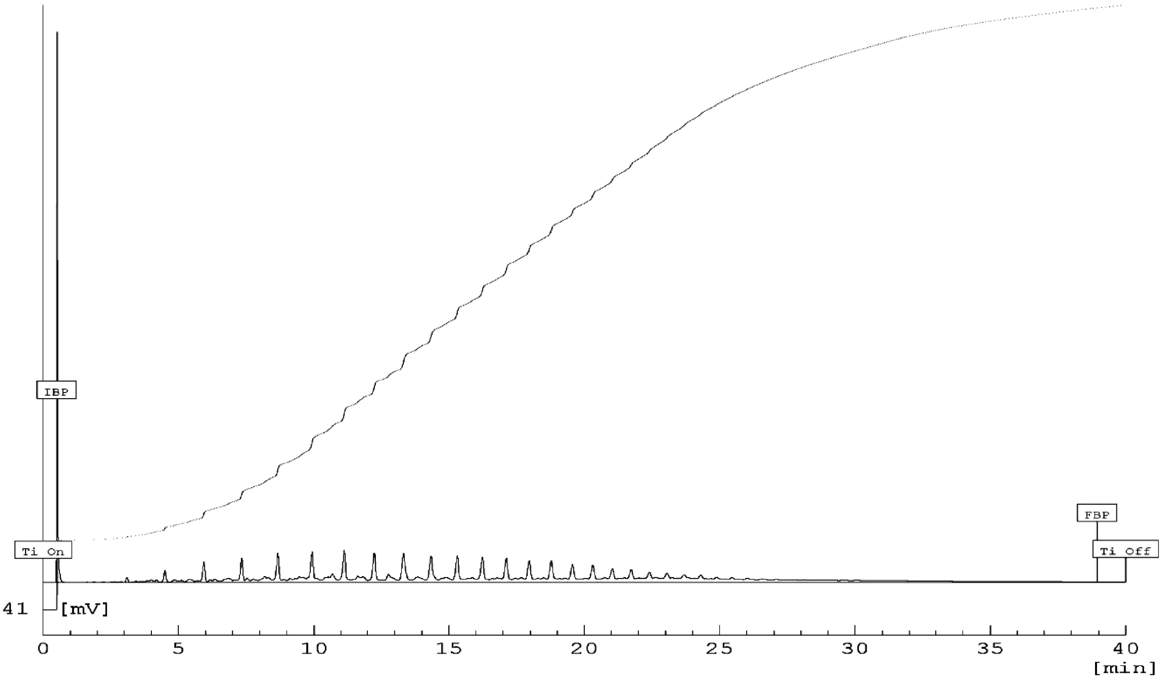
Мұнайдың құрамындағы өнімдердің шығымын анықтау мақсатында атмосфералық қысымда бензин және керосин фракциясы айдалып алынды, айдау шыршалы дефлегматор көмегімен іске асырылды.

Алынған бензиннің октан саны ОКТАН-ИМ (РФ) қондырғысының көмегімен анықталды. Бензиннің, керосиннің және мазуттың жылу бергіштік қасиеті IKA-WERKE фирмасының С2000 калориметрі (Германия) көмегімен зерттелді.

Нәтижелер және талдау

Асфальтендер мен шайырлардан тазартылған мұнайдың фракциялық және толық құрамы мен шығу тегі анықталды.

Нұралы мұнайының фракциялық құрамы жайлы мәліметтер 1-сурет пен 1-кестеде келтірілген.



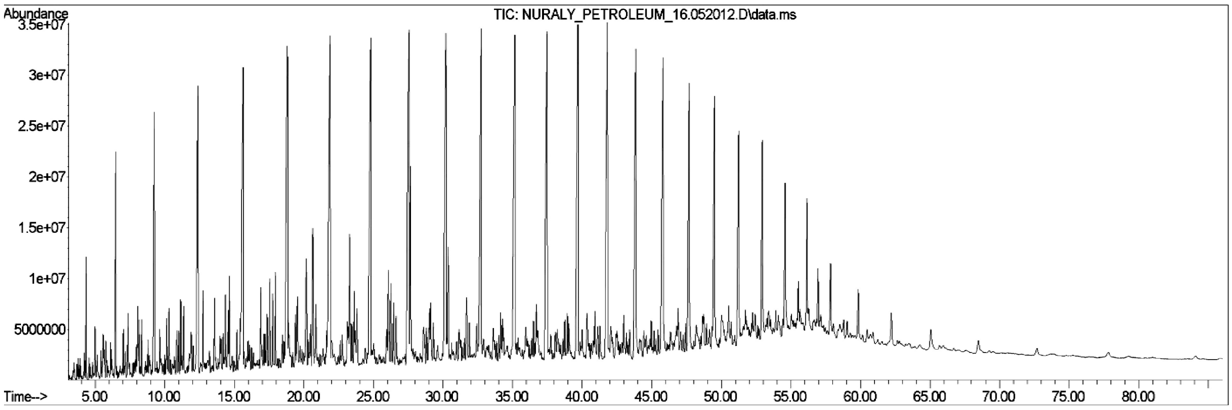
1-сурет. Нұралы мұнайының фракциялық құрамы

1-кесте

Нұралы мұнайының фракциялық құрамы

Шығым, %	Қайнау температурасы, °С	Шығым, %	Қайнау температурасы, °С	Шығым, %	Қайнау температурасы, °С
Қайнаудың басталуы	66,2	10	69,9	98	613,3
1	66,8	50	333,2	99	636,7
2	67,3	90	512,1	100	649,5
5	68,3	95	562,3		

Мұнайдың толық құрамы жайлы мәлімет 2-сурет пен 2-кестеде келтірілген. Асфальтендер мен шайырлардан тазартылған мұнайдың құрамындағы қосылыстардың саны 239.



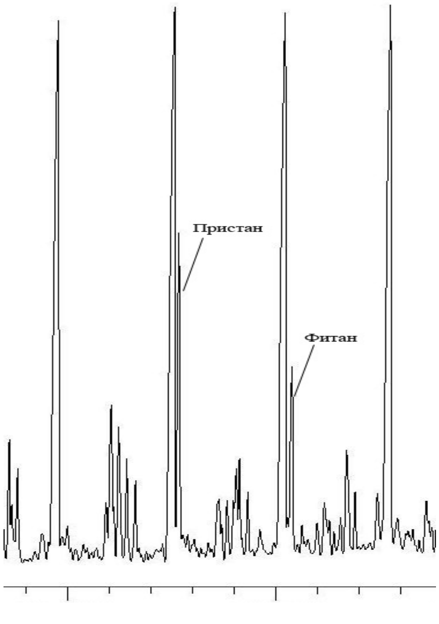
2-сурет. Нұралы мұнайының хроматограммасы

Төменде 2-кестеден Нұралы мұнайының құрамында көмірсутектердің жалпы мөлшері 93,65 %-ды құрайтындығын байқауға болады, 6,35 % әр түрлі күкіртті, оттекті, азотты, галоидты және т.б. қосылыстардан тұрады.

2-кесте

Нұралы мұнайының толық құрамы

Қосылыстар	Массалық үлесі, %
Алкандар	84,12
н-алкандар	66,60
тармақталған алкандар	17,52
Нафтендер	6,76
Ароматты қосылыстар	2,77
Басқа да қосылыстар	6,35



3-сурет. Нұралы мұнайының құрамындағы пристан мен фитанның қатынасы (хроматограмма)

Әдеби мәліметтерде [3, 4] мұнайлардағы пристанның (2,6,10,14-тетраметилпентадекан) фитанға (2,6,10,14-тетраметилгексадекан) қатынасы арқылы олардың шығу тегін анықтауға болады. Егер пристанның фитанға қатынасы 3 немесе одан жоғары болатын болса, ол құрлықта түзілген болып есептеледі, ал 1 немесе одан төмен болатын болса, ол теңіз табанында түзілген, екеуінің аралығындағы болса, жағалауға жақын теңіз табанында түзілген болып есептеледі. Біздің алған мәліметіміз (3-сур.) бойынша пристанның фитанға қатынасы 1,7-ге тең, сол себепті Нұралы кенішінің мұнайы жағалауға жақын теңіз табанында түзілген деген қорытынды жасауға болады.

Мұнайдың құрамындағы өнімдердің шығымын анықтау мақсатында атмосфералық қысымда бензин және керосин фракциясы айдалып алынды, айдау шыршалы дефлегматор көмегімен іске асырылды, бензиннің көлемдік үлесі 9 % (39–180 °С), керосиннің көлемдік үлесі 22 %-ды (180–250 °С) құрайды. Алынған бензиннің октан санының шамасы 85,6-ға, ал моторлы октан санының шамасы 79,6-ға тең. Бензиннің жану жылуы 46,572 кДж/г, керосин мен мазуттың жану жылулары 46,381 және 45,468 кДж/г-ға тең екендігі анықталды (3-кесте).

3-кесте

Мұнай өнімдерінің қасиеттері

Өнім атауы	Шығым, көлемі, %	Қайнау температурасы, °C	Октан саны		Жану жылуы, кДж/г
			зерттеу	моторлы	
Бензин	9	39–180	85,6	79,6	46,572
Керосин	22	180–250	–	–	46,381
Мазут	62,0	–	–	–	45,468

Қорытынды

Осылайша, Нұралы кеніші мұнайының құрамындағы асфальтендер мен шайырлар адсорбциялық бағаналы хроматография әдісімен тазаланып, хромато-масс-спектрометрия көмегімен толық құрамы, имитациялық дистилляция көмегімен фракциялық құрамы және де мұнай құрамындағы пристан мен фитанның қатынасы арқылы оның шығу тегі анықталды. Зерттелген мұнайдың құрамында алкандар 84,12 %-ды (оның ішінде қалыпты алкандар — 66,60, тармақталған алкандар — 17,52 %), циклоалкандар — 6,76, ароматты көмірсутектер — 2,77, басқа да күкіртті, оттекті, азотты, галоидты қосылыстар 6,35 %-ды құрайды. Мұнайдың шығу тегі бойынша жағалауға жақын теңіз табанында түзілгендігі табылды. Мұнайды айдау арқылы өнімдер алынып, олардың қасиеттері зерттелді. Алынған бензиннің зерттеу октан санының шамасы — 85,6-ға, жану жылуы — 46,572 кДж/г-ға, керосин мен мазуттың жану жылулары 46,381 және 45,468 кДж/г-ға сәйкес анықталды. Алынған мәліметтер мұнай өңдеуде қолданыс табуы мүмкін.

Әдебиеттер тізімі

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Н.О.Аппазов, Н.И.Акылбеков, Д.Ж.Ниязова, М.И.Сыздыкбаев, Р.А.Нарманова

Исследование состава и свойств нефти месторождения Нуралы

Применением физико-химических методов анализа определены физико-химические свойства, происхождение (по соотношению пристана к фитану) и фракционный состав нефти месторождения Нуралы. Методом хромато-масс-спектрометрии определен детальный состав нефти, количественный состав соединений, содержащихся в нефти, вычислен способом внутренней нормализации. В качестве библиотеки масс-спектров использована база NIST-08. Из полученной хроматограммы по соотношению 2,6,10,14-тетраметилпентадекана к 2,6,10,14-тетраметилгексадекану найдено происхождение нефти. Фракционный состав нефти и полученных из нее продуктов исследован имитационной дистилляцией. Результаты исследования могут быть применены при переработке нефти.

N.O.Appazov, N.I.Akylbekov, D.Zh.Niyazova, M.I.Syzdykbaev, R.A.Narmanova

Investigation of composition and features of the Nuraly oilfield

By physico-chemical methods of analysis determined physical and chemical properties, origin (as for prystane to phytane), fractional composition (imitational distilaton) of Nuraly oil. Detailed combination of oil was determined using chromate-mass spectrometer, quantitative constitution of compounds containing in oil calculated by internal normalization. Base NIST-08 was used as a mass spectra library. Origin of oil was found out of obtained chromatogram ratio 2,6,10,14-tetramethylpentadecane to 2,6,10,14-tetramethylhexadecane. Fractional composition of oil and its products were examined by simulation distillation. Obtained results can be applied while oil refining.

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Theoretical study of the medium polarity influence on the OH-acids strength

Deprotonation energy for a number of OH-acids theoretically estimated by UHF 6–31G *ab initio* CPCM methods using Gaussian-2009. Reducing of acids deprotonation energy with increasing of the medium polarity is shown by quantum chemical methods. Theoretical justification of EPR spectroscopic data on decrease of rate of the proton exchange reaction between semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl and some carboxylic acids in polar media is given.

Key words: OH-acids, semiquinone radicals, protolytic reaction, proton exchange reaction, deprotonation energy, solvation, acidity and basicity, quantum chemical calculations, *ab initio*, Gaussian-2009.

According to the Brønsted-Lowry acid–base theory, acid is a hydrogenous particle of the substance, capable to be the donor of a proton, and the basis is a particle of the substance, capable to be an acceptor of a proton [1]. Acid-base reactions — is a reaction in which a proton is transferred from the acid to the base. Such reactions are called protolytic reactions. In general protolytic reaction can be described by the following equation:

$$HA + B \leftrightarrow A^{-} + HB^{+}. \qquad (1)$$

Proton-donor and proton-acceptor ability of substances (their acidity and basicity) is determined by the proton affinity. Free proton does not exist in solution. Therefore equation (1) characterizing balance between acid and base, doesn't represent real system Actually all acid-base equilibrium proceed with sH solvent participation:

$$HA + sH \leftrightarrow A^{-} + sH_2^{+}, \qquad (2)$$

where sH_2^{+} — lyonium ion which is resulting from the process of a proton addition, i.e. a solvated proton;

$$B + sH \leftrightarrow s^{-} + HB^{+}, \qquad (3)$$

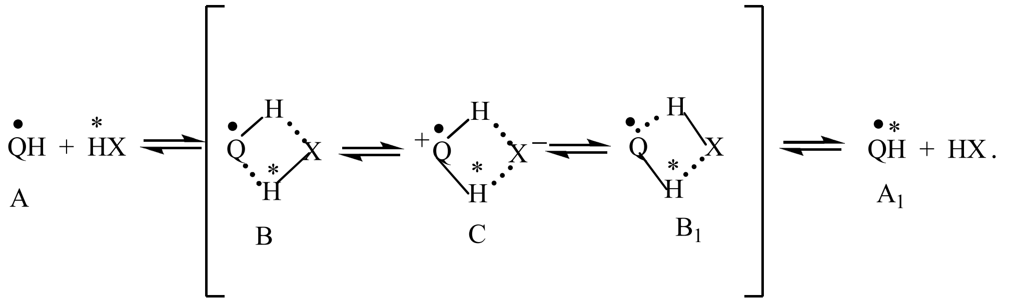
where s^{-} — lyate ion.

Thus, the nature of the solvent has a significant effect on the protolytic equilibrium. Change of solvent can change the direction of the acid-base reaction.

According to its acid-base properties solvents separated on aprotic and protic [2]. Aprotic solvents don't show the acid-base properties. Molecules of such substances don't give and don't attach protons. Benzene, toluene belongs to their number, hexane, carbon tetrachloride, chloroform and some other. Aprotic solvents influence to the acid-base properties of the substances dissolved in them a little.

Protic solvents have strong acid-base properties. Molecules of similar solvents are capable to give or attach protons. In protic solvent the relative strength of acids depends by nature solvent and is determined by the energy necessary for transfer of a proton from a molecule or an ion on infinitely long distance. Influence of solvent is defined by its dielectric permeability and prototropic properties. Thereof the relative strength of acids can change depending on the solvent nature.

The influence of solvated effects on kinetics of an intermolecular proton exchange reaction between semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl (radical I) and some mono-carboxylic fatty acids was previously studied by EPR spectroscopy in KSU [3]. The following general mechanism of intermolecular proton exchange between radical I and OH-acids was proposed on the basis of earlier conducted systematic radio-spectral studies:



(4)

As solvents were used toluene (ε=2,4), 1,4-dioxane (ε=3,0) and nitrobenzene (ε=35,5). All used solvents have the aprotic nature, i.e. their influence on photolytic equilibrium can be characterized by the dielectric constant of the medium.

Using EPR spectroscopy it was found [3] that specific rate of bimolecular reaction is ten times lower in the dioxane medium, than in indifferent solvent toluene, and also that proton exchange rate is slightly decreased with increasing dielectric constant of the medium.

It was interesting to study influence of solvent on the OH-acids strength by quantum chemistry methods. Earlier it was shown [4] that deprotonation energy can serve for the quantum-chemical characteristic of acids strength. Deprotonation energy of acid can be quantum chemical estimated as a difference between the total energy values acid and its anion:

$$HA \rightarrow A^{-} + H^{+}. \qquad (5)$$

The total energy of a proton is equal to zero, therefore:

$$\Delta E_{\text{deprot.}} = E_{\text{total.}}(HA) - E_{\text{total.}}(A^{-}). \qquad (6)$$

As the required differential size ΔE_{deprot} is some orders less than each of counted energy separately, calculations must be carried out as accurately as possible. That's why quantum-chemical evaluation of the deprotonation energy we carried out *ab initio*-UHF method in an extended basis 6–31G. Calculations were carried out by means of Gaussian-2009 software package [5].

The solvent influence at the deprotonation process was taken into account within by the Conducting Polarisable Continuum Model (CPCM). In this model, the solvent is presented as a polarizable continuum and the solute is placed in a cavity within the solvent [6, 7]. The cavity in the classical model PCM defined as a set of overlapping areas, the size of which is proportional to the van der Waals radius the corresponding atoms.

Quantum chemical calculations were performed for a homologous series of mono-carboxylic acids investigated earlier by EPR spectroscopy [3] and also for the semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl — radical I — used as a spin probe. Calculations were carried out with full optimization of geometry by UHF 6–31G *ab initio*-method taking into account solvent within macroscopic model of CPCM. Water (ε=80) and aprotic benzene (ε=2,3), toluene (ε=2,4), chlorobenzene (ε=5,7) were taken as the solvent. Selection of solvents is caused by their different nature, range of dielectric permeability of the medium, and the parameterization of macroscopic polarized continuum model CPCM for a limited number of solvents.

Table 1

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations for a number of the studied OH-acids. Solvent — water

Acid	Acid Formula	Total energy HA, A.U.	Total energy A^{-}, A.U.	$\Delta E_{\text{deprot.}}$, A.U.	pK_a
Formic	$HCOOH$	–188,6767	–188,2053	0,4713	3,75
Acetic	CH_3COOH	–227,7119	–227,2336	0,4782	4,76
Butyric	$CH_3(CH_2)_2COOH$	–305,7487	–305,2707	0,4779	4,82
Valeric	$CH_3(CH_2)_3COOH$	–344,7672	–344,2891	0,4780	4,86
Caproic	$CH_3(CH_2)_4COOH$	–383,7857	–383,3077	0,4780	4,88
Caprylic	$CH_3(CH_2)_6COOH$	–461,8227	–461,3446	0,4781	4,89
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–656,9150	–656,4369	0,4781	–
Palmitic	$CH_3(CH_2)_{14}COOH$	–773,9456	–773,4922	0,4533	–
Stearic	$CH_3(CH_2)_{16}COOH$	–852,0034	–851,5292	0,4742	–
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–691,8277	–691,3333	0,4943	–

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations are presented in table 1 (solvent — water). Handbook [8] values of the p*Ka* for a number of the studied OH-acids are also given in the table 1.

Data presented in table 1 show that with growth of a carbon chain in a homological row OH-acids, acidity is decrease (p*Ka* is increase), deprotonation energy is increase from 0,47 to 0,49 A.U. This is logical, since strong acid easily gives a proton and has a lower deprotonation energy. It should be noted the big size of deprotonation energy for the radical I compared to all investigated carboxylic acids. Therefore, the radical I is the weakest acid in a studied range of OH-acids. It will play a base role in photolytic reactions with carboxylic acids.

It was interesting to present in graphical form relationship between deprotonation energy and handbook value p*Ka* for a studied range of OH-acids (solvent — water; fig. 1).

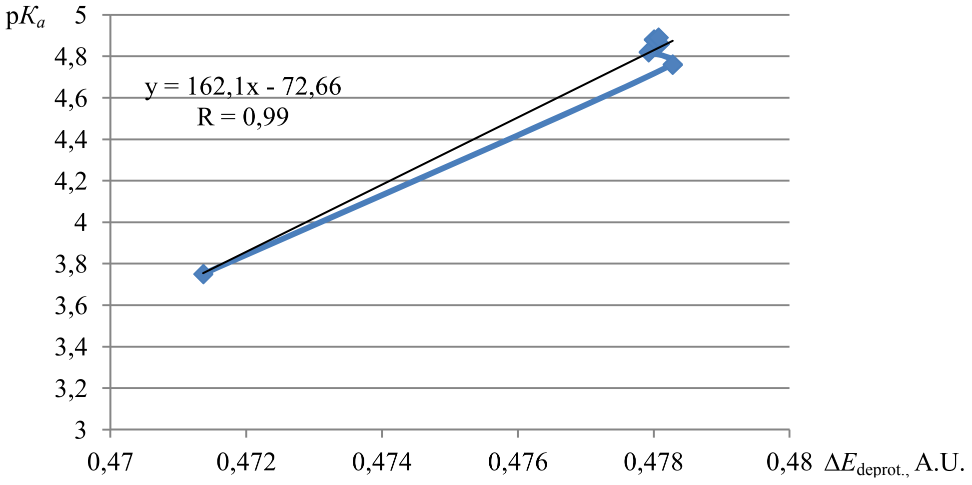


Figure 1. Relationship between deprotonation energy and handbook p*Ka* value
for a studied range OH-acids. Solvent — water

The analysis of the graphic dependence presented in figure 1, showed existence of direct proportional dependence between an indicator of acidity and deprotonation energy of acid in a case when as solvent water was considered. Pearson correlation coefficient for the given relation is large enough (R=0,99), suggesting that there is a high correlation between the deprotonation energy of acid and its acidity.

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations are presented in table 2 (solvent — chlorobenzene). Handbook [8] values of the p*Ka* for a number of the studied OH-acids are also given in the table 2.

Table 2

**Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations
for a number of the studied OH-acids. Solvent — chlorobenzene**

Acid HA	Acid Formula	Total energy HA, A.U.	Total energy A^-, A.U.	$\Delta E_{deprot.}$, A.U.	pK_a
Formic	HCOOH	–188,6699	–188,1869	0,4830	3,75
Acetic	CH_3COOH	–227,7032	–227,2149	0,4883	4,76
Butyric	$CH_3(CH_2)_2COOH$	–305,7414	–305,2522	0,4891	4,82
Valeric	$CH_3(CH_2)_3COOH$	–344,7667	–344,2706	0,4961	4,86
Caproic	$CH_3(CH_2)_4COOH$	–383,7852	–383,2892	0,4960	4,88
Caprylic	$CH_3(CH_2)_6COOH$	–461,8222	–461,3260	0,4961	4,89
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–656,9144	–656,4183	0,4962	–
Palmitic	$CH_3(CH_2)_{14}COOH$	–773,9698	–773,4736	0,4962	–
Stearic	$CH_3(CH_2)_{16}COOH$	–851,9999	–851,5105	0,4893	–
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–691,8254	–691,3178	0,5076	–

Data presented in table 2 show that with growth of a carbon chain in a homological row OH-acids, deprotonation energy is increase from 0,48 to 0,51 A.U. This seems to be correct because the stronger the acid, the easier it gives a proton, the less deprotonation energy. A large amount of deprotonation energy for radical I compared to all investigated carboxylic acids should also be noted. Consequently, the radical I in protolytic reactions with carboxylic acids will act as a base. That's why radical I will play the role of a base in protolytic reactions with carboxylic acids.

It was interesting to present in graphical form relationship between deprotonation energy and handbook value p*Ka* for a studied range of OH-acids (solvent — chlorobenzene; fig. 2).

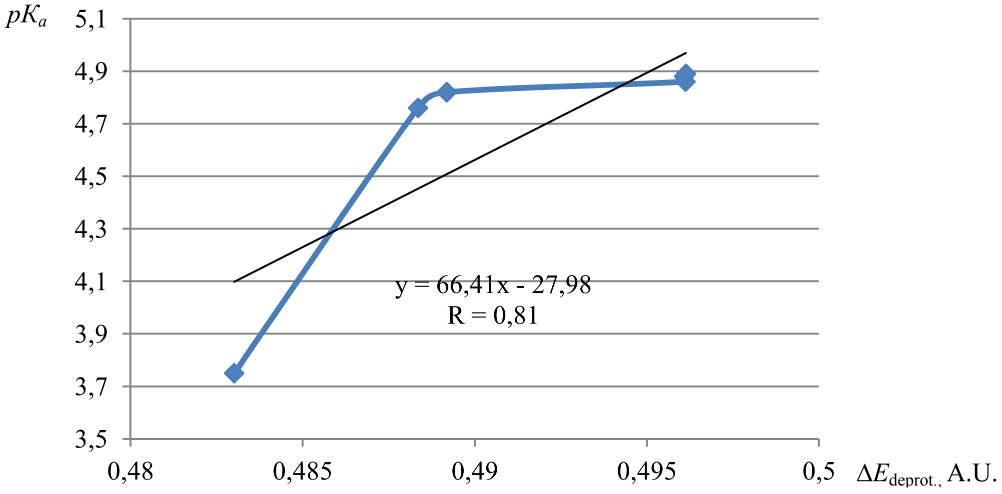


Figure 2. Relationship between deprotonation energy and handbook p*Ka* value for a studied range OH-acids. Solvent — chlorobenzene

The analysis of the graphic dependence presented in figure 2, showed existence of direct proportional dependence between an indicator of acidity and deprotonation energy of acid in a case when as solvent chlorobenzene was considered. Note the smaller value of the Pearson correlation coefficient (R=0,81) compared with the case when the water solvent is taken into account (R=0,99). Limited application of the reference p*Ka* value for the acid strength characteristic in non-aqueous solutions it shows.

Similar quantum chemical UHF 6–31G *ab initio* CPCM calculations for a number of investigated OH-acids (solvents — toluene (ε=2,4) and benzene (ε=2,3)) were performed. Growth of the deprotonation energy from 0.50 to 0,52 A.U. with increasing of the carbon chain in the homologous series of carboxylic acids was also noted in the calculations with toluene and benzene solvents. The fact of reducing the difference between the deprotonation energies of carboxylic acid and radical I in these calculations (≈0,01 A.U.) compared to the previous one when water as the solvent was taken into account (≈0,02 A.U.) has attracted attention. It allows to assume that the difference in strength of carboxylic acids and the radical I is reduced, the acidity of the proton exchange reaction participants becomes comparable in non-polar media. Increasing the speed of the proton exchange in indifferent mediums, fixed by EPR spectroscopy, is the result of it. The difference in the acidity of the proton exchange reaction participants is increased in the polar medium due to the polarizing effect of the solvent. Delay of speed proton exchange reaction in polar media is the result of it.

It was interesting to analyze the obtained settlement quantum chemical data of the deprotonation energy for a studied range OH-acids in the medium of water, chlorobenzene, benzene and toluene (Table 3). Value averages were calculated by us for the comparative analysis:

$$(\Delta E_{\text{deprot.}})_{\text{middle}} = \Sigma(\Delta E_{\text{deprot.}}); \tag{7}$$

$$\Delta_{\text{middle}} = \Delta E_{\text{deprot.}}(\text{radical I}) - (\Delta E_{\text{deprot.}})_{\text{middle}}. \tag{8}$$

The average value $(\Delta E_{\text{deprot.}})_{\text{middle}}$ will allow us to characterize the dependence of the OH-acids deprotonation energy from the medium. The value of Δ_{middle} will allow us to characterize the average difference between the deprotonation energies of carboxylic acids and radical I.

Table 3

Deprotonation energies for a studied range OH-acids. Calculation method — UHF 6–31G *ab initio* CPCM

Acid	Acid Formula	pK_a	$\Delta E_{deprot.}$, A.U. Solvent:			
			water (ε=80)	chlorobenzene (ε=5,7)	toluene (ε=2,4)	benzene (ε=2,3)
Formic	HCOOH	3,75	0,4713	0,4830	0,5056	0,5073
Acetic	CH_3COOH	4,76	0,4782	0,4883	0,5112	0,5130
Butyric	$CH_3(CH_2)_2COOH$	4,82	0,4779	0,4891	0,5117	0,5134
Valeric	$CH_3(CH_2)_3COOH$	4,86	0,4780	0,4961	0,5207	0,5226
Caproic	$CH_3(CH_2)_4COOH$	4,88	0,4780	0,4960	0,5207	0,5226
Caprylic	$CH_3(CH_2)_6COOH$	4,89	0,4781	0,4961	0,5208	0,5227
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–	0,4781	0,4962	0,5208	0,5227
Palmitic	$CH_3(CH_2)_{14}COOH$	–	0,4533	0,4962	0,5216	0,5227
Stearic	$CH_3(CH_2)_{16}COOH$	–	0,4742	0,4893	0,5118	0,5135
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–	0,4943	0,5076	0,5267	0,5282
$(\Delta E_{deprot.})_{middle}$, A.U.			0,4762	0,4938	0,5172	0,5189
Δ_{middle}, A.U.			0,0181	0,0138	0,0095	0,0093

Data presented in table 3 show that the deprotonation energy of acid increases, the difference in energies of deprotonation of carboxylic acids and radical I decreases with decreasing of the solvent polarity.

It was interesting to analyze by graph the relationship between the average of deprotonation energy $(\Delta E_{deprot.})_{middle}$ and dielectric permeability ε of the medium. The obtained graph is shown in figure 3.

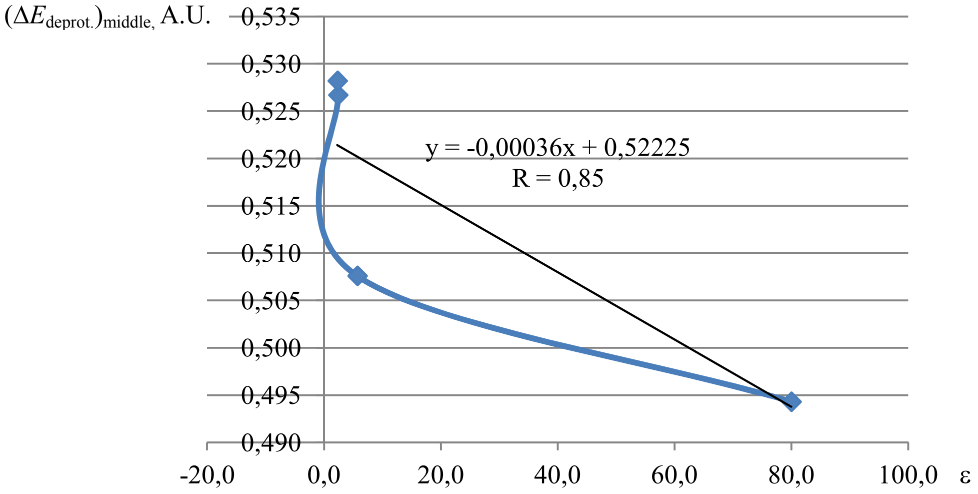


Figure 3. Relationship between the average of deprotonation energy $(\Delta E_{deprot.})_{middle}$ and dielectric permeability ε of the medium

Data presented in figure 3 show that between dielectric permeability of solvent and acid deprotonation energy there is the inverse proportional relationship. Deprotonation energy of acid decreases with increasing of the medium polarity. This indicates an increase of the substances acidity in a polar solvent.

The following conclusions were formulated based on the obtained data:

– Deprotonation energy of acids decreases with increasing of the medium polarity. This suggests that the acidity of substances is higher in polar solvents than in indifferent mediums;

– The difference in acidity of the radical I and carboxylic acids is less in non-polar media. This leads to increased speed of the proton exchange between its in indifferent mediums;

– Radical I is demonstrated more basicity in polar solvents. This causes a slight decrease the rate of the proton exchange reaction in polar media.

The results obtained are in good agreement with the EPR spectroscopic data of proton exchange reactions between carboxylic acids and semiquinone radical I. The results suggest a theoretical justification for the fact a slight decrease the rate of the proton exchange reaction in polar media. Further it would be interesting to continue quantum chemical researches of the OH-acids behavior in other solvents.

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ОН-қышқылдарының күшіне орта полярлығының әсерін теориялық зерттеу

Ab initio UHF әдісінің 6–31G базисінде Gaussian-2009 бағдармалық пакетінің CPCM полярлаушы континуум макроскопиялық моделінің шегіндегі еріткіштің әсерін ескере отырып, ОН-қышқылдар қатарының депротондану энергиясы теориялық бағаланды. Ортаның полярлануының өсуімен қышқылдардың депротондану энергиясының төмендеуі квантықхимиялық көрсетілді. Полярлы ортадағы семихинонды радикал 3,6-ди-үш.бутил-2-оксифеноксилдің карбон қышқылдарымен протон алмасу жылдамдығының ЭПР-спектроскопиялық берілгендерінің төмендеуіне теориялық негіздеме берілді.

И.А.Пустолайкина, К.Ж.Кутжанова, А.Ф.Курманова, Е.Р.Батырова, Д.К.Толеутай

Теоретическое изучение влияния полярности среды на силу ОН-кислот

Методом *ab initio* UHF в базисе 6–31G с учетом влияния растворителя в рамках макроскопической модели поляризуемого континуума CPCM программного пакета Gaussian-2009 теоретически оценены энергии депротонирования ряда ОН-кислот. Квантовохимически показано снижение энергии депротонирования кислот с ростом полярности среды. Дано теоретическое обоснование ЭПР-спектроскопических данных о снижении скорости протонного обмена карбоновых кислот с семихинонным радикалом 3,6-ди-трет.бутил-2-оксифеноксилом в полярных средах.

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Influence of hydroimpulsive discharge on process of dephenolizing of primary coal tar

The maintenance of phenol and its derivatives as a part of coal tar «Sary Arka spetskoks» is defined. The method of removal of phenol and its derivatives from coal tar of coke-chemical productions of the Central Kazakhstan using of energy of hydropulse discharge is developed. For definition's change composition of coal tar gas chromatograph Agilent 7890A with the mass selective detector 5975C Inert MSD was used.

Key words: coal tar, hydroimpulsive discharge, phenol and its derivates, chromatogram, polycyclic aromatic hydrocarbons.

Coal tar is a mixture of bi- and polycyclic aromatic hydrocarbons, and also polycyclic systems with heteroatoms in their rings. Number of all these substances is approximately 95 % of the resin components. Review and study of coal tar as a physico-chemical system open new possibilities for studying its properties and improving its processing technology. Coal tar is a polyazeotrope-polyeutectic system. An intermolecular interaction of the resin components leads to the formation of numerous azeotropes, eutectics and mixed crystals.

High-temperature coal tar, being the product of deep thermal conversion of pyrolysis fuel primary products, consists of the most thermodynamically stable compounds. Therefore, high-temperature coal tar contains only small amounts of paraffinic hydrocarbons, cycloalkanes and also aromatics with long side chains. The content of compounds with functional groups in high- temperature coal tars, in particular phenols, is not big [1]. Coal tar of Shubarkol coal cut contains about 10 % of phenols, 3.2 % of organic bases, preferably of acridine and quinoline series [2]. The most important features of polycyclic compounds are their thermal stability and oxidation stability, and also toxicity to microorganisms. This allows to use technical mixtures based on processing products of coal tar for the manufacture of various protective coatings and antiseptic oils, protecting timber.

Individual cresols and their mixtures have great value and that is why are used for the production of synthetic resins, plasticizers and flame retardants for polymer materials, chemicals for agriculture, various stabilizing additives: antioxidants, polymerization inhibitors and others [3].

Using crude coal tar without processing leads to direct losses of valuable products and adversely affect the environment in the areas of its application. It is estimated that each year worldwide about 7 million tons of coal tar are distillated. Some compounds can be found in coal tar in an amount of 1 % or more, i.e. the resources of each substances and the possibility of their producing are significant [4].

Nowadays in Kazakhstan the problem of recycling and processing of waste products of coal production to high-quality road-building materials exists. In this regard, the purpose of this research is to study the composition of coal tar of Shubarkol cut LLC «Sary Arka Spetckoks» and the identification of phenol and its derivatives in coal tar and also cleaning methods from it for its further processing (producing bitumen from it).

In order to determine the composition of coal tar (CT) of Shubarkol cut, 0.01 g of coal tar was taken and then was dissolved in 10 ml of chloroform The resulting solution was filtered to remove insoluble in chloroform compounds and impurities, which present in the coal tar. The solution was examined with Agilent 7890A gas chromatograph with a mass selective detector 5975C Inert MSD. Processing of the results was performed automatically using the GS-MSD DataAnalysis.

Analysis was carried out under the following conditions:

– column length — 60 m;
– column diameter — 0.25 mm;
– thickness of the adsorbent column — 0.25 micrometers;
– evaporator temperature — 250 ºC;
– thermostat temperature — 60–300 ºC;

– gas carrier — helium;

– flow rate of gas carrier — 1 ml/min;

– sample volume — 0.1 ml.

It was established that coal tar is a complex mixture of aromatic heterocyclic compounds and their derivatives boiling in the wide range of temperatures. The chromatogram of the feedstock is shown in Figure 1.

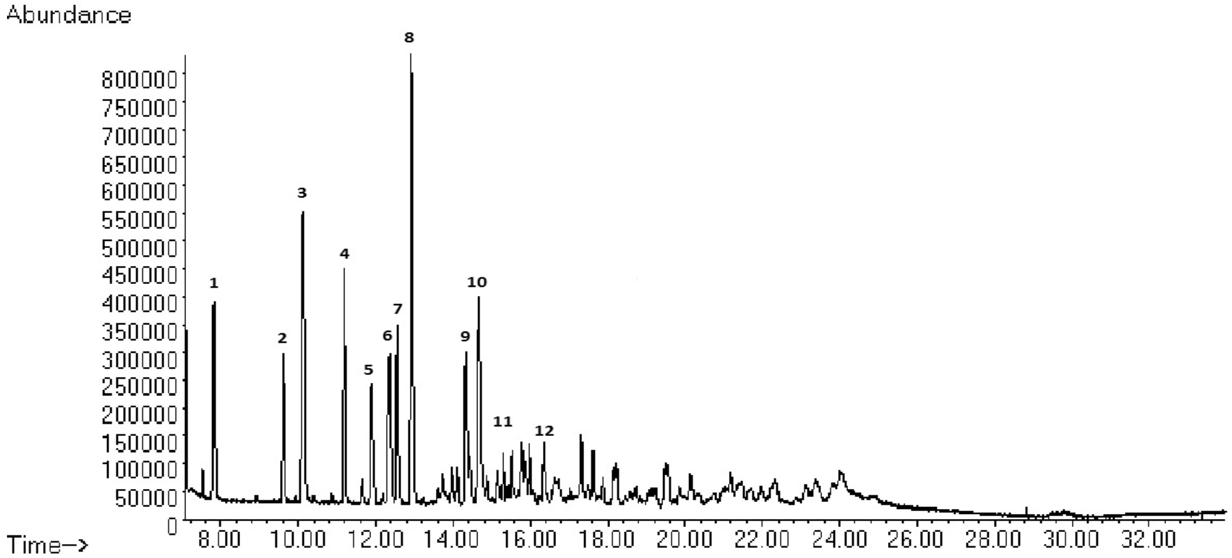

Figure 1. The chromatogram of the coal tar

High content of phenol and its derivatives can be seen from the results of gas chromatographic (GC) analysis of coal tar, which correspond to peaks is visible: 1) phenol; 2) 2-methyl-phenol; 3) 4-methyl-phenol; 4) phenol; 5) 3,4-dimethyl-phenol; 6) 3,4-dimethyl-phenol; 7) 2-methyl-phenol; 8) 4-methyl-phenol; 9) 4-ethyl-phenol; 10) 2-ethyl-phenol; 11) 2,3-dimethyl-phenol; 12) 2-propyl-phenol. Time of a yield of phenol and its some derivatives at different temperatures speaks that in resin the yielded connections are in azeatrope forms. To remove phenols from and for the further processing coal tar was exposed to hydroimpulsive discharge (HID) using catalyst ($NiCl_2$).

Laboratory reactor was designed and assembled in order to carry out experimental works on the processing of coal tar by hydroimpulsive discharge. It allows to carry out tests in a wide range of changes of characteristics of the electric discharge. Laboratorial reactor consists of a cell, a control unit of electrohydraulic apparatus, unit of monitors, high voltage transformer, rectifier, high voltage capacitor with discharger and fault protection scheme on the carcass of generator. A cell have tightly closing (with the help of threaded connection) lid made from high-strength insulating material. Connected through high-voltage cables with controlled discharger of electrohydraulic apparatus electrode of positive polarity where mounted on the cover. Welded to the inner bottom of the container, a metal rod is used as electrode of negative polarity which body is connected to the negative pole of the generator and is grounded. The distance between the electrodes (working discharge interval) is adjustable.

In order to carry out HID, 100 ml of coal tar was heated to 500 ºC and 100 ml of distilled water was added to. The resulting mixture was shaken to form an emulsion. Then this mixture was poured into the cell previously heated with boiled water to 70 °C. Then resulting emulsion was exposed to HID during 15 minutes under the following parameters: $I = 12$ A, $U = 30$ kV, with the frequency of 69–71 pulses/min. At the end of the process, the cell content was poured into a separatory funnel and left till the full disintegration. After disintegration of the solution, upper aqueous layer of dark-red (brown) color was drained. Remaining coal tar was heated to fluid state (~500 ºC), the density was measured, $\rho = 1.06$ g/cm^3.

In order to determine changes in the composition of coal tar, 0.01 g of a tar was taken and then was dissolved in 10 ml of chloroform. The resulting filtrate was also investigated with Agilent 7890A gas chromatograph. Chromatogram of the tar after HID processing is shown in Figure 2.

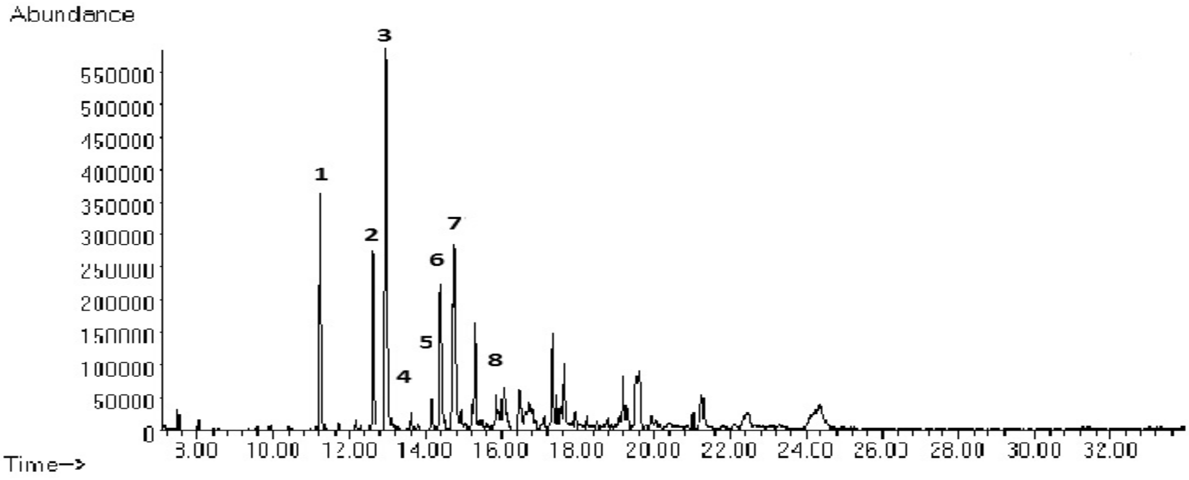

Figure 2. Chromatogram of coal tar after HID

After HID the total of phenol and its derivatives has changed that it is possible to observe on the area of peaks: 1) phenol; 2) 2-methyl-phenol; 3) 4-methyl-phenol; 4) 2,3-dimethyl-phenol; 5) 4-ethyl-phenol; 6) 3,4-dimethyl-phenol; 7) 2-ethyl-phenol; 8) 2-ethyl-4-methyl-phenol. However at the general reduction of phenol from 13,72 % to 9,64 %, 2-methyl-phenol from 9,06 % to 7,28 % and 4-methyl-phenol from 30,36 % to 20,38 %, there is an insignificant increase in its branched more out derivatives, such as 2,3-dimethyl-phenol from 0,44 % to 0,55 %, 3,4-dimethyl-phenol from 7,8 % to 9,82 % and 4-ethyl-phenol from 0,49 % to 1,84 %. Under the chromatogram also it is possible to notice occurrence of new phenol compound — 2-ethyl-4-methyl-phenol. Presumably, it's depend to action of energy of hydroimpulsive discharge there is an addition of methyl- and ethyl- radicals to a phenol ring.

Comparative data of GC analysis of coal tar before and after HID processing is presented in the table.

Table

The content of phenols and its derivatives in coal tar before and after HID processing

Compound	CT before HID, %	CT after HID ($NiCl_2$), %
Phenol	13,72	9,64
2-Methyl-phenol	9,06	7,28
4-Methyl-phenol	30,36	20,38
2,3-Dimethyl-phenol	0,44	0,55
3,4-Dimethyl-phenol	7,8	9,82
2-Ethyl-phenol	14,88	12,77
4-Ethyl-phenol	0,49	1,84
2-Ethyl-4-methyl-phenol	–	1,33
2-Propyl-phenol	0,78	–
Total amount of phenol and its derivates	77,53	63,58

Thereby, preliminary results of the processing of coal tar by means of HID were obtained. According to obtained data from chromatogram, the absence of intense peaks till 11th minute and decrease in the intensity of certain peaks can be observed, which corresponds to the content of phenol and most of its derivatives.

The offered method allows to remove phenol and its derivatives from primary coal tar that in the future allows to apply resin to reception of road and building bitumen. Further use of other kinds of catalysts (including organic) for more effective removal of phenol and its derivatives is supposed. Application organic connection which is scheduled will be hydrogen donators for linkage of formed radicals occurbed at the HID. It will not allow incorporate to free radicals to a phenol ring that methyl-ethyl- of substitution derivates of phenol will promote removal more quantities.

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Біріншілік таскөмір шайырын фенолсыздандыру үрдісіне гидроимпульстік разрядтың әсері

Мақалада «Сары Арқа Спецкокс» ЖШС тас көмір шайырының құрамындағы фенол және оның туындылары анықталды. Гидроимпульстік разряд қуатын қолдана отырып, Орталық Қазақстанның коксхимиялық өндірістерінің тас көмір шайырынан фенолды және оның туындыларын жою әдісі жүзеге асырылды. Тас көмір шайырының құрамындағы өзгерісті анықтау үшін 5975С Inert MSD масс-селективті детектормен жабдықталған Agilent 7890A газдық хроматограф қолданылды.

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Влияние гидроимпульсного разряда на процесс обесфеноливания первичной каменноугольной смолы

В статье определено содержание фенола и его производных в составе каменноугольной смолы ТОО «Сары Арка Спецкокс». Разработан метод удаления фенола и его производных из каменноугольной смолы коксохимических производств Центрального Казахстана с использованием энергии гидроимпульсного разряда. Для определения изменения состава каменноугольной смолы использовался газовый хроматограф Agilent 7890A с масс-селективным детектором 5975C Inert MSD.

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Assessing the environmental pollution of mining and processing plant

It was established that the process of accumulation of heavy metal ions by biological objects can be described by mathematical equations. Application of the received mathematical models gives possible to carry out a prediction regarding the concentration of potential-determining ions, when changing other factors influencing to the process of binding of heavy metal ions by biological objects. Shown that the plants of Chlorophytum type are biosensors that can serve as natural indicators of environmental pollution in industrial areas.

Key words: natural indicators, biosensors, pollution, heavy metal ions, absorption, waste water, mathematical models, plant of Chlorophytum.

Introduction

In mineral processing generate wastes which are suspensions of fine solid particles in water. From the enrichment plant tails direct hydraulic transport in the pond — a complex hydraulic structure, this is an integral part of all mining and processing production. In fact this is a new kind of field — man-made.

The tailings are aggregation of the mining industry waste. The volume of accumulated material in them is estimated in astronomical numbers. They are also the perspective of content and reserves of useful components compared with mining tailing deposits, which are ore-dressing tailings of ferrous and non-ferrous metals. Tails — this is waste of mineral processing, in which the content of a valuable component naturally lower than in the feed, since they are dominated by particles of waste rock. The solid phase of tailings slurry is a mixture of mineral particles of different sizes — from 3 mm to a fraction of a micron. The composition of the particles and their density depends on the mineral composition of the rocks included in the host minerals [1].

The waste of ferruginous quartzite has significant adverse influence on the environment. Transportation of tailings carried by hydro transport with using drainage water. Together with the water in the pond receives various ingredients presented as silicon (63 %), trivalent iron (35 %) and other elements (titanium, manganese, calcium, phosphorus, potassium, etc.) which are amount 2 % [2].

The main sources of environmental pollution by tailings are waste mine dust emissions of heavy metals from the mine, which are tailings of storage tail beneficiation. The soil and vegetation contaminated by gross forms of heavy metals [3].

A significant accumulation of harmful substances in the soil cover leads to lower productivity, a violation of the normal processes of growth and development of crops, poor hygienic quality of the habitat. Possible changes in living organisms, leading to disease. Anthropogenic dust getting into the air during the extraction of ore, blasting operations, drying, sintering ore, quartzite processing by crushing and processing complex, especially when firing pellets at the Pellet Plant, as well as dust blown off the surface of the dumps, dry tailings beaches and hydraulic dump contains increased number of trace heavy metals such as iron, zinc, aluminum, nickel, chromium, copper, lead, manganese, etc. A significant number of pollutants released to the environment from the tailings [4].

Experimental part

Study of the impact of waste water on plants and soil were performed as described [5, 6]. Atomic absorption analysis of samples for metal ions was performed on a grade of AA-140 company «Varian».

Results and discussion

The objects of study were selected plants and soil containing heavy metal ions M^{2+}, where M — Ni^{2+}, Fe^{2+}, Pb^{2+}. To better study of these systems we used the method of mathematical planning, which includes the use matrices (Tables 1–3). The basis of taking was 3-factor 4-tier matrix [7].

Table 1

Scheme of the absorption of heavy metals by root

Water	T_{soil}	τ	C_{met}	Fe_{root}	Pb_{root}	Ni_{root}
				pC		
Waste water (5 day)	–	+	+	1,655	7,240	0,459
Waste water (2 day)	–	–	+	3,96	6,705	0
Waste water (2 day)	+	+	–	1,435	0	0
Water (5 day)	+	–	–	0	0	0

Table 2

Scheme of the absorption of heavy metals by stem

Water	T_{soil}	τ	C_{met}	Fe_{stem}	Pb_{stem}	Ni_{stem}
				pC		
Waste water (2 weeks)	–	+	+	4,867	8,060	0,616
Waste water (2 days)	–	–	+	8,740	6,705	0
Waste water (5 days)	+	+	–	2,976	2,620	2,623
Water (5 day)	+	–	–	0	0	0

Table 3

Scheme of the absorption of heavy metals by soil

Water	T_{soil}	τ	C_{met}	Fe_{soil}	Pb_{soil}	Ni_{soil}
				pC		
Waste water (2 weeks)	–	+	+	0,657	5,160	1,321
Waste water (2 days)	–	–	+	0	0	0
Waste water (5 days)	+	+	–	0	0	0
Water (5 day)	+	–	–	0	0	0

As a variable parameters are defined: the temperature (T) in the range of 278–293 K, the metal concentration (CM) 0.1, and the time (τ) 5 days, 2 days. Mass of soil was 100 g, the flow of solution containing ions of heavy metals to water was 50 ml/day. Composition of test solution after water drainage copper ore is given in Table 4.

Table 4

Composition of test solution after water drainage copper ore

pH	mg/L							
	SO_4	Cl	Mg	Ca	Fe_{sum}	Cu	Zn	H_2SO_4
2,9	5340	350	180	640	406	235	154	123

This solution was used for the evaluation of pollution the soil and plants by iron ions (II) and copper (II). The source of lead and nickel ions served as a solution obtained after the decomposition of iron ore tailings (mine Kentobe) containing 0.652 mg/L of nickel, 2.157 mg/L of lead. As the test plants was used crested plant Chlorophytum (Chlorophytum comosum). Studies have shown that chlorofitum is highly sensitive to water pollution with heavy metals. This differs Bioindicator quick germination of seeds and almost 100 % germination, which significantly reduced in the presence of pollutants. In addition, the roots and stems of Chlorophytum under the influence of pollutants undergo marked morphological changes (stunting and distortion of stems, reducing the length and weight of the roots, the appearance in the leaves of cinnamon-brown spots).

Based on the change in concentration of heavy metals systems were prepared according to each particular factor. Then, using a template, performed for each sample rate factor. The best-known method of finding the optimal parameters — the most of a private function. The processing of the experimental data obtained by the generalized mathematical equation. The resulting mathematical models allow us to find the value of the concentration of heavy metals in all defined terms. Thus, the use of mathematical models makes it possible to carry out prediction of the concentration of potential-determining ions, when the other factors that affect the binding of heavy metal ions of biological objects. Applied mathematical models for the various systems shown below (Table 5).

Table 5

Mathematical models for the various systems M — Ni^{2+}, Fe^{2+}, Pb^{2+}

Object	Function	M^{n+}		
		Ni^{2+}	Fe^{2+}	Pb^{2+}
Root	$C_{M'}=f(T)$	–	$y=1.2\cdot10^{-3}\cdot t-\cdot10^{-2}$	$y=-2\cdot10^{-8}\cdot t+3\cdot10^{-7}$
	$C_{M'}=f(\tau)$	–	$y=9.8\cdot10^{-3}\cdot\tau-1.9\cdot10^{-2}$	$y=-2.33\cdot10^{-8\cdot}\cdot\tau+1,45\cdot10^{-7}$
	$C_{M'}=f(C_M)$	–	$y=-7.2\cdot10^{-3}\cdot C_м+1.8\cdot10^{-2}$	$y=1\cdot10^{-7}\cdot C_м$
Stem	$C_{M'}=f(T)$	$y=-2.0\cdot10^{-2}\cdot t+3.2\cdot10^{-2}$	$y=8,69\cdot10^{-5}\cdot t-8.626\cdot10^{-4}$	$y=1.99\cdot10^{-4}\cdot t-1.99\cdot10^{-3}$
	$C_{M'}=f(\tau)$	$y=4.07\cdot10^{-2}\cdot\tau-8.15\cdot10^{-2}$	$y=1.78\cdot10^{-4}\cdot\tau-3.5\cdot10^{-4}$	$y=3.99\cdot10^{-4}\cdot\tau-7.9\cdot10^{-4}$
	$C_{M'}=f(C_M)$	$y=1.2\cdot10^{-3}\cdot C_м+1.2\cdot10^{-3}$	$y=-5.21\cdot10^{-4}\cdot C_м+5.28\cdot10^{-4}$	$y=-1.199\cdot10^{-3}\cdot C_м+1.19\cdot10^{-3}$

To assess the adequacy of the response function values obtained experimentally and by calculation based on the generalized equations of multiple correlation coefficients were calculated [7], which are presented in Table 6.

Table 6

The correlation coefficients for systems of equations M — Ni^{2+}, Fe^{2+}, Pb^{2+}

Object	Function	M^{n+}					
		Ni^{2+}		Fe^{2+}		Pb^{2+}	
		R	t_R	R	t_R	R	t_R
Root	$C_M=f(T)$	–	–	0.99	8659.82	0.97	59.70
	$C_M=f(\tau)$	–	–	0.94	15.46	0.98	146.35
	$C_M=f(C_M)$	–	–	0.97	59.70	0.99	8659.82
Stem	$C_M=f(T)$	0.99	8659.82	0.99	8659.82	0.99	8659.82
	$C_M=f(\tau)$	0.98	146.35	0.99	8659.82	0.97	59.70
	$C_M=f(C_M)$	0.97	59.70	0.98	146.35	0.98	146.35

By analyzing of obtained results it can be concluded that the using of the developed mathematical models based on probabilistic determined approach is legitimate for these systems. The possibility of using these equations confirmed the values of the correlation coefficient.

Conclusion

Thus, the accumulation of heavy metal ions by biological objects can be described by mathematical equations as confirmed by high values of the correlations. It shows that the plants of Chlorophytum type are biosensors that can serve as natural indicators of environmental pollution in industrial areas.

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Ш.К.Әмірханова

Қоршаған ортаның тау-кен байыту комбинатының қалдықтарымен экологиялық ластануының жағдайы

Биологиялық объектілерінің ауыр металдар иондарын жинақтау процесі, математикалық теңдеулермен сипатталу мүмкіндігі анықталды. Алынған математикалық модельдерді қолдану, ауыр металдардың иондары биологиялық объектілермен байланысуының процесіне әсер ететін, қалған факторлардың өзгеруі кезінде потенциал анықтағыш ионның концентрациясы жөнінде болжамдарды жүргізуге мүмкіндік береді. Хлорофитум түрдегі өсімдіктер өндірістік аймақтардағы қоршаған ортаның ластануының индикаторы қызметін атқара алады және биосенсорлар болатыны анықталды.

Ш.К.Амерханова

Оценка экологического загрязнения окружающей среды ГОК

Установлено, что процесс накопления ионов тяжелых металлов биологическими объектами может быть адекватно описан математическими уравнениями. Применение полученных математических моделей даст возможность проводить прогноз относительно концентрации потенциалоопределяющего иона при изменении остальных факторов, влияющих на процесс связывания ионов тяжелых металлов биологическими объектами. Показано, что растения рода хлорофитум являются биосенсорами, которые могут служить естественными индикаторами загрязнений окружающей среды в промышленных районах.

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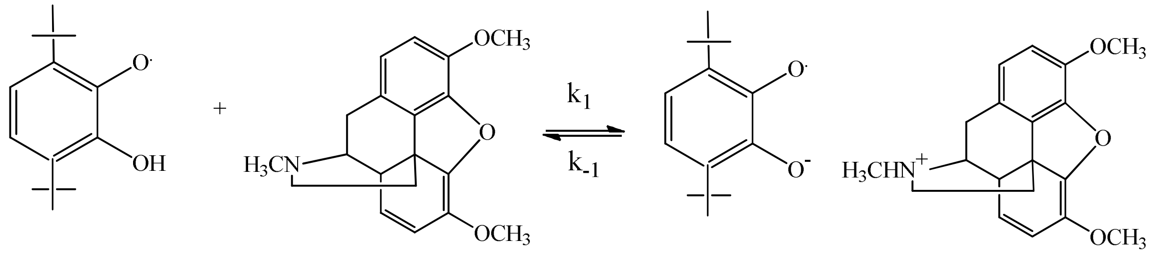
EPR-spectroscopic and quantum-chemical investigations of the fast protolytic reactions of several alkaloids

Kinetic and thermodynamic experimental parameters for the reactions of protonation of alkaloids by spin probe 3,6-di-tert-butyl-2-oxyphenoxyl obtained by ESR spectroscopy in a toluene solution are presented. Values of various physico-chemical data obtained by quantum chemical calculations in the «Gaussian-2009» for some alkaloids, such as ionization potential, electron affinity and proton affinity have been calculated.

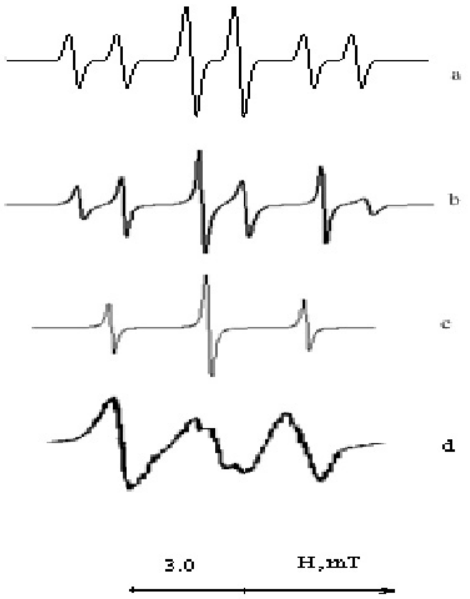
Key words: EPR-spectroscopy, spin probe, 3,6-di-tert.butyl-2-oxyphenoxyl, proton transfer reactions, quantum-chemical investigations, kinetic basicity, alkaloids.

The usage of stable semiquinone free radical 3,6-di-tert.butyl-2-oxyphenoxyl (I) as acid spin probe (XH) allows to investigate the kinetic basicity of many alkaloids (Y) in liquid organic mediums by EPR-spectroscopy method. For example, the fast acid-base protolytic interaction between I and thebaine in toluene solution may be presented with the following working scheme [1]:



(1)

Here k_1 and k_{-1} are the elementary rate constants of direct and reverse protonation reactions in studied system.



Temperature, K: *a* — 310; *b* — 270; *c* — 250; *d* — 230

Figure 1. The dynamic EPR-spectra of toluene solution of protolytic acid-base system I – tebaine at different temperatures

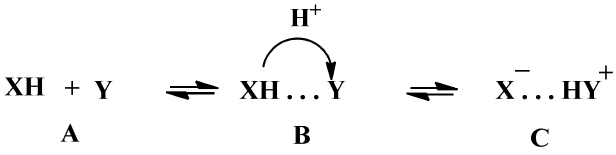
The EPR spectra of spin probe I present as triplet of doublet with hyperfine splitting (hfs) constants equal $a_H = 0.392$ mT for 2 magnetic equivalent benzene ring protons and $a_H = 0.162$ mT for hydroxyl proton (see fig. 1*a*). Figure 1*c* illustrates proton lost process for spin probe I and formed semiquinone anion-radical has EPR spectra as simple triplet with hfs equal $a_H = 0.162$ mT. The figure 1*b* shows the alternating linewidth effect in EPR spectra of acid-base system I – tebaine, connected with kinetic of the fast reversible proton transfer reaction (1) [2]. This effect described by modified theory of F.Bloch for spin relaxation in chemical systems and may be used for determination of the rate constants k_1 and k_{-1} of protolytic reaction (1). On the table 1 physicochemical experimental data for protonation reactions of alkaloids (1), obtained by EPR spectroscopic method are presented.

Table 1

Kinetic and thermodynamic parameters of the fast proton transfer reactions between I and several alkaloids

Base	Solvent	K_e (293) l/mol	$-\Delta H \pm 3{,}0$ kJ/mol	k_1 (293 K) l/mol·c	$E_1 \pm 6{,}0$ kJ/mol	k_{-1} (293 K) c^{-1}	$E_1 \pm 3{,}0$ kJ/mol
Triethylamine	Toluene	9.7	37.7	$7.7 \cdot 10^8$	10.5	$8.7 \cdot 10^7$	48.2
Thebaine	Toluene	1.8	25.3	$5.4 \cdot 10^8$	16.8	$3.0 \cdot 10^8$	42.2
Pseudoephedrine	Toluene	11.3	8.2	$1.8 \cdot 10^9$	28.0	$1.5 \cdot 10^8$	36.2
Triethylamine	THF	6.6	28.0	$3.6 \cdot 10^8$	18.4	$5.5 \cdot 10^7$	46.0
Atropine	THF	9.6	33.0	$7.5 \cdot 10^8$	2.5	$3.7 \cdot 10^7$	85.5
Quinine	THF	26.3	26.7	$1.7 \cdot 10^8$	32.2	$6.3 \cdot 10^6$	58.9

As is generally known, the intermolecular proton transfer (IPT) reaction in acid-base system with hydrogen bonds run in accordance with the scheme:



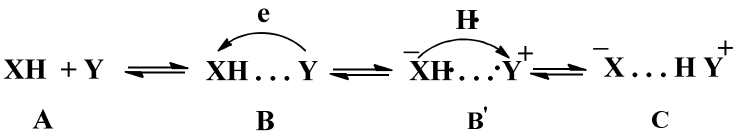
$$\underset{A}{XH + Y} \rightleftharpoons \underset{B}{XH\ldots Y} \rightleftharpoons \underset{C}{X^{-}\ldots HY^{+}} \qquad (2)$$

Here are: B — intermolecular molecular complex with hydrogen bond (MCHB) and C — reactions product, salt or ion pair — ionic complex with hydrogen bond (ICHB). It should be noticed that presented on figure 1 EPR spectra show the molecular dynamic $A \rightleftharpoons C$ (see schemes 1 and 2) [3].

Comparison of the experimental values of equilibrium constants (K_e) and enthalpies (ΔH) for protolytic reaction (1) of triethylamine an thebaine, presented in table 1, demonstrate the dependence of these physicochemical parameters from ionization constants of investigated bases [4]. Relatively low strength of ionic pare (ICHB) of 3,6-di-tert.butylsemiquinone anion-radical with thebainium cation bring to loosening this salt by molecules of solvent tetrahydrofurane (THF). The strong solvation decrease rates of acid-base reaction (1) in THF medium, but THF — molecules cannot separate the contact ionic pare of semiquinone anion-radical with triethylammomium cation.

The superposition of EPR spectra on figure 1*d* shows that thebaine form 2 types ionic pare with spin probe I at low temperatures in toluene medium. Simple triplet with hfs constant from 2 magnetic equivalent protons $a_H = 0.335$ mT belongs to ionic pare with the fast intramolecular transition of ammonium cation between oxygen atoms of 3,6-di-tert.butylsemiquinone anion-radical. This EPR spectra is similar to spectra presented on figure 1*c*. The next low-temperature EPR spectra is doublet of doublet with hfs constants $a_H = 0.30$ and $a_H = 0.37$ mT. The disappearance of the magnetic equivalence of 2 benzenes ring protons of 3,6-di-tert.butylsemiquinone anion-radical indicates on absence of fast tautomerism in this ionic pare with specific structural geometry.

But our EPR-investigations showed that for formation of salt C base Y have to the appropriate ionization potential (IP). For example: the stable paramagnetic H-acid semiquinone radical 3,6-di-tert.butyl-2-oxyphenoxyl (I) form only MCHB with very strong proton-acceptor as hexametapol. The ionic pair C or ICHB generates by addition of donors of electron: alkaline metals, amines to I — hexametapol mixture. On the basis of available data and acid-base theory of M.I.Usanovitch the next alternative scheme of the proton transfer reaction may be suggested [5–7]:



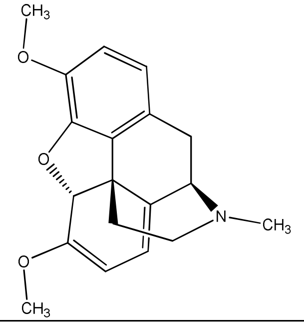
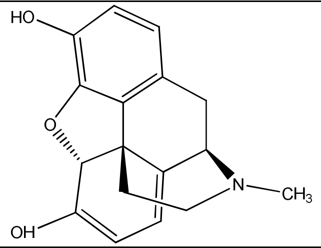
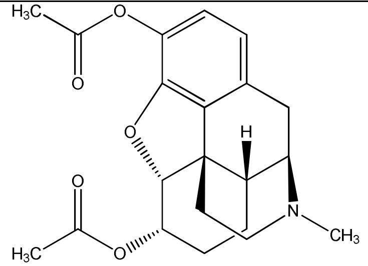
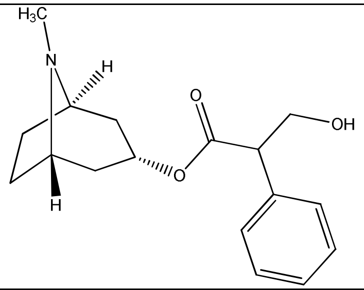
$$\underset{A}{XH + Y} \rightleftharpoons \underset{B}{\overset{e}{XH\dots Y}} \rightleftharpoons \underset{B'}{\overset{H}{\overset{-}{X}H\dots \overset{+}{Y}}} \rightleftharpoons \underset{C}{\overset{-}{X}\dots H\overset{+}{Y}} \tag{3}$$

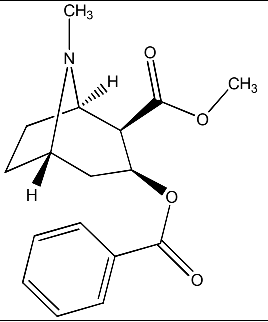
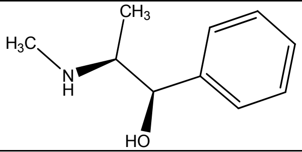
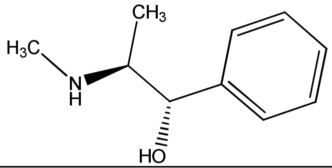
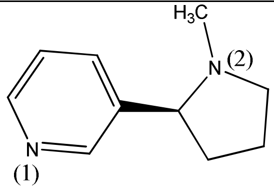
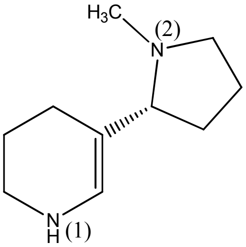
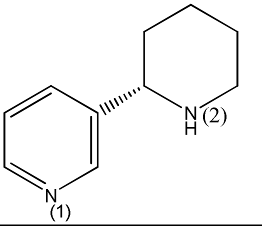
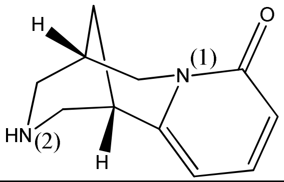
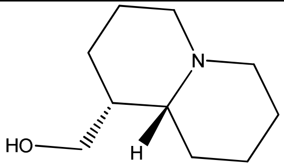
In accordance with this scheme (3) the quantum transfer of electron from bases molecule to acid provokes fast decoupling and transfer of hydrogen atom and formation of ICHB C.

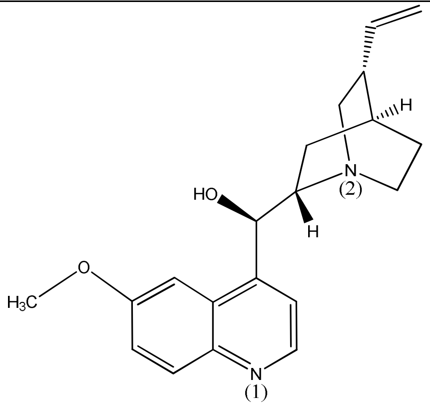
The values of different physicochemical data, obtained by quantum chemical calculations with programs packet of «Gaussian-2009» are presented in table 2 [8–10].

Table 2

The physicochemical data of several alkaloids obtained by quantum chemical calculation with UHF 3–21G method

Alkaloids	Molecular structure	Ionization potential, eV	Electron affinity, eV	Proton affinity, eV
1	2	3	4	5
Thebaine		5,8430	1,5280	11,0949
Morphine		5,9673	2,4389	11,3813
Heroin		5,8720	1,3767	10,9469
Atropine		5,8614	1,9745	10,9958

1	2	3	4	5
Cocaine		5,9850	0,9391	10,7010
Ephedrine		6,0997	2,6516	11,1359
Pseudoephe-drine		6,0465	2,6368	11,1135
Nicotine		6,0730	2,2490	10,9033 (N1) 10,7764 (N2)
Tetrahydro-nicotine		5,4015	3,5282	10,6665 (N1) 11,3851 (N2)
Anabasine		6,4674	2,1728	10,7980 (N1) 10,6864 (N2)
Cytisine		6,3451	1,4274	8,7136 (N1) 10,4824 (N2)
Lupinin		5,3819	5,2183	11,2183

1	2	3	4	5
Quinine		5,9042	0,9696	11,2935 (N1) 11,5659 (N2)

If the experimental values of ionization potentials for alkaline metals are equal 3–5 eV and for small molecules of water 12.6 eV, ammonia 10.0 eV, then the calculated values of adiabatic IP for contained in table 2 big molecules of alkaloids change in range 5–6 eV [4]. It is very interesting that narcotic molecules of morphine and heroin have appropriate equal values of adiabatic IP as a molecule of thebaine. Analogous effect be observed for narcotic cocaine and similar molecules of atropine.

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Кейбір алкалоидтардағы протондану реакцияларын ЭПР-спектроскопиялық және кванттықхимиялық зерттеу

Толуол ерітінділеріндегі ЭПР-спектроскопия әдісі арқылы алынған спиндік зонд 3,6-ди-үш. бутил-2-оксифеноксилмен алкалоидтардың протондану реакцияларының кинетикалық және термодинамикалық тәжірибелік өлшемдері көрсетілген. Кейбір алкалоидтар үшін инондану потенциалы, электронға жақындығы және протонға жағындығы тәрізді әр түрлі физика-химиялық қасиеттерінің кванттықхимиялық мәндері «Gaussian-2009» бағдарламасында есептелді.

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ЭПР-спектроскопические и квантово-химические исследования быстрых протолитических реакций некоторых алкалоидов

Представлены кинетические и термодинамические экспериментальные параметры для реакций протонирования алкалоидов спиновым зондом 3,6-ди-трет-бутил-2-оксифеноксилом, полученные методом ЭПР-спектроскопии в растворе толуола. Для некоторых алкалоидов квантовохимически рассчитаны значения различных физико-химических данных, такие как потенциал ионизации, сродство к электрону и сродство к протону, полученные в программе «Gaussian-2009».

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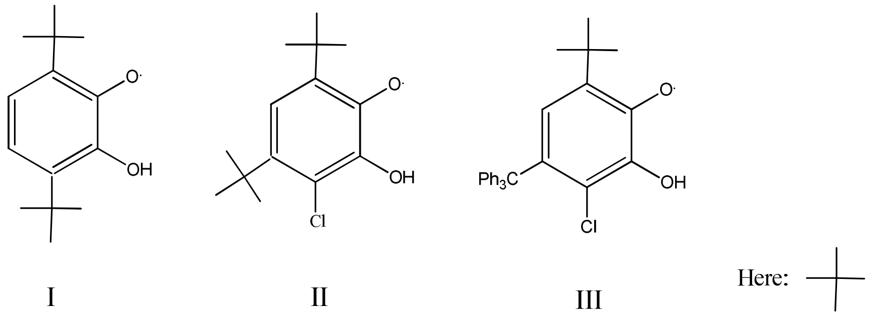
EPR-spectroscopy of the fast proton exchange reactions in solutions

Kinetic parameters of the fast intermolecular proton exchange reactions between radical 3,6-di-tert.butyl-2-oxyphenoxyl and different H-acids in toluene solutions obtained by ESR spectroscopy method are presented. NH-acids have more protolytic reactivity than carboxylic acids. Values of various physico-chemical properties for some H-acids, such as ionization potential, electron affinity, proton affinity and energy of deprotonation were obtained by quantum chemical calculations in the program «Gaussian-2009».

Key words: EPR-spectroscopy, semiquinone radicals, H-acids, proton exchange reactions, quantum-chemical investigations.

The stable semiquinone radicals were used as acid spin probes (XH) for EPR-spectroscopic determination of the rate constants of fast intermolecular proton transfer (IPT) and exchange (IPE) reactions in solutions [1]. For example, stable semiquinone radicals: 3,6-di-tert.butyl-2-oxyphenoxyl (I), 4,6-di-tert.butyl-3-clorine-2-oxyphenoxyl (II) and 4-triphenylmethyl-6-tert.butyl-3-clorine-2-oxyphenoxyl (III) generated by mixture corresponding to orthoquinone and pyrocatecol in EPR glass-tube, containing organic solution of investigated chemical systems [2, 3].

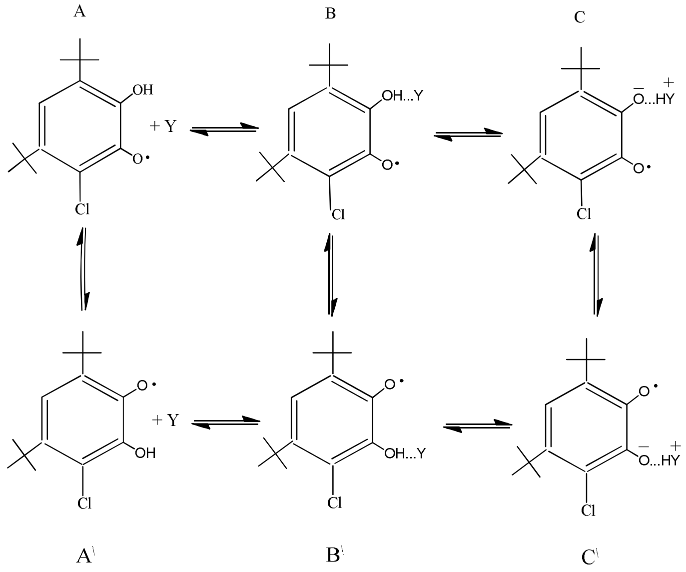


I II III

Here: is tert.butyl group

(1)

It is necessary to say that the high intramolecular mobility of hydroxyl hydrogens atom in semiquinone radicals I – III determine nanosecond homolytic tautomerism. Therefore radicals I – III have property of the dual protolytic reactivity. With a glance of tautomerism the general scheme of intermolecular proton transfer reactions for spin semiquinone probes represents as:



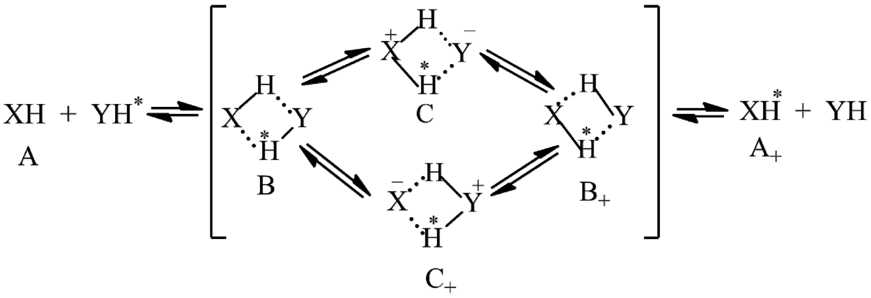
(2)

Here: Y is the molecule of proton-acceptor, for example, tertiary amine

If for spin probe I intramolecular tautomerism A ↔ A’ will be degenerate process, but in stable radicals II and III it has nongenerate character, since oxyphenoxyls have the different structure of isomers. Each path of this two-channel protolytic reaction (2) may be describe by known scheme [2]:

$$\underset{\mathrm{A}}{\mathrm{XH} + \mathrm{Y}} \rightleftharpoons \underset{\mathrm{B}}{\mathrm{XH}\ldots\mathrm{Y}} \rightleftharpoons \underset{\mathrm{C}}{\overset{-}{\mathrm{X}}\ldots\mathrm{H}\mathrm{Y}^{+}} \tag{3}$$

The each channel of IPE-reaction for spin probes I – III with different organic OH- and NH-acids (YH) go according to following scheme [3]:



(4)

Here: asterisk denote the acids proton with another orientation of spin

The figure 1 illustrate typical changes of dynamic EPR-spectra corresponding to different intermolecular proton exchange fast reactions in organic acid-base systems, containing, for example, solution of spin probe I and various carbon acids, alcohols, primary and secondary amines, alkaloids and another H-acids [2–4].

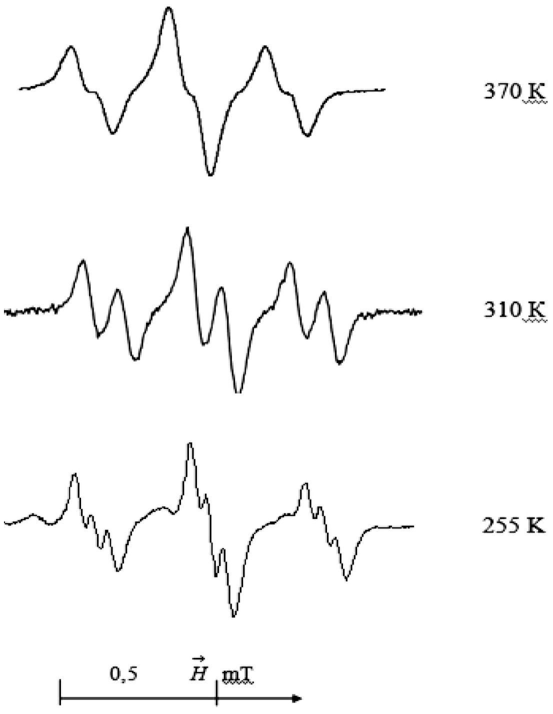


Figure 1. The dynamic EPR-spectra of acid-base system: I – anabasine in toluene medium

The EPR spectra of toluene solution of pure spin probe I presents triplet of doublets, with splitting constant a_H = 0.392 mT from hyperfine interaction on unpaired electron with two magnet-equivalent benzene ring protons and each component of this triplet split to doublet of hydroxyl proton of I with $a_{\mathrm{H}}^{\mathrm{OH}}$ = 0.162 mT.

The computation of kinetic parameters like this fast IPE reactions in liquids was made in accordance with modified F.Bloch equations for several magnetic resonance line broadening effects, connecting with chemical protons spin exchange processes [1].

$$\nu_{ex} = \frac{\gamma_e \tilde{a}_{\mathrm{H}}^{\mathrm{OH}}}{2\sqrt{2}} \left[1 - \left(\frac{\tilde{a}_{\mathrm{H}}^{\mathrm{OH}}}{a_{\mathrm{H}}^{\mathrm{OH}}} \right)^2 \right]^{\frac{1}{2}} . \qquad (5)$$

Simulation of dynamic EPR spectra was made by the use of fortran program of N.Hirota, adapted for our IPE-reactionary system (2)–(4) [1, 5]. It should be said that short-lived intermediates of IPE-reaction B, B_+ and C, C_+ do not appear and dynamic EPR spectra (see figure 1) contains summarized kinetic information about two-channel IPE-reaction (4).

Table 1

Kinetic parameters of the fast IPE-reactions between radical I and different H-acids in toluene solutions

H-acid	k_{ex} (293 K) l/mol·s	E_a kJ/mol	pK_a
Formic	$(4{,}5 \pm 0{,}2)\cdot 10^7$	7,1±0,3	3,75
Acetic	$(5{,}1 \pm 0{,}7)\cdot 10^7$	13,4±0,4	4,75
Succinic	$(8{,}4 \pm 0{,}5)\cdot 10^6$	11,1±0,6	4,21
Abietic	$(2{,}2 \pm 0{,}1)\cdot 10^8$	7,7±0,3	–
Diethylamine	$(3{,}1 \pm 0{,}7)\cdot 10^9$	4,0±0,4	10,93
Diocthylamine	$(2{,}3 \pm 0{,}1)\cdot 10^9$	3,7±0,5	11,01
Ethylenediamine	$(6{,}8 \pm 0{,}1)\cdot 10^9$	10,4±0,2	–
Hexamethylenediamine	$(7{,}2 \pm 0{,}1)\cdot 10^9$	8,7±0,9	–
Ephedrine	$(3{,}7 \pm 0{,}2)\cdot 10^9$	2,3±0,5	–
Pseudoephedrine	$(4{,}6 \pm 0{,}2)\cdot 10^8$	26,0±0,5	–
Anabasine	$(8{,}7 \pm 0{,}1)\cdot 10^8$	5,3±0,3	

EPR-spectroscopic kinetic data represented in table 1 show that NH-acids have more protolytic reactivity than carboxylic acids. For explanation of this kinetic effect we have studied several physicochemical properties of known molecules presented in table 2 by ab-initio method contained in quantum chemical programs packet «Gaussian-2009» [6–11].

Table 2

The physicochemical properties of different simple acids and bases, obtained by UHF 3–21G ab-initio method

H-acids	–IP, eV	–EA, eV	PA, eV	–DPE, eV
HOH	10,2881	5,8816	8,3070	19,5200
CH_3OH	9,0160		8,8956	18,3197
$\dot{C}H_2OH$	7,0663	2,4965	8,3747	17,4008
CH_3CH_2OH	8,7268		9,0871	18,1611
$\dot{C}H_2CH_2OH$	8,0106	2,1823	9,1255	18,1082
$CH_3CH_2CH_2OH$	8,6453		9,1468	18,0965
$\dot{C}H_2CH_2CH_2OH$	7,8003	2,4527	9,1064	17,9920
HCOOH	9,4855	2,6624	7,5833	16,2066
CH_3COOH	8,8767	2,7611	8,1016	16,3585
CF_3COOH	10,3745	0,9973	6,9294	15,0084
CCl_3COOH	12,0497			14,6575
HCl	11,8418		4,9062	14,0372
HNO_3	10,2874	–0,3313	7,2328	14,7820
H_3PO_4	8,1912	1,7598	8,0519	15,3807
H_2SO_4			7,3467	14,1206
NH_3	8,0530	6,5410	9,8411	20,0334
CH_3NH_2	7,2285	6,3192	10,2776	19,4600
$(CH_3)_2NH$	6,6263		10,5609	18,9794

For calculation of indicated physicochemical data known formulas were used, for example: the value of ionization potential of molecule (IP) is equal to

$$IP = E_M - E_M^+, \tag{6}$$

where E_M — molecules' total energy; E_M^+ — total energy of correspondent cation of this molecule. The value of proton affinity (PA) is equal to:

$$PA = E_M - E_{MH}^+. \tag{7}$$

Here: E_{MH}^+ — total quantum-chemical energy of protonated molecule. Electron affinity (EA) presented with the following expression:

$$EA = E_M - E_M^-. \tag{8}$$

The energy of deprotonation (DPE) of H-acid molecules (MH) is equal to:

$$DPE = E_{MH} - E_M^-. \tag{9}$$

It seems from scheme (4) that the fast IPE reaction is the cooperative concerted process going in four-centered cyclic complex with 2 hydrogen bonds. It is naturally to suppose that molecular dynamic in hydrogen bridge with more strong acid-base pair will be determine the value of common rate of the fast IPE reaction in liquid medium. For example in case of mixture I — secondary amine the strength of hydrogen bridge OH…N higher than in acid-base system I – OH-acids and the first tunneling of acid proton inside OH…N-bridge involves next return the proton of conjugate acid to more slow second acid-center. The calculated data presented in table 2 show that the proton-acceptor ability of basic molecules depends on values of ionization potentials: the lowest value of IP the more value of PA of bases [10].

The amino-alcohol ephedrine exchange in IPE-reaction its NH-proton and produce ionic pair C_+ on cooling reactive mixture. The ionic pair C generate in reactions radical I with more stronger H-acids. The difference between kinetic values for alkaloids ephedrine and pseudoephedrine may be explained with availability of intramolecular hydrogen bond in threo-isomer of 1-phenyl-2-methylaminoproranol-1. The necessity of destruction this hydrogen bond bring to increasing activation energy and decreasing the rate constant of IPE reaction for pseudoephedrine in regard to ephedrine. The values of experimental by EPR derived kinetic data for irreversible IPT-reaction between spin probe I and pseudoephedrine were obtained: $k_1(293K) = 1.8 \cdot 10^9$ l/mol·c, $E_1 = 28{,}0$ kJ/mol.

$$\underset{A}{XH + Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C}{\overset{-}{X}\ldots HY^+} \tag{10}$$

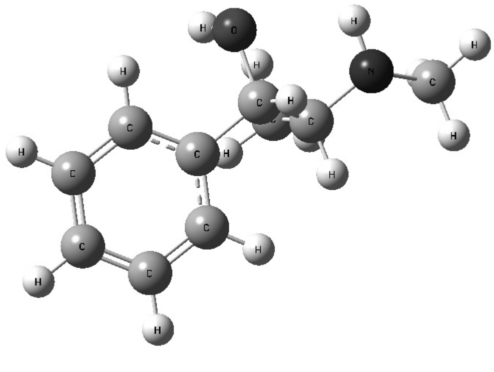


Figure 2. Ab-initio (3–21G)-structure of pseudoephedrine molecule with intramolecular hydrogen bond

Due to the presence of intramolecular hydrogen bond pseudoephedrine molecule may be display the nature of tertiary amines i.e. realize fast irreversible reaction of proton transfer according to schemes (2) and (3).

Alkaloid anabasine has two basic centers, but in protolityc reaction only morpholinyl substituent with NH-group participates. The dynamic EPR spectra of fast IPE reaction between spin probe I and anabasine shown in figure 1. Under cooling of reactionary system form the contact ionic pair with hyperfine splitting on nitrogen's atom of ammonium cation.

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Ерітінділердегі жылдам протон алмасу реакцияларының ЭПР-спектроскопиясы

ЭПР-спектроскопия әдісі арқылы алынған толуол ерітінділеріндегі әр түрлі Н-қышқылдарының 3,6-ди-үш.бутил-2-оксифеноксил радикалымен молекулааралық жылдам протон алмасу реакцияларының кинетикалық өлшемдері көрсетілген. Карбон қышқылдарымен салыстырғанда NН-қышқылдары жоғары протондану реакциялық қабілеттілігіне ие екендігі көрсетілген. «Gaussian-2009» бағдарламасында кванттықхимиялық есептеулер көмегімен кейбір Н-қышқылдар үшін инондану потенциалы, электронға жақындығы, протонға жағындығы және депротондану энергиясы тәрізді әр түрлі физика-химиялық қасиеттерінің мәндері алынды.

А.С.Масалимов, А.Ф.Курманова, С.Н.Никольский, А.У.Оспанов, А.А.Тур

ЭПР-спектроскопия быстрых реакций протонного обмена в растворах

Представлены кинетические параметры быстрых межмолекулярных реакций протонного обмена между радикалом 3,6-ди-трет. бутил-2-оксифеноксилом и различными Н-кислотами в растворе толуола, полученные методом ЭПР-спектроскопии. Показано, что NH-кислоты имеют большую протолитическую реакционную способность, чем карбоновые кислоты. В программе «Gaussian-2009» с помощью квантовохимических расчетов получены значения различных физико-химических свойств для некоторых Н-кислот, таких как потенциал ионизации, сродство к электрону, сродство к протону и энергия депротонирования.

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Диаграмма редокс-потенциал – pH системы Cu–S–H_2O в стандартных условиях

В статье теоретически исследована и построена более полная, чем известная в литературе, диаграмма *E*–pH системы Cu–S–H_2O в стандартных условиях, определены области стабильного существования, условия взаимопревращений сульфидов и оксидов меди. Впервые установлено образование в системе сульфида Cu_7S_4. Медь, его сульфиды и оксиды расположены в ряд по убыванию их восстановительных свойств. Показано, что сульфиды меди могут располагаться в области гидротермального рудообразования.

Ключевые слова: система, редокс-потенциал, pH, медь, сера, вода, сульфиды, оксиды.

Термодинамическую устойчивость электрохимических систем в водных средах удобно характеризовать на основе диаграммы потенциал (активность электрона) — отрицательный логарифм активности водородных ионов (активность протона H^+) — диаграммы *E*–pH, получившей название диаграммы Пурбэ.

Диаграмма Пурбэ может служить химико-термодинамической основой при решении вопросов устойчивости того или иного состояния системы и возможности протекания какой-либо реакции. Ею, в частности, можно пользоваться при рассмотрении вопросов (самопроизвольного или анодного) окисления металлов.

Чтобы понять причины отложения сульфидов в природе, а также условия образования их в различных гидрохимических и гидрометаллургических технологических процессах, необходимо выяснить поведение металлов и серы в водных растворах. Получаемая при этом информация может быть особенно полезной и ценной при проведении целенаправленного гидрохимического синтеза сульфидов, так как она позволяет расширить представление о сульфидных фазовых равновесиях и обеспечивает базу для выращивания монокристаллов, которые можно использовать для определения структурных параметров и физико-химических свойств сульфидов.

Диаграмма Пурбэ позволяет оценить термодинамически вероятное поведение химических элементов, установить пределы потенциалов и pH, внутри которых данное соединение элемента должно быть устойчивым, выяснить химическую природу продуктов окисления, находящихся в контакте с соединением (элементом) при данных значениях потенциалов и pH. Кроме того, она дает указания на то, за счет какой реакции — выделения водорода или восстановления кислорода — идет растворение вещества.

В настоящей работе теоретически исследовано взаимопревращение в системе Cu–S–H_2O при стандартных условиях ($T = 298{,}15$ К и $P_{\text{общ.}} = 101{,}3$ кПа) в зависимости от редокс-потенциала (*E*) и pH. Изучение физико-химических условий образования сульфидов меди в водной среде представляет большой теоретический и практический интерес. Эта система исследовалась и ранее. Например, в [1–4] показано образование только двух сульфидов: Cu_2S и CuS.

Между тем в системе Cu–S, кроме халькозина Cu_2S и ковеллина CuS, известны [5] и другие сульфиды: джарлеит $Cu_{49}S_{25}$-III ($Cu_{1,96}S$), дигенит Cu_9S_5-III и анилит Cu_7S_4.

Для построения диаграммы *E*–pH использованы все сульфиды (кроме $Cu_{49}S_{25}$) и оксиды (Cu_2O, CuO) меди, водные ионы: $Cu^+_{(в)}$, $Cu^{2+}_{(в)}$, $HCuO^{2-}_{2(в)}$, $CuO^{2-}_{2(в)}$, $HS^-_{(в)}$, $S_2^{2-}{}_{(в)}$, $HSO_4^-{}_{(в)}$, $SO^{2-}{}_{4(в)}$ и $H_2S_{(в)}$, их стандартные термодинамические данные ($\Delta G^0{}_{298}$, $S^0{}_{298}$ и $\Delta H^0{}_{298}$) для расчета $\Delta G^0_{298,p}$, взятые из известных термодинамических справочников, а также полученные путем сравнительного и приближенного методов расчета, и методика, описанная в [1].

Обычно диаграммы *E*–pH строят для четырех значений активности ионов, отличающихся друг от друга на два порядка: 10^{-6}, 10^{-4}, 10^{-2} и 10^0 моль/л. В данной работе активность твердых (кристаллических) соединений и чистых жидкостей принята равной единице. В тех уравнениях окислительно-восстановительных процессов, где сера участвует в той или иной водорастворимой форме, ее активность (концентрация) принята равной 10^{-1} моль/л. Такая величина выбрана в связи с тем, что она приблизительно соответствует активности H_2S в растворе, насыщенном им при стандартных условиях. Активность медьсодержащих ионов принята равной 10^{-6} моль/л. При равновесной активности ионов элемента в растворе, равной 10^{-6} моль/л и менее, его можно считать устойчивым к окислению.

Для определения состояния устойчивости конденсированных фаз составляли все уравнения реакций их образования из одних и тех же исходных веществ с учетом всех комбинаций и перестановок, затем устанавливали метастабильные реакции и на диаграмму наносили линии зависимости *E*–pH, соответствующие стабильным равновесиям. Стабильность или метастабильность оксред-реакций определялась в направлении окисления от нижней части диаграммы к верхней. Все вычисления электродного потенциала (*E*) проведены при $T = 298{,}15$ К и $P = 101{,}3$ кПа общего давления.

Уравнения оксред-реакций, осуществляемых в системе Cu–S–H_2O, зависимость оксред-потенциала *E* от pH среды, активность ионов и водорастворимых молекул серы, ионов меди, значения $\lg K_p$ и pH представлены в таблице 1, а диаграмма *E*–pH — на рисунке. На диаграмме границы между полями стабильности твердых фаз обозначены сплошными линиями, растворенных компонентов — пунктирными. Номера линий на диаграмме соответствуют номерам уравнений равновесных химических процессов и зависимости *E*–pH.

Таблица 1

Возможные окислительно-восстановительные реакции в системе Cu-S-H_2O и их электродные потенциалы в стандартных условиях ($P_{общ} = 101{,}3$ кПа, $T = 298{,}15$ К)

№ реакции	Уравнение реакции	$\Delta G^0_{298,p}$, $\frac{кДж}{моль}$	Уравнение редокс-потенциала $E = E_0 + (0{,}05916/n)\times\lg([Ox]/[Red])$, В; значение $\lg K_p$	pH взаимодействия; активность [], моль/л
1	2	3	4	5
1	$2Cu + H_2S_{(в)} \rightleftharpoons Cu_2S + 2H^+_{(в)} + 2e^-$	–58,0	–0,300–0,0592pH–0,0296lg[H_2S]	[H_2S] = 10^{-1}
2	$9Cu + 5H_2S_{(в)} \rightleftharpoons Cu_9S_5 + 10H^+_{(В)} + 10e^-$	–254,0	–0,263–0,0592pH–0,0296lg[H_2S]	
3	$7Cu + 4H_2S_{(в)} \rightleftharpoons Cu_7S_4 + 8H^+_{(В)} + 8e^-$	–204,0	–0,264–0,0592pH–0,0296lg[H_2S]	
4	$Cu + H_2S_{(в)} \rightleftharpoons CuS + 2H^+_{(в)} + 2e^-$	–21,6	–0,112–0,0592pH–0,0296lg[H_2S]	
5	$2Cu + HS^-_{(в)} \rightleftharpoons Cu_2S + H^+_{(в)} + 2e^-$	–97,9	–0,508–0,0296pH–0,0296lg[HS^-]	[HS^-] = 10^{-1}
6	$2Cu + S^{2-}_{(в)} \rightleftharpoons Cu_2S + 2e^-$	–177,8	–0,921–0,0296lg[S^{2-}]	[S^{2-}] = 10^{-1}
7	$2Cu_2S + H_2S_{(в)} \rightleftharpoons 2Cu_9S_5 + 2H^+_{(в)} + 2e^-$	13,9	0,072–0,0592pH–0,0296lg[H_2S]	

1	2	3	4	5
8	$7Cu_2S + H_2S_{(в)} \rightleftharpoons$ $\rightleftharpoons 2Cu_7S_4 + 2H^+_{(в)} + 2e^-$	–2,1	$-0{,}011-0{,}0592pH-0{,}0296lg[H_2S]$	
9	$Cu_2S + H_2S_{(в)} \rightleftharpoons$ $\rightleftharpoons 2CuS + 2H^+_{(в)} + 2e^-$	14,8	$0{,}077-0{,}0592pH-0{,}0296lg[H_2S]$	$[H_2S] = 10^{-1}$
10	$7Cu_2S + H_2S^-_{(в)} \rightleftharpoons$ $\rightleftharpoons 2Cu_7S_4 + H^+_{(в)} + 2e^-$	–42,1	$-0{,}218-0{,}0296pH-0{,}0296lg[H_2S]$	
11	$7Cu_2S + H_2S^{2-}_{(в)} \rightleftharpoons$ $\rightleftharpoons 2Cu_7S_4 + 2e^-$	–122,0	$-0{,}632-0{,}0296lg[S^{2-}]$	$[S^{2-}] = 10^{-1}$
12	$7Cu_7S_4 + 3H_2S_{(в)} \rightleftharpoons$ $\rightleftharpoons 7CuS + 6H^+_{(в)} + 6e^-$	52,9	$0{,}091-0{,}0592pH-0{,}0296lg[H_2S]$	
13	$Cu_7S_4 + 3HS^-_{(в)} \rightleftharpoons$ $\rightleftharpoons 7CuS + 3H^+_{(в)} + 6e^-$	–67,0	$-0{,}116-0{,}0296pH-0{,}0296lg[HS^-]$	
14	$Cu_7S_4 + 3S^{2-}_{(в)} \rightleftharpoons$ $\rightleftharpoons 7CuS + 6e^-$	–306,6	$-0{,}530-0{,}0296lg[S^{2-}]$	
15	$7CuS + 12H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons Cu_7S_4 + 3HSO^-_{4(в)} +$ $+21H^+_{(в)} + 18e^-$	616,9	$0{,}355 - 0{,}0690pH + 0{,}0099\lg[HSO_4^-]$	$[HSO_4^-] = 10^{-1}$
16	$7CuS + 12H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons Cu_7S_4 + 3SO^{2-}_{4(в)} +$ $+24H^+_{(в)} + 18e^-$	649,5	$0{,}374 - 0{,}0789pH + 0{,}0099\lg[SO_4^{2-}]$	$[SO_4^{2-}] = 10^{-1}$
17	$2Cu_7S_4 + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 7Cu_2S + HSO_4^- +$ $+7H^+_{(в)} + 6e^-$	225,4	$0{,}389 - 0{,}0690pH + 0{,}0099\lg[HSO_4^{2-}]$	
18	$2Cu_7S_4 + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 7Cu_2S + SO^{2-}_{4(в)} +$ $+8H^+_{(в)} + 6e^-$	236,3	$0{,}408 - 0{,}0789pH + 0{,}0099\lg[SO_4^{2-}]$	
19	$Cu_2S + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 2Cu^{2+}_{(в)} + HSO^-_{4(в)} +$ $+7H^+_{(в)} + 10e^-$	411,2	$0{,}426 - 0{,}0414pH +$ $+0{,}0118\lg[Cu^{2+}] + 0{,}0059\lg[HSO_4^-]$	$[Cu^{2+}] = 10^{-6}$
20	$Cu_2S + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 2Cu^{2+}_{(в)} + SO^{2-}_{4(в)} +$ $+8H^+_{(в)} + 10e^-$	422,1	$0{,}437 - 0{,}0473pH +$ $+0{,}0118\lg[Cu^{2+}] + 0{,}0059\lg[SO_4^{2-}]$	
21	$Cu_2S + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 2Cu + SO^{2-}_{4(в)} +$ $+8H^+_{(в)} + 6e^-$	292,1	$0{,}505 - 0{,}0789pH + 0{,}0099\lg[SO_4^{2-}]$	
22	$Cu_7S_4 + 16H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 7Cu^{2+}_{(в)} + 4HSO^-_{4(в)} +$ $+28H^+_{(в)} + 38e^-$	1551,9	$0{,}423 - 0{,}0436\ pH +$ $+0{,}0109\lg[Cu^{2+}] + 0{,}0062\lg[HSO_4^-]$	
23	$CuS + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons Cu^{2+}_{(в)} + HSO^{2-}_{4(в)} +$ $+7H^+_{(в)} + 8e^-$	309,8	$0{,}401 - 0{,}0518pH +$ $+0{,}0074\lg[Cu^{2+}] + 0{,}0074\lg[HSO_4^-]$	

1	2	3	4	5
24	$CuS \rightleftharpoons Cu^{2+}_{(в)} + S + 2e^-$	113,9	$0{,}590–0{,}0296\lg[Cu^{2+}]$	
25	$H_2S_{(в)} \rightleftharpoons S + 2H^+_{(в)} + 2e^-$	27,4	$0{,}142–0{,}0592pH–0{,}0296\lg[H_2S]$	
26	$H_2S^-_{(в)} \rightleftharpoons S + H^+_{(в)} + 2e^-$	–12,6	$–0{,}065–0{,}0296pH–0{,}0296\lg[HS^-]$	
27	$S + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons HSO^-_{4(в)} + 7H^+_{(в)} + 6e^-$	195,9	$0{,}338 - 0{,}0690pH + 0{,}0099\lg[HSO_4^-]$	
28	$S + 4H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons HSO^{2-}_{4(в)} + 8H^+_{(в)} + 6e^-$	206,8	$0{,}357 - 0{,}0790pH + 0{,}0099\lg[SO_4^{2-}]$	
29	$Cu_7S_4 \rightleftharpoons$ $\rightleftharpoons 7Cu^{2+}_{(в)} + 4S + 14e^-$	768,3	$0{,}569+0{,}0296\lg[Cu^{2+}]$	
30	$Cu_2S \rightleftharpoons 2Cu^{2+}_{(в)} + S + 4e^-$	215,3	$0{,}558+0{,}0296\lg[Cu^{2+}]$	
31	$Cu \rightleftharpoons Cu^{2+}_{(в)} + 2e^-$	65,0	$0{,}337+0{,}0296\lg[Cu^{2+}]$	
32	$2Cu + H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons Cu_2O + 2H^+_{(в)} + 2e^-$	90,8	$0{,}471–0{,}0592pH$	
33	$Cu_2O + H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 2CuO + 2H^+_{(в)} + 2e^-$	129,2	$0{,}669–0{,}0592pH$	
34	$Cu_2O + 2H^+_{(в)} \rightleftharpoons$ $2Cu^{2+}_{(в)} + H_2O_{(ж)} + 2e^-$	39,1	$0{,}203+0{,}0592pH+0{,}0592\lg[Cu^{2+}]$	
35	$Cu_2O + 3H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons 2CuO^{2-}_{2(в)} + 6H^+_{(в)} + 2e^-$	493,9	$2{,}560 - 0{,}1776pH + 0{,}0592\lg[CuO_2^{2-}]$	$[CuO_2^{2-}] = 10^{-6}$
36	$Cu + 2H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons CuO^{2-}_{2(в)} + 4H^+_{(в)} + 2e^-$	292,4	$1{,}515 - 0{,}1183pH + 0{,}0296\lg[CuO_2^{2-}]$	
37	$Cu^{2+}_{(в)} + H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons CuO + 2H^+_{(в)}$	45,0	–7,89	$pH = 3{,}94–0{,}5\lg[Cu^{2+}]$
38	$CuO + H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons CuO^{2-}_{2(в)} + 2H^+_{(в)}$	182,4	–31,95	$pH = 16{,}0 + 0{,}5\ \lg[CuO_2^{2-}]$
1’	$H_2S_{(в)} \rightleftharpoons H^+_{(в)} + HS^-_{(в)}$	40,0	–7,0	$pH = 7{,}0 + \lg([HS^-]/[H_2S])$
2’	$HS^-_{(в)} \rightleftharpoons H^+_{(в)} + S^{2-}_{(в)}$	79,9	–14,0	$pH = 14{,}0+\lg([S^{2-}]/[HS^-])$
3’	$HSO^-_{4(в)} \rightleftharpoons H^+_{(в)} + SO^{2-}_{4(в)}$	10,9	–1,91	$pH = 1{,}91 + \lg([SO_4^{2-}]/[HSO_4^-])$
4’	$Cu^{2+}_{(в)} + 2H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons HCuO^-_{2(в)} + 3H^+_{(в)}$	152,4	–26,7	$pH = 8{,}9 + \lg([HCuO_2^-]/$ $/[Cu^{2+}])$
5’	$HCuO^-_{2(в)} \rightleftharpoons H^+_{(в)} + CuO^{2-}_{2(в)}$	75,0	–13,13	$pH = 13{,}1 + \lg([CuO_2^{2-}]/$ $/[HCuO_2^-])$
6’	$Cu^+_{(в)} \rightleftharpoons Cu^{2+}_{(в)} + e^-$	14,8	$0{,}153+0{,}0592\cdot\lg([Cu^{2+}]/[Cu^+])$	$[Cu^+] = 10^{-6}$
7’	$Cu^+_{(в)} + 2H_2O_{(ж)} \rightleftharpoons$ $\rightleftharpoons HCuO^-_{2(в)} + 3H^+_{(в)} + e^-$	167,8	$1{,}739 - 0{,}1775pH +$ $+0{,}0592 \cdot \lg([CuO_2^-]/[Cu^+])$	$\left[HCuO_2^-\right] = 10^{-6}$
8’	$Cu^+_{(в)} + 2H_2O_{(ж)} \rightleftharpoons$ $CuO^{2-}_{2(в)} + 4H^+_{(в)} + e^-$	242,2	$2{,}510 - 0{,}2366pH +$ $+0{,}0592 \cdot \lg\left(\left[CuO_2^{2-}\right]/[Cu^+]\right)$	
а	$O_{2(г)} + 4H^+_{(в)} + 4e^- \rightleftharpoons 2H_2O_{(ж)}$		$1{,}228–0{,}0592pH$	
в	$2H^+_{(в)} + 4e^- \rightleftharpoons H_{2(г)}$		$–0{,}0592pH$	

Примечание. Агрегатное состояние твердого вещества в уравнениях реакций не указано.

Для водных сред наиболее важной в диаграмме *E*–pH является условие электрохимического равновесия воды. В таблице 1 нижний предел существования воды при $P(H_2) = 101{,}3$ кПа описан уравнениями реакции разложения воды (восстановлением ионов H^+) с выделением H_2 и потенциала $E = -0{,}0592$pH (уравнения «в»), верхний предел устойчивости воды при $P(O_2) = 101{,}3$ кПа описан уравнениями реакции восстановления кислорода до воды и потенциала $E = 1{,}228\text{–}0{,}0592$pH (уравнения «а»). Нижний и верхний пределы устойчивости воды на диаграмме показаны штрихпунктирными линиями «в» и «а». При изменении pH раствора от –2 до 16 потенциал водородного электрода (линия «в») изменяется от 0,1183 В до –0,9466 В ($E = 0$ при pH = 0), а потенциал кислородного электрода (разложения H_2O с образованием O_2), т.е. линия «а», описывающая верхний предел устойчивости воды, изменяется от 1,3463 В до 0,2814 В ($E = 1{,}228$В при pH = 0).

Таким образом, на диаграммах *E*–pH область, ограниченная линиями «а» и «в», разграничивает область электрохимической устойчивости воды, т.е. в этой области разложение воды термодинамически невозможно.

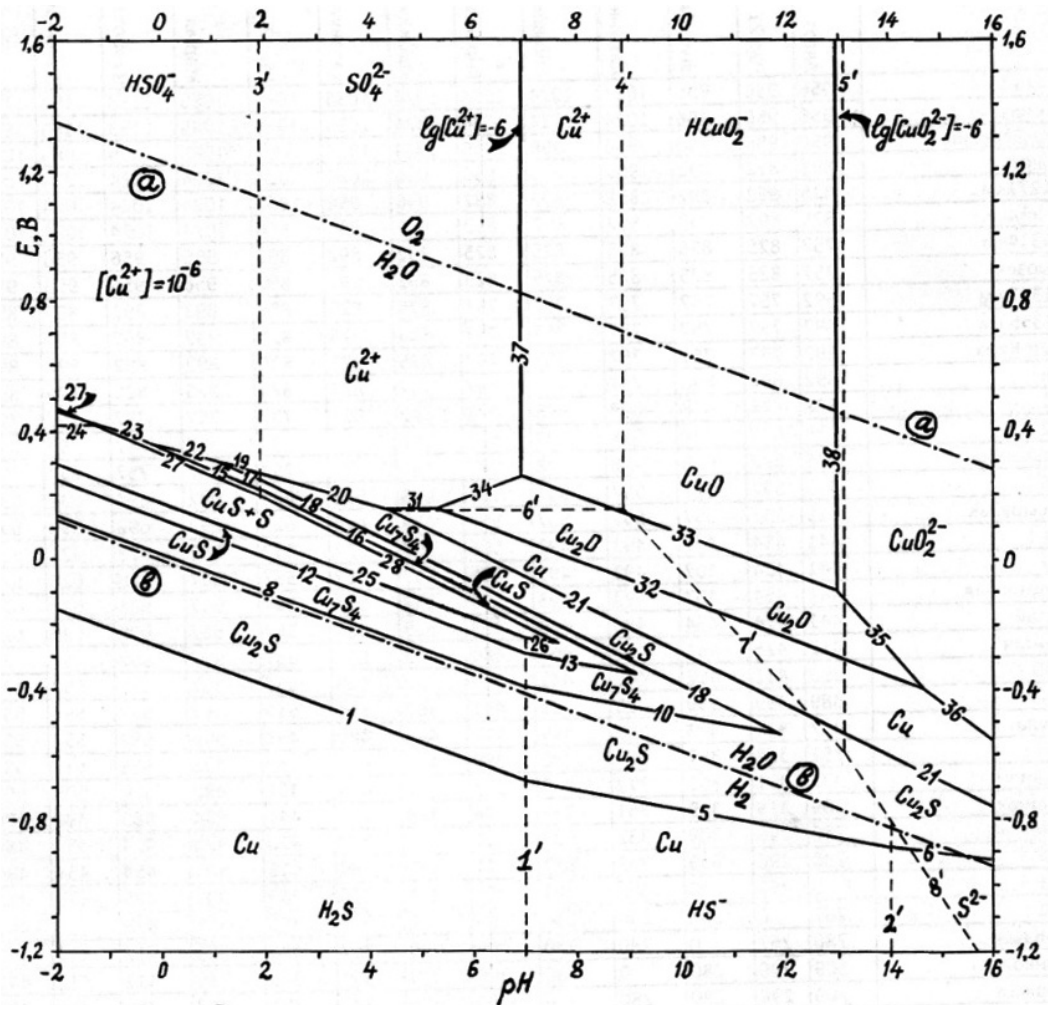

Рисунок. *E*–pH диаграмма системы Cu–S–H_2O при $T = 298{,}15$ К и $P_{общ} = 101{,}3$ кПа

Как видно из диаграммы (см. рис.), в центре ее левой половины расположена область устойчивости серы от потенциала 0,290 В (pH = –2) до –0,243 В (pH = 7) и далее до $E = -0{,}260$ В (pH = 7,63) (линии 25, 26 снизу). Сверху область устойчивости серы ограничена линией 27 с потенциалами 0,466 В (pH = –2) и 0,197 В (pH = 1,9); линией 28 с потенциалами 0,197 В (pH = 1,9) и –0,260 В (pH = 7,63). Линии 26 и 28 пересекаются при pH = 7,63, что свидетельствует об ограничении области существования серы справа от него. Согласно уравнению (линии) 27 между pH = –1,13 и –2 и соответствующих потенциалов от 0,412 В до 0,466 В сера взаимодействует с $H_2O_{(ж)}$ и переходит в ионы

$HSO_4^-{}_{(в)}$. Таким образом, сера стабильна в области диаграммы, ограниченной линиями 25,26 снизу и 27, 28 сверху.

Область S окружает область устойчивости ковеллина CuS, ограниченная линиями 12 и 13 снизу; 24, 23, 15 и 16 сверху. Линии 13 и 16 пересекаются при pH = 9,13, что ограничивает область существования CuS справа от него.

Далее, область CuS окружает более большая область существования сульфида Cu_7S_4, ограниченная линиями 8, 10 снизу и 22, 17, 18 сверху. Линии 10 и 18 пересекаются при pH = 11,88. Поэтому при pH больше чем 11,88 CuS не может существовать. Область стабильности Cu_7S_4 определена впервые.

Область стабильности сульфида Cu_7S_4 окружена самой большой областью существования халькозина Cu_2S, ограниченной линиями 1, 5, 6 снизу; 19, 20 и 21 сверху. Линии 6 и 21 пересекают ось ординаты-потенциала E справа при pH = 16 с $E = –0,893$ В и –0,767 В соответственно.

Области стабильности серы, сульфидов CuS, Cu_7S_4, Cu_2S слева ограничиваются осью потенциала E (ординаты) при pH = –2.

Ниже нижней области, ограниченной линиями (уравнениями) 1, 5, 6, и выше верхней области стабильности Cu_2S, ограниченной линиями 21, 31, 32, 36 и осью E (pH = 16), находится металлическая медь.

Выше линии 32, в области, ограниченной этой линией и линиями 34, 33, 35, находится область стабильности куприта Cu_2O.

В области, ограниченной осью ординаты слева (потенциал E при pH = –2 больше чем 0,412 В) и линиями 24, 23, 22, 19, 20, 31, 34, вертикальной линией 37, существуют ионы $Cu^{2+}{}_{(в)}$. В области, ограниченной линией 33, вертикальными линиями 37 при pH = 6,95 и 38 при pH = 13, существует тенорит CuO. Область существования ионов $CuO_2^-{}_{(в)}$ ограничена вертикальной линией 38, осью ординаты E справа при pH = 16 и линиями 35, 36.

Для анализа процессов, происходящих в системе, составили таблицу 2, представляющую пределы потенциалов и pH среды, которая позволяет описать процессы образования соединений и их взаимопревращения.

При взаимодействии твердой (кристаллической) меди с $H_2S_{(в)}$ термодинамически вероятно образование сульфидов Cu_2S, Cu_9S_5, Cu_7S_4, CuS (для всех $\Delta G^0_{298,\ p} < 0$). Однако, в соответствии с уравнениями реакций 1–4 (табл. 1), сульфиды Cu_9S_5, Cu_7S_4 и CuS метастабильны, так как их электродные потенциалы (уравнения 2–4 для E) при одинаковых pH и концентрации $H_2S_{(в)}$ больше, чем E реакции образования Cu_2S (уравнение 1). Поэтому из всех возможно образуемых сульфидов только Cu_2S является стабильным и на диаграмму наносятся линии, соответствующие уравнениям реакций взаимодействия Cu с $H_2S_{(в)}$ (линия 1 от потенциала –0,152 В при pH = –2 до –0,685 В при pH = 7), с $HS^-{}_{(в)}$ (линия 5 от потенциала –0,685 В при pH = 7 до –0,893 В при pH = 14) и с $S^{2-}{}_{(в)}$ (линия 6, параллельная оси pH, при потенциале –0,893 В).

Далее, при взаимодействии Cu_2S с $H_2S_{(в)}$ (уравнения реакций 7–9) термодинамически вероятно образование только сульфида Cu_7S_4 (уравнение 8, $\Delta G^0_{p,298} = –2{,}1$ кДж/моль). Сульфиды Cu_9S_5, CuS метастабильны (уравнения 7, 9), так как их электродные потенциалы выше, чем E для Cu_7S_4, являющегося стабильным. По уравнению реакции 10 и соответствующему ему потенциалу при взаимодействии Cu_2S с $HS^-{}_{(в)}$ также образуется стабильный Cu_7S_4.

Таким образом, линия 8 от потенциала 0,137 В (pH = –2) до потенциала –0,540 В (pH = 11,88) соответствует переходу Cu_2S на Cu_7S_4.

При дальнейшем повышении потенциала Cu_7S_4, взаимодействуя с $H_2S_{(в)}$, по уравнениям реакции и потенциалу 12, в пределах потенциалов 0,240 В (pH = –2) и –0,294 В (pH = 7), и с $HS^-{}_{(в)}$ по уравнениям реакции и потенциалу 13, в пределах потенциалов –0,294 В (pH = 7) и –0,357 В (pH = 9,13), переходит в CuS.

В соответствии с линией и уравнением 25, в пределах потенциалов 0,290 В (pH = –2) и –0,243 В (pH = 7) из $H_2S_{(в)}$, и далее в соответствии с линией 26 до потенциала –0,260 В (pH = 7,63) из $HS^-{}_{(в)}$ образуется сера. При повышении потенциала S, взаимодействуя с водой по уравнению 27, в пределах потенциалов 0,466 В (pH = –2) и 0,197 В (pH = 1,9) превращается в ионы $HSO_4^-{}_{(в)}$ и далее в соответствии с уравнением 28 до потенциала –0,260 В (pH = 7,63) переходит в ионы $SO_4^{2-}{}_{(в)}$.

Сульфид CuS, взаимодействуя с водой в соответствии с уравнением (линией) 16, в пределах потенциалов –0,357 В (pH = 9,13) и 0,214 В (pH = 1,9), переходит в сульфид Cu_7S_4 и ионы $SO_4^{2-}{}_{(в)}$, далее в соответствии с линией 15 до потенциала 0,345 (pH = 0) — в Cu_7S_4 и ионы $HSO_4^{2-}{}_{(в)}$, затем в соответствии с уравнением 23 до потенциала 0,412 В (pH = –1,13) — в ионы $Cu^{2+}{}_{(в)}$ и $HSO_4^-{}_{(в)}$.

Таблица 2

Пределы редокс-потенциалов (*E*) и pH среды равновесных химических реакций, происходящих в системе $Cu–S–H_2O$ при стандартных условиях

Номера уравнений реакций	Схемы уравнений равновесных химических процессов	Потенциалы (*E*), В		pH среды	
		слева	справа	слева	справа
1	$Cu + H_2S_{(в)} \rightarrow Cu_2S$	–0,152	–0,685	–2	7
5	$Cu + HS^-_{(в)} \rightarrow Cu_2S$	–0,685	–0,893	7	14
6	$Cu + S^{2-}_{(в)} \rightarrow Cu_2S$	–0,893	–0,893	14	16
8	$Cu_2S + H_2S_{(в)} \rightarrow Cu_7S_4$	0,137	–0,396	–2	7
10	$Cu_2S + HS^-_{(в)} \rightarrow Cu_7S_4$	–0,396	–0,540	7	11,88
12	$Cu_7S_4 + H_2S_{(в)} \rightarrow CuS$	0,240	–0,294	–2	7
13	$Cu_7S_4 + HS^-_{(в)} \rightarrow CuS$	–0,294	–0,357	7	9,13
25	$H_2S_{(в)} \rightarrow S$	0,290	–0,243	–2	7
26	$HS^-_{(в)} \rightarrow S$	–0,243	–0,260	7	7,63
27	$S + H_2O_{(ж)} \rightarrow HSO_4^-{}_{(в)}$	0,466	0,197	–2	1,9
28	$S + H_2O_{(ж)} \rightarrow SO_4^{2-}{}_{(в)}$	0,197	–0,260	1,9	7,63
16	$CuS + H_2O_{(ж)} \rightarrow Cu_7S_4 + SO_4^{2-}{}_{(в)}$	–0,214	–0,357	1,9	9,13
15	$CuS + H_2O_{(ж)} \rightarrow Cu_7S_4 + HSO_4^-{}_{(в)}$	0,345	0,214	0	1,9
23	$CuS + H_2O_{(ж)} \rightarrow Cu^{2+}_{(в)} + HSO_4^-{}_{(в)}$	0,412	0,345	–1,13	0
24	$CuS \rightarrow Cu^{2+}_{(в)} + S$	0,412	0,412	–2	–1,13
18	$Cu_7S_4 + H_2O_{(ж)} \rightarrow Cu_2S + SO_4^{2-}{}_{(в)}$	0,248	–0,540	1,9	11,88
17	$Cu_7S_4 + H_2O_{(ж)} \rightarrow Cu_2S + HSO_4^-{}_{(в)}$	0,301	0,248	1,13	1,9
22	$Cu_7S_4 + H_2O_{(ж)} \rightarrow Cu^{2+}_{(в)} + HSO_4^-{}_{(в)}$	0,345	0,301	0	1,13
21	$Cu_2S + H_2O_{(ж)} \rightarrow Cu + SO_4^{2-}{}_{(в)}$	0,160	–0,767	4,31	16
20	$Cu_2S + H_2O_{(ж)} \rightarrow Cu^{2+}_{(в)} + SO_4^{2-}{}_{(в)}$	0,271	0,160	1,9	4,31
19	$Cu_2S + H_2O_{(ж)} \rightarrow Cu^{2+}_{(в)} + HSO_4^-{}_{(в)}$	0,301	0,271	1,13	1,9
31	$Cu \rightarrow Cu_{(в)}$	0,160	0,160	4,31	5,29
32	$Cu + H_2O_{(ж)} \rightarrow Cu_2O$	0,160	–0,395	5,29	14,63
36	$Cu + H_2O_{(ж)} \rightarrow CuO_2^{2-}{}_{(в)}$	–0,395	0,555	14,63	16
34	$Cu_2O + 2H^+_{(в)} \rightarrow Cu^{2+}_{(в)}$	0,160	0,258	5,29	6,95
33	$Cu_2O + H_2O_{(ж)} \rightarrow CuO$	0,258	–0,101	6,95	13
35	$Cu_2O + H_2O_{(ж)} \rightarrow CuO_2^{2-}{}_{(в)}$	–0,101	–0,395	13	14,63
37	$Cu^{2+}_{(в)} + H_2O_{(ж)} \rightarrow CuO$	–	–	6,95	–
38	$CuO + H_2O_{(ж)} \rightarrow CuO_2^{2-}{}_{(в)}$	–	–	13	–

В соответствии с параллельной оси pH линией 24 сульфид CuS при потенциале 0,412 В и в пределах pH от –1,13 до –2 переходит в ионы $Cu^{2+}_{(в)}$ и S.

Сульфид Cu_7S_4, взаимодействуя с водой, в соответствии с уравнением (линией) 18, в пределах потенциалов –0,540 В (pH = 11,88) и 0,248 В (pH = 1,9), превращается в сульфид Cu_2S и ионы $SO_4^{2-}{}_{(в)}$, затем, в соответствии с уравнением и линией 17 до потенциала 0,301 В (pH = 1,13), переходит в Cu_2S и ионы $HSO_4^-{}_{(в)}$ и далее, в соответствии с уравнением и линией 22 до потенциала 0,345 В (pH = 0) — в ионы $Cu^{2+}_{(в)}$, $HSO_4^-{}_{(в)}$.

Сульфид Cu_2S при взаимодействии с водой согласно уравнению (линии) 19, в пределах потенциалов 0,301 В (pH = 1,13) и 0,271 В (pH = 1,9), переходит в ионы $Cu^{2+}_{(в)}$ и $HSO_4^-{}_{(в)}$, затем в соответствии с уравнением и линией 20 до потенциала 0,160 В (pH = 4,31) — в ионы $Cu^{2+}_{(в)}$ и $SO_4^-{}_{(в)}$ и далее в соответствии с уравнением и линией 21 до потенциала –0,767 В (pH = 16) — в элементарную медь и ионы $SO_4^{2-}{}_{(в)}$.

Медь в соответствии с уравнением и линией 31, параллельной оси pH, при потенциале 0,160 В в пределах pH от 4,31 до 5,29 окисляется до ионов $Cu^{2+}_{(в)}$.

При понижении потенциала до –0,395 В (pH = 14,63) медь в соответствии с уравнением и линией 32, взаимодействуя с водой, образует Cu_2O и затем в интервале потенциалов –0,395 В (pH = 14,63) и –0,555 В (pH = 16) согласно уравнению и линии 36 переходит в ионы $CuO_2^{2-}{}_{(в)}$.

Оксид Cu_2O, взаимодействуя по уравнению 34 с протонами ($H^+_{(в)}$), в интервале потенциалов 0,160 В (pH = 5,29) и 0,258 В (pH = 6,95), образует ионы $Cu^{2+}_{(в)}$ и воду, затем, взаимодействуя с водой по уравнению 33, в интервале потенциалов 0,258 В (pH = 6,95) и –0,101 В (pH = 13), переходит в оксид CuO и далее по уравнению 35, в интервале потенциалов –0,101 В (pH = 13) и –0,395 В (pH = 14,63), — в ионы $CuO_2^{2-}{}_{(в)}$. Ионы $Cu^{2+}_{(в)}$ при взаимодействии с водой по уравнению 37 (вертикальной линии) при pH = 6,95 образуют CuO, который, взаимодействуя с водой по уравнению 38 (вертикальной линии), переходит в ионы $CuO_2^{2-}{}_{(в)}$.

Пунктирными линиями представлены процессы диссоциации водорастворимых молекул и ионов: $H_2S_{(в)}$ (линия 1'); $HS^-_{(в)}$ (2'); $HSO_4^-{}_{(в)}$ (3'); $HCuO_2^-{}_{(в)}$ (5'); взаимодействие $Cu^{2+}_{(в)}$ с водой с образованием $HCuO_2^-{}_{(в)}$ (4'); окисление $Cu^+_{(в)}$ до $Cu^{2+}_{(в)}$ (6'); взаимодействие $Cu^+_{(в)}$ с водой с образованием $HCuO_2^-{}_{(в)}$ (7') и $CuO_2^{2-}{}_{(в)}$ (8').

Полученная диаграмма системы Cu–S–H_2O при $T = 298{,}15$ К и $P = 101{,}3$ кПа позволяет заключить, что по восстановительным свойствам медь, его сульфиды и оксиды в зависимости от pH и E можно расположить в следующие убывающие ряды:

$$Cu > Cu_2S > Cu_7S_4 > CuS;\ Cu_2S > Cu > Cu_2O > CuO.$$

Как видно из диаграммы E–pH системы Cu–S–H_2O, наиболее широкими полями стабильности обладают сульфид Cu_2S, затем Cu_7S_4 и наименьшими полями — CuS, затем сера. При этом площадь стабильности как сульфидов, так и серы увеличивается при переходе от щелочной к кислой среде. Например, для Cu_2S между линиями устойчивости 6 (нижняя) и 21 (верхняя) ΔE в сильно щелочной среде (pH = 16) составляет 0,124 В; в нейтральной среде (pH = 7) — $\Delta E = 0{,}628$ В; затем в кислой среде (pH = 4) — $\Delta E = 0{,}678$ В.

Области стабильности Cu_7S_4, CuS ограничиваются справа значениями pH = 11,88 и 9,13 соответственно. Поэтому эти сульфиды могут хорошо растворяться в щелочах при pH бóльших, чем указанные, и не растворяются или совсем плохо растворяются в кислотах.

Таким образом, построена более полная, чем известные в литературе, диаграмма E–pH системы Cu–S–H_2O, которую можно использовать для определения и контроля условий получения сульфидов (Cu_2S, Cu_7S_4, CuS) и оксидов (Cu_2O, CuO) меди, оценки их поведения в водном растворе в присутствии электричества, определения порядка окисления и восстановления сульфидов меди и Cu_2O, выбора необходимых условий (E, pH, концентрация ионов) для перевода меди в раствор, превращения в сульфиды и оксиды. Впервые в системе Cu–S–H_2O установлено образование сульфида Cu_7S_4.

Диаграмма также позволяет предсказать условия образования сульфидов Cu в природных условиях, так как область гидротермального рудообразования описывается уравнениями

$E = 0{,}2631 - 0{,}0592$pH [1] или $E = 0{,}3148 - 0{,}0592$pH [6] — для верхнего предела;

$E = 0{,}1725 - 0{,}0592$pH [1] — для нижнего предела.

Все сульфиды меди в соответствии с диаграммой E–pH могут располагаться в области гидротермального рудообразования в зависимости от E и pH среды.

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М.И.Жамбек

$Cu–S–H_2O$ жүйесінің стандарттық жағдайлардағы редокс-потенциал – pH диаграммасы

Мақалада стандарттық жағдайларда $Cu–S–H_2O$ жүйесінің *E*–pH диаграммасы әдебиеттерде келтірілгендерге қарағанда толығырақ теориялық зерттелген және құрылған, мыс сульфидтері мен оксидтерінің тұрақты орналасу аумағы, өзара алмасуы анықталған. Жүйеде Cu_7S_4 сульфидінің пайда болуы бірінші рет көрсетілген. Мыс, оның сульфидтері мен оксидтері тотықсыздандырғыштық қасиеттерінің кемуі бойынша қатарға орналастырылған. Мыс сульфидтерінің кеннің гидротермалдық пайда болу аймағында орналасу мүмкіндігі көрсетілген.

M.I.Zhambek

The redox-potential – pH diagrams systems $Cu\text{-}S\text{-}H_2O$ in the standard conditions

More detailed than known in literature E-pH diagram of the system $Cu\text{-}S\text{-}H_2O$ in the standard conditions was built and theoretically studied in this article. The areas of stable existence of copper sulfides and oxides and their interchange reactions were determined. The formation of the sulfide Cu_7S_4 was established for the first time. Copper, its sulfides and oxides were placed to the row according to decreasing their reduction properties. It was shown that copper sulfides can be placed in the area hydrothermal ore-formation.

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Ultrasonic cavitation processing of diesel fuel

The influence of ultrasonic cavitation on diesel fraction of oil in the presence of iron-based catalysts was investigated to identify the chemical transformations of hydrocarbons and clarify possible practical applications of cavitation for oil cracking processes. The change of individual chemical composition of diesel fuel is established at the aspect of increase the amount of light fractions.

Key words: ultrasound cavitation processing, diesel fuel, cracking process, chemical transformations of hydrocarbons, individual chemical composition of diesel fuel.

Currently, the main aim of fuel industry is improvement of the quality and cost-effective use of petroleum fuel, so more stringent requirements are toughened up on this issue [1]. The petroleum industry of foreign countries (USA, Russia, the Ukraine, China, Brazil) benefits from industrial applications of the cavitation as it results in substantial energy savings, reduced fuel costs, and corresponds to a step towards greater energy independence [2].

Cavitation is one of the most important method of purposeful change of physical and chemical characteristics of motor fuel. All physical and chemical characteristics of petroleum fuels depend on its fractional and component composition, so it is possible to manage the properties of fuels by changing their fractional and component composition [3]. Although much experimental work has been done on the cavitation processing of fuels, there is still a demand by the industry for an economical and efficient commercial process [3, 4].

Literary analysis shows that the influence of catalytic cavitation on the chemical transformations of hydrocarbons remains unexplored. It was assumed that the use of catalysts in cavitation processing of crude oil can increase the quantity and quality of light fractions. Thus, in the present work cavitation processing of diesel fuel was investigated in the presence of iron-based catalysts.

Experimental studies were carried out in air atmosphere using the ultrasonic cavitation which allows to conduct the high-intensity processing of small volumes of liquid with a capacity about 600 watts. The intensity of the ultrasonic processing is 250 W/cm^2, the operating frequency is ±22 kHz.

The diesel fraction was obtained by direct distillation of crude oil at temperature range 200–300 ºC. To study the influence of catalytic cavitation processing on chemical transformations of hydrocarbons of diesel fuel the iron-based catalysts (FeS_2 and nanocatalyst Fe_2O_3) were used due to their low cost, high activity, low toxic and eco-friendly performance. Nanocatalyst Fe_2O_3 was prepared according to the procedure [5]. The processing time was 1 min 30 sec, the volume of processed samples was 50 ml.

The fraction composition of the hydrocarbons of diesel fuel was detected by high performance liquid chromatography Agilent Technologies 5975 and identification of compounds was quantified by mass spectral database NIST 98. The products field of diesel fuel processed by ultrasonic cavitation is given in the Table 1.

Table 1

The products field of diesel fuel after ultrasonic cavitation

Compounds	Product yield, %			
	Initial diesel fuel	Diesel fuel after cavitation	Diesel fuel after cavitation in the presence of catalyst FeS_2	Diesel fuel after cavitation in the presence of nanocatalyst Fe_2O_3
Decane	5.87	6.37	8.35	11.63
Undecane	3.63	1.75	3.46	4.06
Dodecane	2.82	1	3.54	2.53
2,6,11-Trimethyldodecane	6.35	2.12	0.84	1.14
Tridecane	10.62	12.99	12.47	11.15
Tetradecane	2.33	1.84	3.8	2.95
Pentadecane	1.91	9.8	1.19	1.01
Nonadecane		7.78	8.54	4.07
1-Hexadecene	1.56	5.45	1.32	4.73
1-Nonadecene	–	5.07	1.62	0.45
1,2,3-Trimethylbenzene	4.15	1.59	1.18	–
4-Ethyl-1,2-dimethylbenzene	2.56	0.42	0.24	3.49
2,3,6-Trimethylnaphthalene	4.3	6.1	3.19	1.91
2,7-Dimethylnaphthalene	3.68	1.75	–	1.65

It is established that the destruction reactions proceed intensively in the cavitation processing of diesel fuel. As a result of these processes in the system «activated» particles were accumulated [6]. Lifetime of activated particles is short, however some of them possess the defined stability and are capable to exist individually for definitive time. The disappearance of radicals proceed in two ways: such as a result of disproportionation and recombination. As a result of repeating stages of growth and chain breakage the number of *n*-alkanes accumulates in the reaction system.

The obtained data illustrate that the cavitation allows to impact on the conversion of organic mass of diesel fuel. The amount of light fractions increases due to destruction of heavier fractions. During the destruction of hydrocarbons of diesel fuel atomic hydrogen obtained by dehydrogenation processes stabilizes the radical products. It is suggested that in the presence of hydrogen donors cavitation processing provides destruction of C–C bonds and increases the content of the light fractions.

The chemical group composition of diesel fuel after cavitation is shown in the Table 2.

Table 2

The chemical group composition of diesel fuel

Name	Initial diesel fuel	Diesel fuel after cavitation processing	Diesel fuel after cavitation in the presence of catalyst FeS_2	Diesel fuel after cavitation in the presence of catalyst Fe_2O_3
Alkanes	38.24	43.65	45.02	47.4
Alkenes	3.99	11.43	4.2	7.25
Naphthenes	2.86	0.78	1.1	4.19
Arenes	14.69	9.86	5.93	7.24

There is a noticeable change of chemical composition of diesel fuel after the cavitation processing which describes with increase of alkanes, alkenes and decrease of arenes. The alkane yield increases from 38.24 % to 43.65 % after cavitation processing without catalysts. In the presence of catalysts FeS_2 and Fe_2O_3 the alkane yields are 45.2 % and 47.4 %, respectively. The arenes yield decreases about twice in the presence of catalyst Fe_2O_3. In the presence of both catalysts the conversion of hydrocarbons is deeper than without them in the cavitation processing of diesel fuel. The decrease of arenes yield can be explained by the activity of catalysts. It is known from literary analysis that oxide and pyrite catalysts accelerate the hydrogenation of polyaromatic hydrocarbons. The high activity of pyrite is connected with participation of H_2S in the hydrogenation process by following scheme [7]:

$$H_2S + R^{\cdot} \rightarrow HS^{\cdot} + RH \quad (1)$$

$$HS^{\cdot} + R_1H \rightarrow H_2S + R_1 \quad (2)$$

R — radical; R_1H — hydrogen donor. It is known that polycyclic aromatic hydrocarbons are more active hydrogen donors in the hydrogenation process, so they can cause of a deep conversion of a feedstock.

It should be noted that the size of particles of catalyst FeS_2 decreases from 140,66 nm to 119,78 nm after cavitation processing of diesel fuel (Fig. 1, 2). It should be pointed out that cavitation processing has effect on specific surface which is proportional to chemical activity of catalyst, so the same catalysts can be used for several times at cavitation processing of fuels, moreover, the activity and selectivity of this catalysts will be improved after each application.

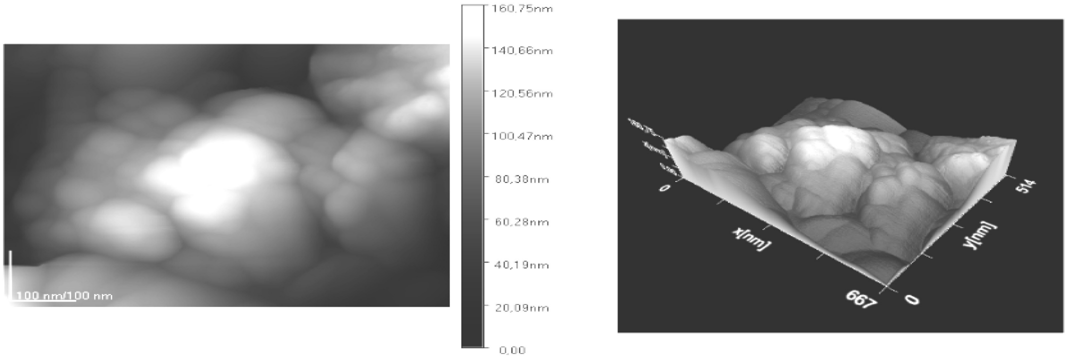

Figure 1. The surface topography of catalyst FeS_2 before the cavitation processing

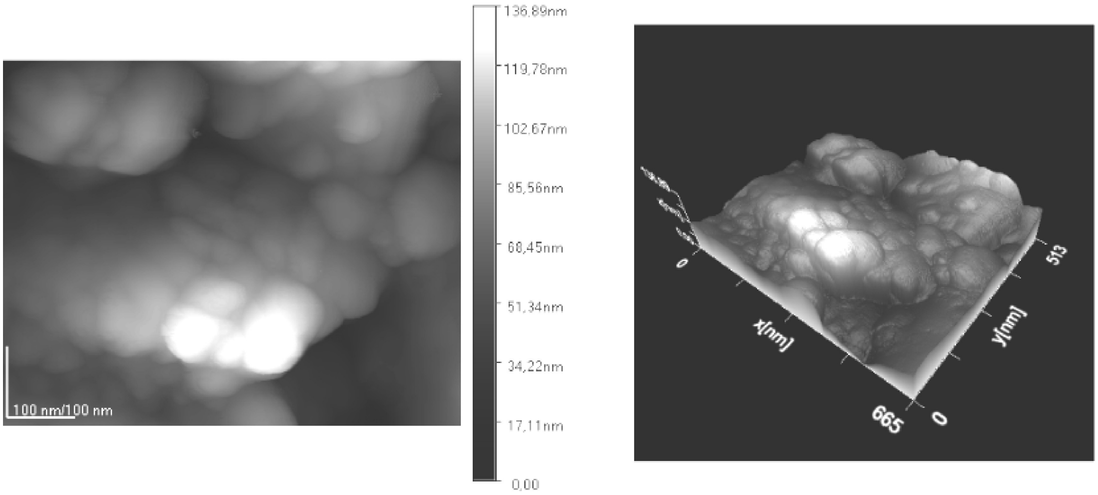

Figure 2. The surface topography of catalyst FeS_2 after the cavitation processing

Thus, the study of the cavitation processing of diesel fuel shows that the conversion of hydrocarbons proceeds on complex mechanisms including hydrocracking by C–H and C–C bonds with forming low-molecular alkanes and olefins which take part in the secondary processes of hydrogenation, cyclization and alkylation on catalyst surface.

Overall, cavitation processing of diesel fuel can provide destruction processes of hydrocarbons and increase the content of light fractions of fuels. Cavitation processing of petroleum fuels can be used in technological processes of oil-refining industry, particular for obtaining light fractions from heavy oil.

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Дизельді отынның ультрадыбыстық кавитациялық өңдеуі

Мұнай өндіру саласында көмірсутектердің крекинг үрдісі үшін практикалық қолдану мүмкіндігі мен көмірсутектердің химиялық айналымдарды анықтау мақсатымен әр түрлі катализаторлар қатысында мұнайдың дизель отынның фракциясына ультрадыбыстық кавитациялық әсері зерттелген. Дизельді отынның құрамындағы жеңіл қайнайтын фракциялардың артуы байқалған.

Хинтай Су, М.И.Байкенов, А.Б.Татеева, А.Ж.Матаева, Б.Есебаев,
А.Мадреимов, Г.Мукышева, Р.С.Бержанова, Б.Ш.Сарсембаев

Ульразвуковая кавитационная обработка дизельного топлива

Исследовано влияние ультразвуковой кавитации на дизельную фракцию нефти в присутствии различных катализаторов с целью выявления химизма превращений углеводородов, а также выяснения возможности практического использования кавитации для крекинга углеводородов в нефтепереработке. Установлено изменение индивидуального состава дизельного топлива в сторону увеличения количества легких фракций в результате кавитационной обработки.

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Influence of nanocatalytic systems on the hydrogenation of model object — anthracene

The influence of nanocatalysts β-FeOOH, Fe(OA)$_3$, Fe_3O_4 and spherical catalysts NiO/SiO_2, Fe_2O_3/SiO_2 on the hydrogenation process of model object is evaluated. These catalysts are established to be new developed catalytic additives promoted deeper chemical modification and destruction of hydrocarbons, as a result they can increase the yield of light products. It is shown that spherical catalysts NiO/SiO_2 and Fe_2O_3/SiO_2 can be used for hydrogenation of multiplet systems, such as coal, coal tar or its fractions.

Key words: hydrogenation of model object, antracene, nanocatalytic systems, multiring hydrocarbon, destruction, spherical catalysts, donor of hydrogen.

Nowadays the search of new catalysts and technologies of solid hydrocarbonaceous materials and oil residues is one of the most important directions in the development of the petrochemical industry. A significant issue in the hydrogenation of heavy hydrocarbon feedstocks is improving the efficiency of heterogeneous catalytic reactions. Therefore, great attention is paid for the development of scientific approaches in creating new catalytic systems possessing the activity and selectivity. Many alternatives of catalysts, in particular nanocatalysts for hydrogenation process are prepared [1].

Selection of effective catalysts and their use in the destructive hydrogenation of heavy hydrocarbon feedstock make possible to carry out the process in milder conditions and increase the conversion of the organic mass and the quality of distillate products. Model compounds, such as anthracene, phenanthrene, pyrene, naphthalene, etc. often are used to determine the activity and selectivity of selected catalysts in the hydrogenation process. It is allowed to reveal the mechanisms for processing of heavy coal and elaborate the science-based methods for predicting their behavior [2]. Altough much experimental work has been done on the hydrogenation of polyaromatic hydrocarbons, there is still a demand by the industry for an economical and efficient commercial process. Therefore, in the present work the catalytic hydrogenation process of model object was investigated in the presence of nanocatalytic systems.

Experimental Part

To study the influence of nanocatalysts and spherical catalysts on the product yield of model objects in the hydrogenation process several experiments were carried out. The conditions are given in the Table 1. Premixed input components were placed in a pressure reactor (autoclave). The moment of reaching operating temperature by autoclave is considered at the beginning of reaction. The heating rate of the autoclave was 10 ºC per min. The products of hydrogenation were washed by benzene.

Table 1

Conditions for hydrogenation of antracene in the presence of nanocatalysts β-FeOOH, Fe(OA)$_3$, Fe_3O_4 and spherical catalysts NiO/SiO_2, Fe_2O_3/SiO_2

№	Antracene, g	Nanocatalytic systems					*T*, ºC	*P*, MPa	τ, min
		β-FeOOH	Fe(OA)$_3$	Fe_3O_4	NiO/SiO_2	Fe_2O_3/SiO_2			
1	1	0,01	–	–	–	–	400	3	60
2		–	0,01	–	–	–			
3		–	–	0,01	–	–			
4		–	–	–	0,01	–			
5		–	–	–	–	0,01			
6		–	–	–	0,01	–	300		
7		–	–	–	–	0,01			

Nanocatalysts β-FeOOH, $Fe(OA)_3$ and Fe_3O_4 were prepared according to the procedure [3–5]. Spherical catalysts NiO/SiO_2, Fe_2O_3/SiO_2 were prepared by an impregnation method. Ash from thermal power station was used as the substrate, the content of which has been investigated by X-ray method: SiO_2=55,391 %, Al_2O_3=2,014 %, Fe_2O_3=7,715 %, TiO_2=1,745 %, CaO=2,606 %, K_2O=2,354 %, MgO=1,531 %, Na_2O=2,734 %, other unidentified compounds=1 %. The substrate was impregnated by 10 % solutions of the salts of nickel and iron ($NiCO_3$ and $FeSO_4 \cdot 9H_2O$) followed by drying and kilning. The surface topography of spherical catalysts was observed by probe microscope GSPM-5400. The parameters of the porous structure of the samples were studied by gas adsorbtion instument ASAP Micromeritics (USA). The fractional composition of the hydrocarbon part of model object was detected by high performance liquid chromatography Agilent Technologies 5975 and identification of compounds was quantified by mass spectral database NIST 98.

Discussion of Results

It is shown from Figures 1–3 that the synthesized catalysts have retained a spherical structure which is similar to conformation of substrate. It can be assumed from these data that the nature of the substrate played a key role in getting the nanoscale particles and highly refined structure. It is showed that more efficient catalysts in processing of hydrocarbon raw materials are superfine particles distributed uniformly throughout the volume of raw materials [6–9]. Appropriateness of application of nanoparticles in catalysis is connected with the chemical activity which is proportional to the specific surface of the catalyst. Many properties of nanoparticles depend on their size, so it is possible to manage activity and selectivity of nanocatalysts by changing its ones [10].

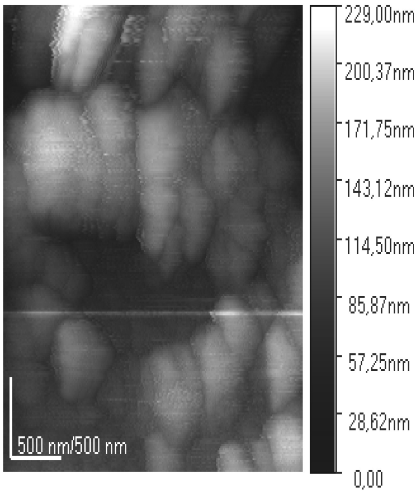


Figure 1. The surface topography of substrate SiO2

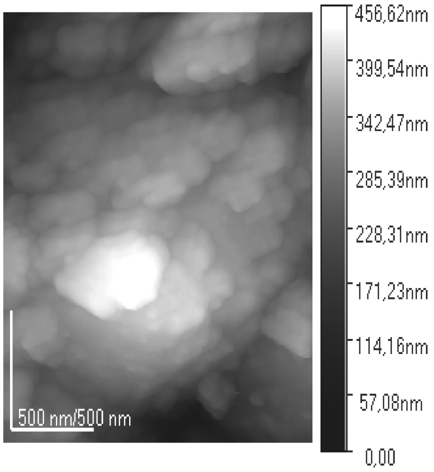


Figure 2. The surface topography of spherical catalyst NiO/SiO2

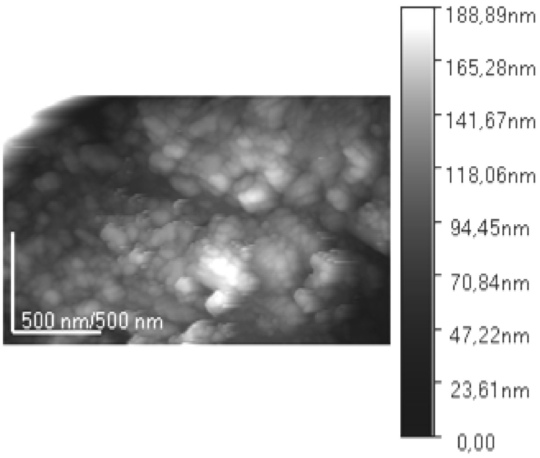
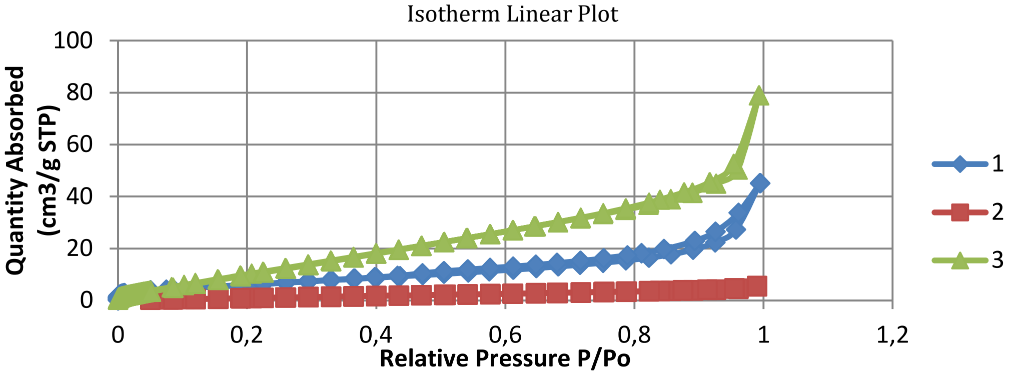


Figure 3. The surface topography of spherical catalyst Fe_2O_3/SiO_2

The analysis of the adsorbtion isotherms of nitrogen on the synthesized catalysts showed the different pore sizes (Fig. 4). The isotherms (curves 1, 3) can be attributed to type 4. which has hysteresis loop. Shape of the hysteresis loops varies considerably for different porous materials. It should be pointed out that the adsorption for this type of isotherm is summarized by micropores and mesopores with the capillary condensation. The adsorbtion isotherm (curve 2) is characteristic for microporous adsorbents and such isotherms are considered to determine only volume of micropores.



1 — substrate SiO_2; *2* — spherical catalyst Fe_2O_3/SiO_2; *3* — spherical catalyst NiO/SiO_2

Figure 4. The adsorbtion isotherms of nitrogen on the spherical catalysts

Pore size distribution analysis of spherical catalysts by the method DFT indicates that the spherical catalyst Fe_2O_3/SiO_2 has micro-mesoporous structure and spherical catalyst NiO/SiO_2 is characterized by presence of only mesopores (Fig. 5, 6).

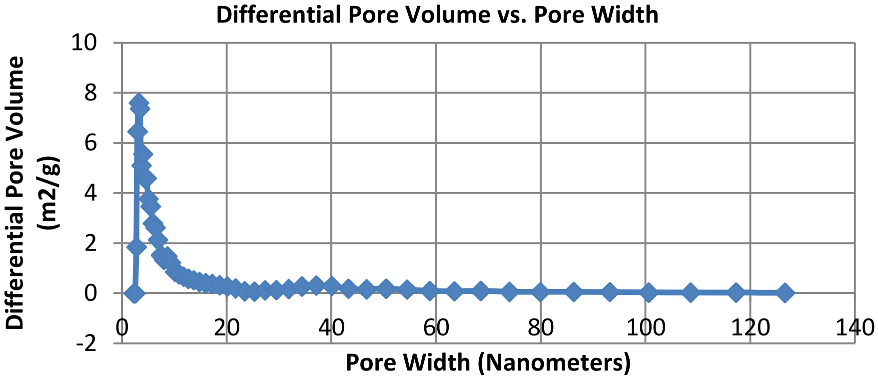


Figure 5. Pore size distribution of spherical catalyst Fe_2O_3/SiO_2 by the method DFT

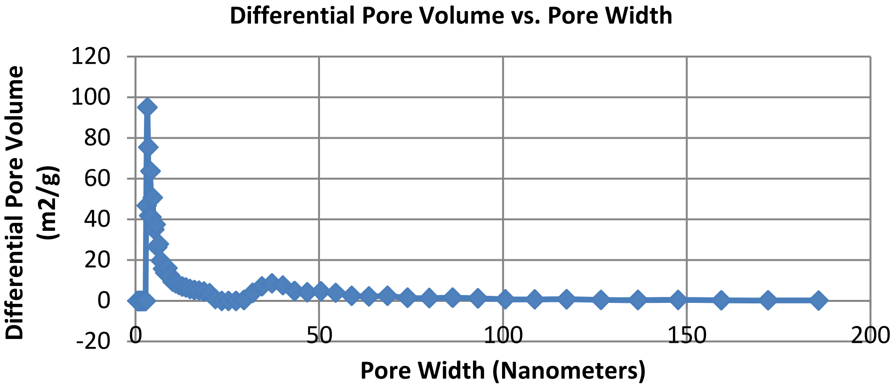


Figure 6. Pore size distribution of synthesized catalyst NiO/SiO2 by the method DFT

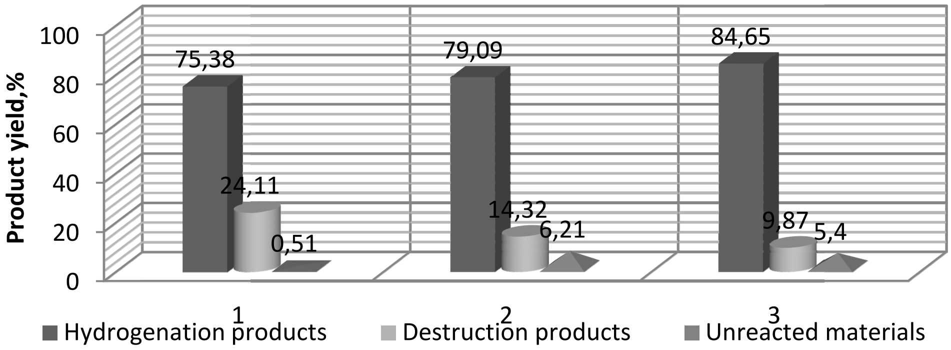
The product yield of hydrogenation process of anthracene in the presence of nanocatalysts β-FeOOH, $Fe(OA)_3$ and Fe_3O_4 is shown in the Table 2.

Table 2

The product yield of hydrogenation process of anthracene

Name	Nanocatalysts		
	β-FeOOH	$Fe(OA)_3$	Fe_3O_4
Naphtalene	2.15	2.43	2.7
1-Butylnaphtalene	20.93	11.04	5.5
2-Ethyldiphenyl	1.03	0.85	2
1,2,3,4-Tetraantracene	59.4	55.55	7.3
9,10-Dihydroantracene	15.98	23.54	77.12
Antracene	0.51	6.21	5.4

It follows from this data that in the hydrogenation of anthracene using nanocatalyst β-FeOOH the hydrogenation product yield is 75.38 % and degradation product yield is 24.11 % and unreacted material yield is 0.51 %. In the case using the nanocatalyst $Fe(OA)_3$, the hydrogenation product yield is 79.09 % and degradation product yield is 14.32 %, an unreacted material yield is 6.21 %. By adding 1 % Fe_3O_4 hydrogenation product and degradation product yields are 84.65 % and 9, 87 %, respectively, unreacted material yield is 5,4 %. Comparison of these results showed a significant change in the ratio of hydrogenation and hydrogenolysis products and the ratio of conversion. At the point of hydrogenolysis product yield and unreacted materials, the most efficient nanocatalyst is β-FeOOH; at the point of the hydrogenation products yield, the most effective nanocatalyst is Fe_3O_4 (Fig. 7). On the contrary, authors [11] noted that the destruction of the hydrocarbons did not happen at the hydrogenation of anthracene and naphthalene in tetralin due to less activity of the catalyst.



1 — β-FeOOH; 2 — $Fe(OA)_3$; 3 — Fe_3O_4

Figure 7. The ratio of hydrogenation and hydrogenolysis products in the presence of nanocatalysts

The product yield of hydrogenation process of anthracene in the presence of spherical catalysts NiO/SiO_2, Fe_2O_3/SiO_2 at 300 ºC and 400 ºC is shown in the Table 3.

Table 3

The product yield of hydrogenation process of anthracene

Name	Spherical catalysts			
	NiO/SiO_2		Fe_2O_3/SiO_2	
	300 ºC	400 ºC	300 ºC	400 ºC
1-Methylnaphtalene	1.68	0.71	–	8.22
1,6-Dimethylnaphtalene	0.11	24.78	–	4.34
1,2,3,4-Tetraantracene	65.48	0.18	88.72	86.474
9,10-Dihydroantracene	32.73	69.48	10.26	–
Antracene	–	0.74	1.02	0.1

In the hydrogenation of anthracene at 300 ºC the hydrogenation products yield is 98.2 % in the presence of spherical catalyst NiO/SiO_2. At 400 ºC the hydrogenation product and degradation product yields are 69,66 % and 25,49 %, respectively. There is negligible quantity in the content of unreacted materials. In the presence of spherical catalyst Fe_2O_3/SiO_2 hydrogenation product yield is 98.98 % at 300 ºC. At 400 ºC the hydrogenation product is 86.47 %, degradation product yield is 11,56 %. Based on these data, the spherical catalysts NiO/SiO_2 and Fe_2O_3/SiO_2 are the most efficient ones at the point of hydrogenation product yield and are not inferior to nanocatalysts β-FeOOH, $Fe(OA)_3$ and Fe_3O_4, furthermore these catalysts have a number of advantages, such as the availability and low cost.

Authors [12] describes the hydrocracking of polycyclic hydrocarbons by multistep mechanism including hydrogenation, hydroisomerization, cracking and repeated hydrogenation. Similarly, antracene is hydrogenated to di- and tetraatracene at the first stage of step-wise transformation. Then cyclohexane rings of tetraantracene are subjected to cracking and isomerization to naphthalene. It is known that hydrogenated polycyclic aromatic hydrocarbons are more active hydrogen donors, so they can cause of a deep conversion of a feedstock. Therefore, the high hydrogenation product yield can be explained by catalytic action which relates to the hydrogenation of aromatic polycyclic hydrocarbons.

Thus, the influence of nanocatalysts β-FeOOH, $Fe(OA)_3$, Fe_3O_4 and spherical catalysts NiO/SiO_2, Fe_2O_3/SiO_2 on the hydrogenation process of model object is evaluated. It is established that the nanocatalysts and spherical catalysts increase the formation rate of hydro-deritatives of anthracene, in particular 9,10-dihydroanthracene and 1,2,3,4-tetrahydroantracene. The most optimum amount of the catalyst systems at ratio of 1 % allows to increase of hydrogen donor which prevents condensation reactions and decreases the stability of the associates. It is demonstrated that spherical catalysts NiO/SiO_2 and Fe_2O_3/SiO_2 can be used for hydrogenation of multiplet systems, such as coal, coal tar or its fractions. These catalysts are established to be new developed catalytic additives promoted deeper chemical modification and destruction of hydrocarbons, as a result spherical catalysts can increase the yield of light products.

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Нанокаталитикалық жүйелердің модельдік объекті — антраценнің гидрогенизация үрдісіне әсері

Модельді объект — антраценнің гидрогенизациясын жүргізудегі β-FeOOH, $Fe(OA)_3$, Fe_3O_4 нанокатализаторларының және NiO/SiO_2, Fe_2O_3/SiO_2 сфералық катализаторларының әсері бағаланған. Синтезделген каталитикалық жүйелер көмірусутектік шикізаттың деструкциясы мен терең химиялық модификациясына әсер ететіні анықталған. Көмір, тасқөмір шайыры немесе оның фракциялары тәрізді мультиплеттік жүйелердің гидрогенизациясында синтезделген катализаторлар қолданыла алатыны көрсетілген.

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Влияние нанокаталитических систем на гидрогенизацию модельного объекта — антрацена

Проведена оценка влияния нанокатализаторов β-FeOOH, $Fe(OA)_3$, Fe_3O_4 и сферических катализаторов NiO/SiO_2, Fe_2O_3/SiO_2 на процесс гидрогенизации модельного объекта — антрацена. Установлено, что синтезированные каталитические системы способствуют более глубокой химической модификации и деструкции углеводородного сырья. Показано, что синтезированные нанокатализаторы могут быть использованы для гидрогенизации мультиплетных систем, таких как уголь, каменноугольная смола или их фракции.

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Analysis of the effectiveness of dispersant for oil spills

The acceptability and effectiveness in some situations, the practical application of dispersants for oil spill at sea is now well recognized and recorded in official documents in many countries and international organizations. To evaluate the quality offered to control the oil spills dispersants in our laboratory studies were conducted using the recommended techniques. Studies have been conducted on the impact of the proposed dispersant Kashagan oil in sea water of the Caspian Sea. On the basis of research has been done evaluating the effectiveness of dispersants at 5 ºC, 25 ºC and is given recommendation for their use.

Key words: crude oil, topped oil, oil spill, emulsification, dispersants, salinity, viscosity, density.

Oil and petroleum products are a significant reasons of environmental pollution, particularly water of oceans and seas [1]. Contact with petroleum hydrocarbons in the marine environment has a negative impact on almost all of its components, including fisheries, phyto-and zooplankton, algae, benthos, marine mammals and birds [2, 3].

One of the most important means for the elimination of accident consequences are dispersants which are designed to dissipate (emulsification) floating oil slicks in a large volume of water in the form of crushed oil droplets. When this is achieved by lowering the concentration of oil in the vicinity of the spill, enhanced biodegradation processes of pollution of the marine environment is restored interaction with the atmosphere, reduced fire hazard spill, preventing the possibility of contamination of the coastal strip, emersion of «chocolate mousse» [4, 5].

In connection with the prospects of oil production in the Kazakhstan sector of the Caspian Sea (KSCS), the question arises about analysis opportunities and the efficient use of different dispersants for oil spills [6].

The purpose of this study was to evaluate the effectiveness of a number of dispersants towards the Kashagan oil using artificial sea water of different salinity at different ambient temperatures. In the experiments were used Kashagan oil, artificial seawater (salinity 0, 6, 12, 18, 35 ‰), dispersants of various manufacturers: Corexit EU 9500, Dasic Slickgone, Inipol IP- 90, Inipol IPF, FLD-1, FLD-2, Bioversal HC (Table 1).

Table 1

Several dispersants accepted for use in oil spills

Dispersant	Approved for use in the following countries:
Corexit EU 9500	France (for use at sea), UK, USA
Inipol IP-90	France (for use at sea)
Inipol IPF	France (for use in freshwater)
Dasic Slickgone NS	France (for use at sea), the UK, Cyprus, Norway
Bioversal HC	Italy, Spain

Oil spills on water natural weathering processes occur light petroleum oil fractions, so test the effect of dispersants in the model is carried out under reduced crude.

Topped oil fraction was obtained at atmospheric pressure by ST RK ISO 3405–2008. Crude and topped oil tested for viscosity and density to determine the suitability of dispersants at the temperature 5–25 ºC. Kinematic viscosity of crude and topped oil measured capillary viscometer IWF-2. Density was determined by areometers.

Kinematic viscosity of Kashagan oil — 11,6 mm^2/s^2, density — 0,846 g/cm^3.

Topped oil at 250 ºC oil is too high in viscosity and is not suitable for further work. Oil topped in a temperature range up to 220 ºC at ambient temperature of 5 ºC solidifies and becomes uncomfortable for the study. Thus, the test proved to be suitable oil, topped at 200 ºC (Table 2).

Conducted to determine the effectiveness of dispersants according to the procedure adopted in the UK as the standard for analysis of dispersants, WSL 448 LR [7].

Table 2

Kinematic viscosity and density of reduced crude

№	Distillation temperature, ºC	Measurement temperature, ºC	Density, g/cm^3	Viscosity, mm^2/s^2
1	200	20	0,862	12,1
2	220	20	0,870	16
3	250	20	1,014	559,9
4	200	5	0,870	15,4
5	220	5	0,880	Not measured

Efficiency index dispersant defined as the mass fraction of the oil were tested, which is dispersed as fine droplets in the aqueous phase at the test conditions.

The concentration of oil in water was measured by an extraction-photometric method: oil dispersed in the aqueous phase was extracted with chloroform, and then the optical density of the oil chloroform solutions at 580 nm. For operation was used the spectrophotometer UV-1800, a light absorbing layer length — 10 mm. Oil concentration was determined using the calibration curve — dependence of the optical absorption of the oil concentration of the solution in chloroform (Fig. 1).

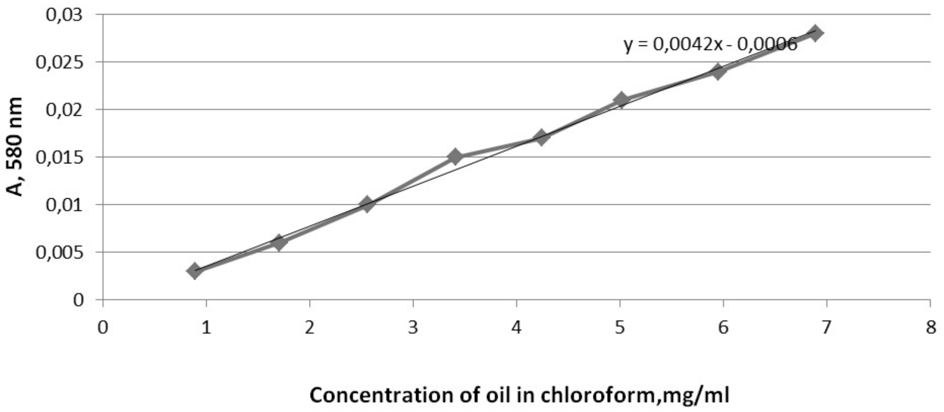

Figure 1. Calibration graph of optical density the concentration of the oil in chloroform (oil, topped at 200 ºC)

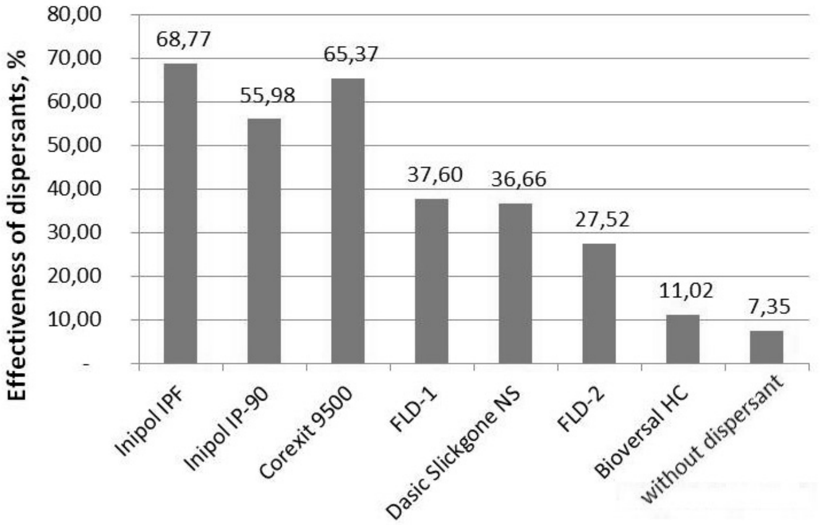

Figure 2. Effectiveness of dispersants at 25 ºC, salinity 16 ‰

Thus, for selected conditions, in particular at a temperature of 25 ºC and salinity 16 ‰ dispersant is most effective mark Inipol IPF, followed dispersants Corexit 9500, Inipol IP-90. FLD-1, Dasic Slickgone

NS, FLD-2 and Bioversal HC dispersants are weakly dispersing agents for the Kashagan oil under these conditions (Fig. 2).

Effectiveness of dispersants is strongly dependent on the ambient temperature (Fig. 3, 4).

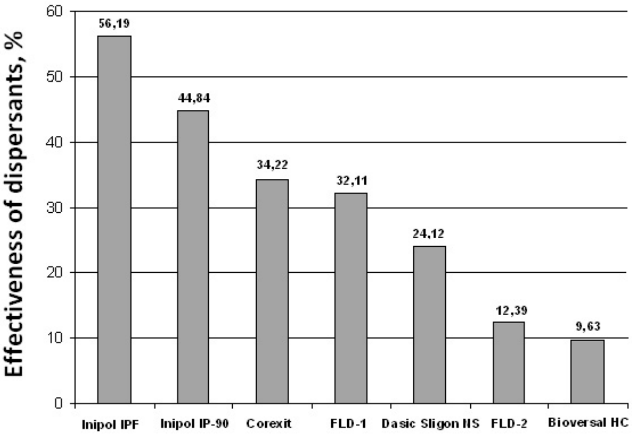

Figure 3. Effectiveness of dispersants at 5 °C

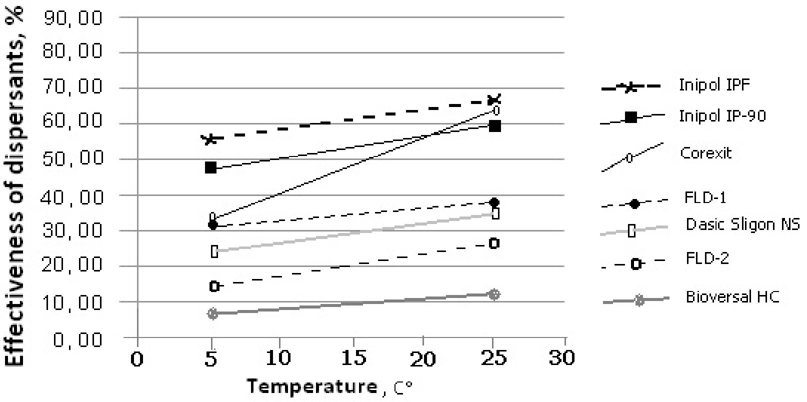

Figure 4. Dependence of the efficiency of dispersants by temperature

The effectiveness of dispersants increases with increasing temperature, while the differences in the efficiency of dispersants are stored — the most effective dispersant Inipol IPF, hereinafter — Inipol IP-90, FLD-1, and least effective dispersants — FLD-2, Bioversal HC.

Dispersants are manufactured primarily for use in ocean waters with an average salinity of 35 ‰. Salinity of the Caspian Sea below the ocean, especially in the KSCS which varies in the range 6–16 ‰. Therefore, we conducted research on the effectiveness of dispersants for different values of salinity in the range of 0–35 ‰ (Table 3).

Table 3

Comparison of the dispersants effectiveness at different salinities (25 °C)

Salinity, ‰	Dispersants					
	Inipol IPF	Inipol IP90	Corexit9500	Bioversal HC	Dasic Slickgone NS	Without dispersant
0	18,23	17,31	18,92	5,34	9,94	3,87
6	38,49	33,88	44,93	10,86	18,23	8,7
12	60,58	42,17	51,38	20,07	30,20	6,28
16 (sea water, Aktau)	68,77	48,85	65,37	11,02	36,66	7,35
35	55,06	41,25	95,57	9,02	86,36	3,87

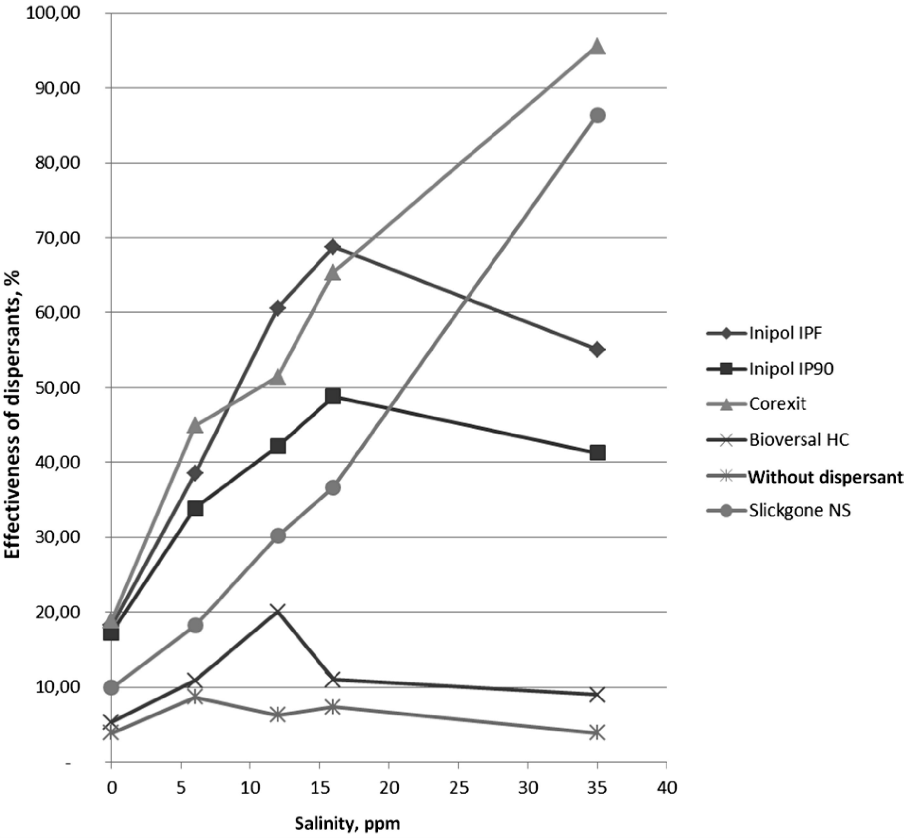

Figure 5. The dependence of the efficiency of dispersants depending on the salinity of the water

As can be seen, salinity of water influences different to the effectiveness of dispersants. Most effective in saltwater ocean with corresponding 35 ‰ are Corexit 9500 and Dasic Slickgone NS. However, their effectiveness at a salinity of the Caspian Sea (from 6 to 16 ‰) is significantly reduced, while Corexit 9500 is one of the preferred dispersants and Dasic Slickgone NS sharply reduces its effectiveness with 86,36 to 36,66 %.

The most effective at salinity of the Caspian Sea (from 6 to 16 ‰) can be considered Inipol IPF and Corexit 9500. Inipol IP-90 is less effective than the above Inipol IPF and Corexit 9500. Dasic Slickgone NS, Bioversal HC and FLD-1, FLD-2 for the Caspian Sea are unacceptable due to low efficiency values (Fig. 5).

Conclusions

1. Effectiveness of dispersants.

At a temperature of 25 °C and 16 ‰ salinity is the most effective dispersant brand Inipol IPF, whose efficiency is 77,84 %, followed by dispersing Inipol IP-90 — 55,10 % and FLD-1 — 45,01 %. Dispersants FLD-2 — 27,03 % and Bioversal HC — 20,77 % are weakly dispersing agents for the Kashagan oil under these conditions. It should be noted that in the absence of dispersants, natural conditions give 14,62 % of the dispersion at 25 °C.

Thus, in the case of Kashagan oil spills possible to use dispersants discussed the following reagents: Inipol IPF, Corexit 9500 and Inipol IP-90.

2. Temperature influence.

The effectiveness of dispersants decreases with decreasing temperature. However, the sequence number of reagents for dispersing activity is fully preserved. So, at 5 ºC the best dispersant properties against Kashagan oil dispersant showed brand Inipol IPF, whose efficiency is 56,19 % and dispersant Inipol IP-90 — 44,84 %. Dispersants FLD-1 — 32,11 % and FLD-2 — 12,39 % are weakly dispersing agents for the Kashagan oil under these conditions. Dispersant Bioversal HC 9,63 % with efficiency at a temperature of 5 ºC practically no effect, as dispersing natural conditions at this temperature give 8,60 % of the dispersion.

3. Effect of salinity.

Reducing salinity of the water in tests reduces the efficiency of dispersants. Most effective in saltwater corresponding to ocean water with 35 ‰ are Corexit 9500 and Dasic Slickgone NS, with salt water from 6 to 16 ‰ the most effective are Inipol IPF and Corexit 9500.

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Мұнай төгілгендегі қолданылатын диспергенттер тиімділігінің сараптамасы

Қазіргі кезде теңіздегі мұнай төгілу салдарын жою үшін бірқатар жағдайда диспергенттерді іс жүзінде қолдану көптеген елдерде және халықаралық ұйымдарда кең көлемде танылған және ресми құжаттарда бекітілген. Мұнай төгілу салдарымен күресу үшін ұсынылып отырған диспергенттердің сапасын бағалау барысында біздің зертханада кеңес етілген әдістемелердің көмегімен зерттеулер жүргізілді. Аталмыш диспергенттердің Каспий теңізінің суында Қашаған мұнай кен орнының мұнайына әсері анықталған. Жүргізілген зерттеулер нәтижесінде 5 ℃, 25 ℃ температураларда диспергенттерді қолдану тиімділігін бағалау жүргізілді және оларды қолдану бойынша кеңестер берілді.

Е.С.Мустафин, И.М.Пудов, А.К.Айтымов

Анализ эффективности диспергентов для применения при разливах нефти

Приемлемость и эффективность в ряде ситуаций практического применения диспергентов для ликвидации нефтяных разливов в море в настоящее время общепризнаны и зафиксированы в официальных документах во многих странах и международных организациях. Для оценки качества предлагаемых для борьбы с разливами нефти диспергентов нашей лабораторией проводились исследования с помощью рекомендованных методик. Были проведены исследования влияния предлагаемых диспергентов на нефть Кашаганского месторождения в морской воде Каспийского моря. На основании проведенных исследований была сделана оценка эффективности диспергентов при температурах 5 ℃, 20 ℃ и дана рекомендация по их применению.

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